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

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Version of record first published: 04 Oct 2006

To cite this article: J. J. Tsaih & L. J. Yu (1997): Mesogenic Behavtors of 4-Cafboxy- and 4-Propenyloxy-Benzo-15-Crown-5 Stilbazolyl Esters, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 302:1, 339-344

To link to this article: http://dx.doi.org/10.1080/10587259708041846

*Mol. Cryst. Liq. Cryst.*, 1997, Vol. 302, pp. 339–344
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# MESOGENIC BEHAVIORS OF 4-CARBOXY- AND 4-PROPENYLOXY-BENZO-15-CROWN-5 STILBAZOLYL ESTERS

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Abstract Mesogens without terminal chain were obtained by connecting benzo-15-crown-5 and stilbazole with carboxy and propenoic acids. A nematic phase was observed for the later on cooling from 145 to 129°C. Hydrogen bond induced nematic and smectic A phases with wide temperature ranges were observed for mixtures containing para- and meta-alkyloxybenzoic acids as proton donors.

## INTRODUCTION

There has been a great deal of studies about crown ethers since the first report by Pedersen in 1967[1]. Macrocyclic polyamine crownethers exhibited disclike mesogenic behaviors were reported by Lehn et al. in 1985.[2] Rodlike molecules consisted of crown ethers as the central cores and connected with two mesogenic terminal chains were reported by Xie et al.[3] and Tuffin et al.[4], enantiotropic mesophases were observed in some cases. Rodlike molecules containing benzocrown ether as the terminal group were reported by He et al.[5] and Percec et al.[6], nonmesogenic or monotropic behaviors were observed.

Incorporation of photoactivity with the functions of crown ether has attracted attentions and interesting behaviors were reported.[7,8] Stilbazole and 4-alkyloxy-4'-stilbazole were known to undergo photoisomerization and photodimerization.[9] When the alkyloxy chain were replaced by 4-alkyloxy-benzoyloxy group, much wider and higher mesophase temperatures were observed.[10] These single terminal chain mesogens behaved as proton acceptors due to the pyridine ring at the other end. Various mesophases could be induced with suitable proton donors.[11]

In the present study, the stilbazole was connected to benzo-15-crown-5 by an ester and an acrylate, SPBCE and SPCCE, respectively. These molecules possessed no terminal group and exhibited mesophases. With the presence of 4-alkyloxy benzoic acid

(CnOBA) and 3- alkyloxy benzoic acid(m-CnOBA), wide nematic and smectic A phases were induced due to the formation of hydrogen bond.

## EXPERIMENTAL

The synthetic proceduces of SPBCE were shown in Scheme 1. The proceduces for SPCCE were the same except that caffeic acid was the starting reagent. The results of elemental analysis and proton NMR spectra for all the intermediates and final products agreed with those of desired structures.[12]

The mixtures contained 1:1 mole ratio of proton donor and acceptor were prepared by weighing adequate amounts of components into vials and heated to isotropic for mixing. The textures displayed between microscopic slide and coverslip were characterized with an optically polarized microscope (NIKON, OPTIPHOT-POL) equipped with a heating stage (Mettler FP800 and FP82). The transition enthalpy was measured by a differential scanning calorimeter (Mettler FP800 and FP85). The NMR spectra were recorded by a Bruker AC 300 NMR spectrometer. The elemental analysis was carried out by a Heraeus CHN-O-RAPID elemental analyzer and molecular mass was determined by a VG BIOTHECH Trio-2000 GC Mass spectrometer.

## RESULTS

The crystals of SPBCE melted into isotropic liquid at 147-150°C. Upon quench cooling a nematic texture immediately followed by crystallization was observed. However, when the cooling rate was programmed(<10°C/min) no mesophase was observed. The crystals of SPCCE became isotropic at 180-182°C. The isotropic liquid changed to Schlieren texture of nematic phase with 2- and 4-brush at 146°C on cooling (rate 5°C/min), which crystallized at 128°C.

The mesophase behaviors for mixtures of SPBCE and CnOBA and m-CnOBA were shown in Table I and II, respectively. Enantiotropic nematic phases were observed for CnOBA/SPBCE with $n \leqq 6$ for the alkyloxy chain. Monotropic nematic and smectic A phases were observed for n=7, and nearly so for n=8. Enantiotropic nematic and smectic A for n=9 and 10. Only enantiotropic smectic A was observed for $n \geqq 12$. For the mixtures of m-CnOBA/SPBCE, monotropic nematic phase was observed for $n \leqq 5$, and enantiotropic smectic A for $n \geqq 7$.The temperature ranges of these hydrogen bond induced mesophases were apparently narrower than those of CnOBA/SPBCE mixtures.

When compound SPCCE was employed as the proton acceptor, much wider mesophase temperature ranges with higher isotropic temperatures were observed, Fig.1 and 2. For mixtures of CnOBA/SPCCE, enantiotropic nematic for n=4 and 5, and

enantiotropic nematic and smectic A for n=6 up to 12 were observed. For mixtures of m-CnOBA/SPCCE, enantiotropic nematic and smectic A for n=4 up to 7, and enantiotropic smectic A for n≧8 were observed. The mixtures of m-CnOBA/SPCCE remained as smectic A at room temperature for days.

## DISCUSSION

The molecules SPBCE and SPCCE consisted of a stilbazole at one end and a benzo-15-crown-5 at the other. These molecules possessed no terminal groups, unlike the typical rod-like mesogens. Forthermore, the diameter of the 15C5 moiety is about 2 times that of a benzene or pyridine ring. Therefore the formation of mesophase would be less likely as compared to the typical rod-like molecules of the same molecular weight. As a matter of fact, 4-alkyloxy-4'-stilbazole homologues exhibited smectic B phases(~10°C) and 4-[4'-alkyloxy benzoyloxy]-4"stilbazole homologues exhibited nematic and smectic A phases (60-100°C). These were also stilbazole containing molecules but with one terminal chain. Apparently, it was due to the bulky factor of the crown moiety the stability of the meso-phase was reduced.

The formation of mesophases were expected when proton donors were mixed with these two proton acceptors. For the hydrogen bonded complexes, the molecular length was increased and a flexible chain was attached. These factors strongly stabilized the mesophases although the complexes still consisted of a benzocrown moiety.

The mixtures consisted of m-CnOBA as the proton donor exhibited narrower mesophase temperature ranges and lower isotropic temperatures. These effects were attributed to the meta-position substitution of the alkyloxy chains. A lateral substitution would reduce the mesophase temperature range.

Acknowledgment:This work was supported by the National Science Council under contract numbers: NSC84-2113-M032-004 and NSC85-2113-M032-002.

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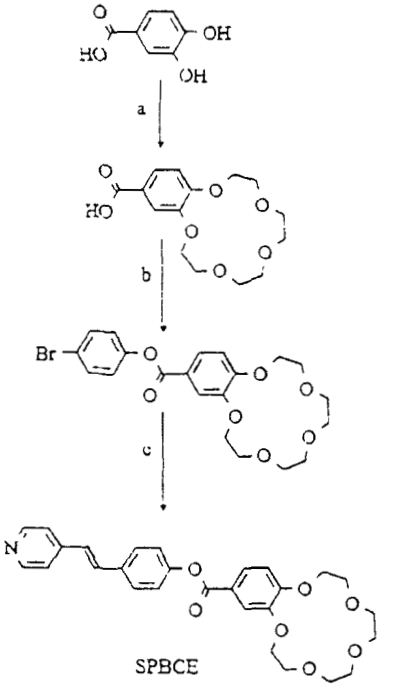
12. The results of elemental analysis of SPBCE ($C_{28}H_{29}O_7N$) were (% ) calcd: C 68.43, H 5.90,N 2.85, found C 68.32, H 5.89, N 2.97. The MS: m/e(rel.intensity,% ) $M^+$ 491(10),295(98), 197(48),163(100).
Those of SPCCE ($C_{30}H_{31}O_7N$)were(% ) calcd: C69.60, H6.00, N2.70,found C 69.53, H 6.10,N 2.76. MS:m/e(rel.int.,% ),$M^+$517(10),321(50),197(60),189(100).

Scheme 1




a : bis-[2-(2-chloroethoxy)-ethyl]-ether , NaOH , NaI , MeOH

b : 4-bromophenol , DCC , DMAP , $CH_2Cl_2$

c : 4VP , $Pd(OAc)_2$ , $PPh_3$ , $Et_3N$ , $CH_3CN$

Table I The phase behaviors of 1:1 mole ratio mixture of p-alkyloxy benzoic acid (CnOBA) and SPBCE .Temperature in ℃.

| n | K | $S_A$ | N | I |
|---|---|---|---|---|
| 4 | . 153 | | . 171 | . |
| 5 | . 132 | | . 167 | . |
| 6 | . 149 | | . 164 | . |
| 7 | . 166 | (. 128) | (. 160) | . |
| 8 | . 155 | (. 134) | . 158 | . |
| 9 | . 114 | . 147 | . 163 | . |
| 10 | . 117 | . 154 | . 161 | . |
| 12 | . 115 | . 156 | | . |
| 14 | . 124 | . 168 | | . |

Table II The phase behaviors of 1:1 mole ratio of m-alkyloxy benzoic acid (m-CnOBA) and SPBCE .Temperature in ℃.

| n | K | $S_A$ | N | I |
|---|---|---|---|---|
| 3 | . 104 | | (. 97) | . |
| 4 | . 102 | | (. 91) | . |
| 5 | . 89 | | (. 75) | . |
| 6 | . 91 | | . 93 | . |
| 7 | . 85 | . 92 | | . |
| 8 | . 83 | . 97 | | . |
| 9 | . 87 | . 104 | | . |
| 10 | . 97 | . 105 | | . |

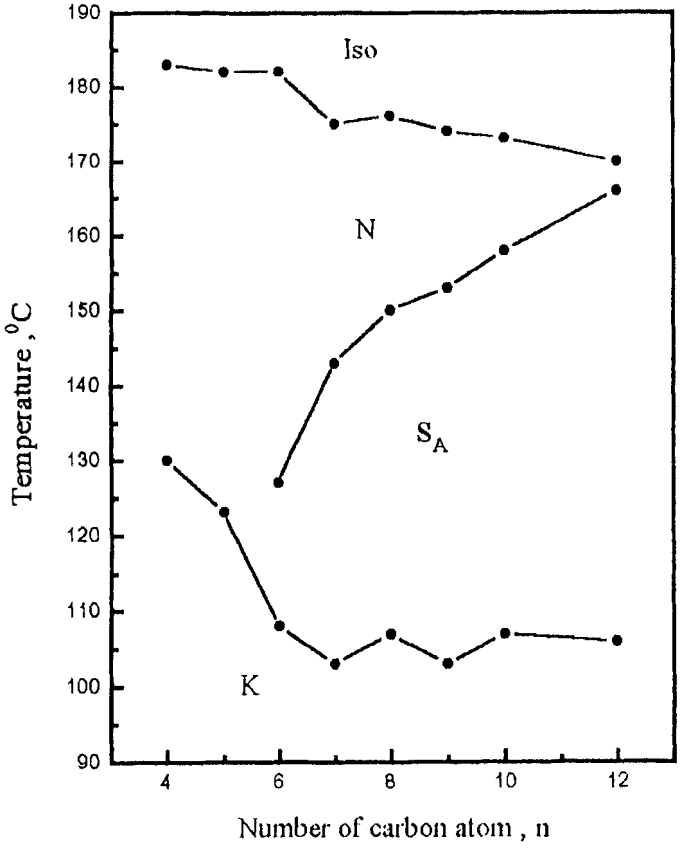



Figure 1 The phase diagram of 1:1mole ratio of p-alkyloxy benzoic acid (CnOBA) and SPCCE.

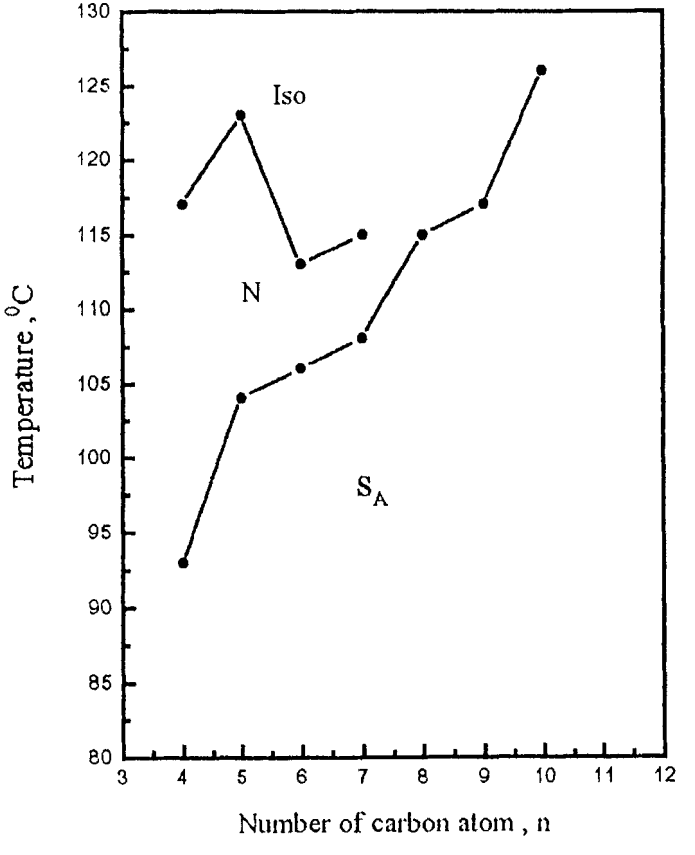



Figure 2 The phase diagram of 1:1mole ratio of m-alkyloxybenzoic acid (m-CnOBA) and SPCCE.