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L. J. Yu [a] & K. Y. Chen [a]
[a] Department of Chemistry, Tamkang University Tamsui, 25137, Taiwan, Republic of China
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THE MESOGENIC 6-ALKOXY-2-(2-(4-PYRIDYL)ETHENYL)NAPHTHALENE HOMOLOGUES

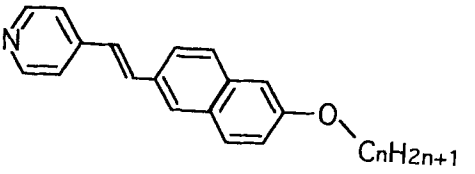
L. J. YU and K. Y. CHEN
Department of Chemistry, Tamkang University
Tamsui, Taiwan 25137, Republic of China

Abstract Enantiotropic smectic B phases were observed for the homologues of 6-alkoxy-2-(2-(4-pyridyl)ethenyl) naphthalene. Chiral nematic and chiral smectic C phases were observed for mixtures with terephthalic acid mono-(2-methylbutyl) ester as chiral proton donor. These behaviors were similar to that of 4-alkoxy-4'-stilbazole.

INTRODUCTION

The photochemically active materials have attracted a great deal of attention because of their application in optical data storage. Association of liquid crystal properties with these materials would bring more advantages due to the mesophase behaviors. It was reported recently that the 4-alkoxy-4'-stilbazole (C_nOSB) exhibited just these behaviors.[1,2] Furthermore, it was shown that C_nOSB homologues behaved as proton acceptors and ferroelectric liquid crystals were obtained by mixing with chiral proton donors.[3]

In the present study, a naphthyl moiety was used to replace the phenyl ring of C_nOSB. The mesophases and hydrogen bond induced mesophases were reported for 6-alkoxy-2-(2-(4-pyridyl)ethenyl)naphthalene ($6NPC_n$) homologues.



6NPCn

EXPERIMENTAL

The synthesis of 6-alkoxy-2-(2-(4-pyridyl)ethenyl)naphthalene ($6NPC_n$)homologues followed that of 4-alkoxy-4'-stilbazole.[3,4,5] The results of elemental analysis and proton NMR spectra agreed well with the required structures.

The nonmesogenic chiral mono-(2-methylbutyl) ester of terephthalic acid (MBTA) was used as chiral proton donor. The mixtures of a 1:1 molar ratio of MBTA and $6NPC_n$ were obtained by weighing the components into a vial and heating to isotropic for mixing. The mesophase textures were characterized by a polarizing optical microscopy (Nikon, OPTIPHOT-POL) in conjunction with a heating stage (Mettler, FP 80-82). The transition temperatures were checked, and enthalpy values were measured by a differential scanning calorimetry (Perkin-Elmer,DSC-2).

RESULTS AND DISCUSSION

The results of elemental analysis of the obtained $6NPC_n$ homologues were given in Table 1. As can be seen from the table, these results agreed well with the calculated values. The proton NMR spectra showed a coupling constant of 16 cps for the ethenyl protons indicated that the obtained products consisted of trans-configuration.

The mesophase behaviors observed for these homologues were shown in Table 2 and also shown in Figure 1. The lower members of the $6NPC_n$ homologues (n = 1,

TABLE 1 The elemental results of 6-alkoxy-2-(2-(4-pyridyl)ethenyl)-naphthalene homologues, $6NPC_n$

n	Formular		C,%	H,%	N,%
1	$C_{18}H_{15}NO$	calcd	82.76	5.75	5.36
		obsed	82.21	5.80	5.32
4	$C_{21}H_{21}NO$	calcd	83.17	6.93	4.62
		obsed	83.03	7.03	4.67
5	$C_{22}H_{23}NO$	calcd	83.28	7.26	4.42
		obsed	83.12	7.45	4.47
6	$C_{23}H_{25}NO$	calcd	83.39	7.55	4.23
		obsed	83.26	7.67	4.27
7	$C_{24}H_{27}NO$	calcd	83.45	7.82	4.06
		obsed	83.38	7.86	4.13
8	$C_{25}H_{29}NO$	calcd	83.57	8.08	3.90
		obsed	83.55	8.12	3.94
9	$C_{26}H_{31}NO$	calcd	83.60	8.31	3.75
		obsed	83.67	8.39	3.77
10	$C_{27}H_{32}NO$	calcd	83.72	8.53	3.62
		obsed	83.74	8.55	3.63
12	$C_{29}H_{37}NO$	calcd	83.86	8.92	3.37
		obsed	83.54	8.96	3.44
14	$C_{31}H_{41}NO$	calcd	83.97	9.26	3.16
		obsed	83.81	9.27	3.18

Table 2 The phases, transition temperatures (°C) and enthalpy (kJ/mol, in parenthesis) of 6-alkoxy-2-(2-(4-pyridyl)ethenyl)naphthalene homologues.

n	Phase behavior
1	K ---(186- 188)---> I
4	K ---(139 - 141)---> I
5	K ---(122 - 126)---> I
6	K ---(118, 19.06)---> S_B ---(130, 14.29)---> I
7	K ---(104, 19.94)---> S_B ---(126.5, 14.09)---> I
8	K ---(106.5, 19.36)---> S_B ---(127, 12.36)---> I
9	K ---(98, 18.28)---> S_B ---(126.5, 12.65)---> I
10	K ---(104.5, 26.96)---> S_B ---(125.4, 16.34)---> I
12	K ---(103.5, 26.0)---> S_B ---(123, 13.0)---> I
14	K ---(106.9, 32.14)---> S_B ---(120, 15.45)---> I

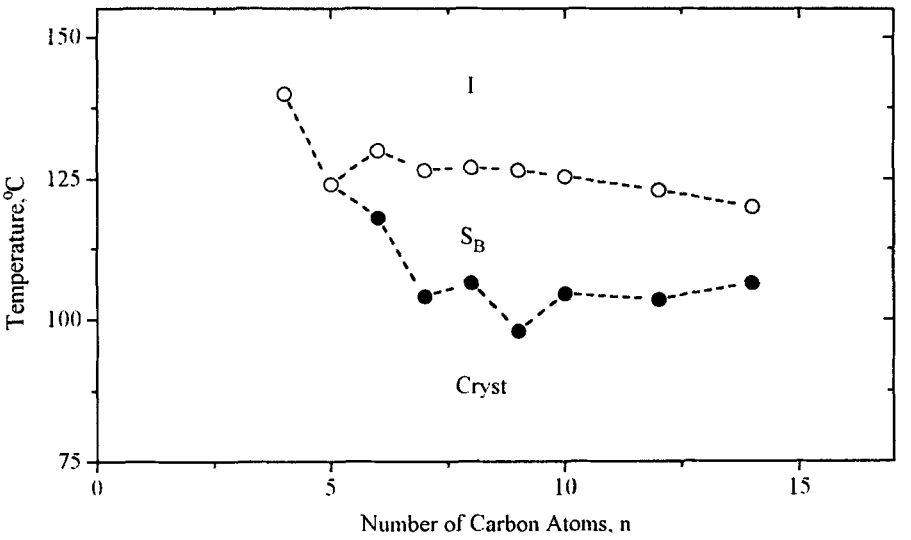


FIGURE 1 Phases as a function of carbon number of 6-alkoxy-2-(2-(4-pyridyl)ethenyl)-naphthalene homologues, $6NPC_n$.

4 and 5) exhibited a direct transition from crystal to isotropic with temperatures higher than those of phenyl analogues (C_nOSB) by about 40-50 degrees.[5] For the members with longer end chains ($n \geq 6$) a single enantiotropic smectic B phase was observed.

The temperatures of crystal to S_B and S_B to isotropic were in general higher than those of C_nOSB by 20 and 40 degrees, respectively. The smectic B phases of $6NPC_n$ existed at higher temperatures and with wider temperature ranges. However, the enthalpy values for S_B to isotropic were the same as those of C_nOSB homologues.[3,5] These observations were consistent with those of general believes, and the increases of melting and clearing points were attributed to the replacement of phenyl ring by a naphthyl moiety.

The mesophases observed for the mixtures consisted of a 1:1 molar ratio of MBTA and $6NPC_n$ were given in Table 3. For mixtures contained lower members (n = 1 and

Table 3 The mesophases observed for the mixtures of chiral terephthalic acid mono(2-methylbutyl)ester and 6-alkoxy-2-(2-(4-pyridyl)ethenyl)naphthalene homologues in a 1:1 molar ratio.

n	Phase behavior
1	K --133--> S_A --136.5--> N^* --179--> I
4	K --103--> S_A --176.8--> N^* --186--> I
5	K --113--> S_A --174--> I
6	K --118--> S_A --183--> I
7	K --112--> S_A --182--> I
8	K --117--> S_C^* --123--> S_A --183--> I
9	K --118--> S_C^* --128--> S_A --178--> I
10	K --118--> S_C^* --128--> S_A --182--> I
12	K --105--> S_C^* --126--> S_A --178--> I
14	K --98--> S_C^* --130--> S_A --177--> I

4), only enantiotropic S_A and N^* were observed, and no blue phase was observed. For mixtures with n =5, 6, and 7, only smectic A phase was obtained. Enantiotropic chiral smectic C and smecticA were observed for mixtures consisted of members with longer end chains ($n \geq 8$). As compared with those of C_nOSB mixtures,[3] the transition temperatures were in general about 10 degrees higher for the present case. The absence of blue phase in the present mixtures indicated that the helical pitch of chiral nematic phase was larger than those of C_nOSB mixtures. The slight increase of transition temperatures was resulted from the presence of naphthyl moiety.

In conclusion, the thermal behaviors of $6NPC_n$ homologues were similar to those of C_nOSB homologues but with higher thermal stability. This effect was attributed to the stronger intermolecular interactions in $6NPC_n$ than in C_nOSB.

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