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Novel bent-shaped liquid crystalline compounds: IV. Dimesogenic compounds containing 2-hydroxy-1,3-dioxypropylene and azobenzene mesogens

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Abstract

Three bent-shaped dimesogenic liquid crystalline compounds having odd-numbered terminal alkyloxy chains ($n = 5, 7, 9$) with a 2-hydroxy-1,3-dioxypropylene as central linking unit and two identical azobenzene mesogens were synthesized. Their mesomorphic properties were then characterized by polarized light microscopy and differential scanning calorimeter. The terminal alkoxy chain length was the key factor to provide the liquid crystallinity in this series. The compound of $n = 7$ showed a monotropic SmC phase, and that of $n = 9$ displayed an enantiotropic SmC phase. The compound of $n = 5$, however, did not show liquid crystal phase. The thermal stability of the smectic phases also increased with the terminal alkoxy length.

Keywords: Bent-shaped liquid crystal; Dimer; Azobenzene; Smectic C; Thermal stability

1. Introduction

Liquid crystalline dimesogens (dimers, bimesogens, twins, etc.) are attracting much attention in recent years because they exhibit variety of phases, and serve as useful models for semi-flexible, main-chain liquid crystal polymers [1–3]. In typical dimesogens, two individual mesogenic entities are linked to each other via flexible polymethylene spacer units. Of special interest are those containing mesogens based on azobenzene moiety. Azobenzenes can undergo reversible *trans–cis* (*E*/*Z*) isomerization upon irradiation with UV/vis light, which allows one to change physical properties of these materials by simple irradiation. A survey of liquid crystals composed of bent-shaped molecules revealed that compounds with azo linkages have hardly been studied. Nevertheless, azo compounds are very attractive for their high thermal stability and for the photo-induced effects as well as for the potential applications in liquid crystal displays and devices, reversible optical storage systems, nonlinear optical waveguides, photorefractive switches, and holographic gratings. Precise placement of photochromic moieties within the liquid crystal dimesogen also could lead to reversible photo-induced configurational and constitutional changes [4]. Recently, our group reported [5] that the bent-shaped azobenzene-typed dimers ($2A_n$) with an even-numbered terminal chains ($n = 6, 8, 10, 12$) showed smectic C mesophase for the compounds of $n = 8$, 10 and 12, but not with the compound of $n = 6$.

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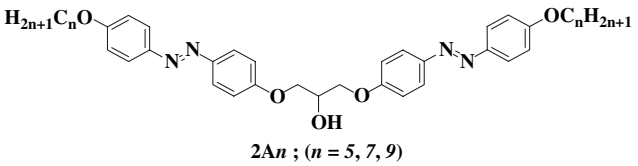


Fig. 1. Structure of liquid crystalline dimesogens ($2A_n$).

In the present work, we synthesized homologous compounds with odd-numbered terminal chains, and investigated for their liquid crystallinity. This article reports the synthesis and the mesomorphic properties of odd-membered dimers ($2A_n$: $n = 5$, 7 and 9) in comparison with the already reported even-membered dimers [5,6]. The materials containing two azobenzene mesogenic units with terminal alkoxy chains are depicted in Fig. 1.

2. Experimental

2.1. Materials

Anhydrous ethanol, *p*-toluenesulfonic acid (PTSA), 4-nitrophenol, 1-bromopentane, 1-bromoheptane, 1-bromononane, palladium on activated carbon (10% Pd/C), hydrazine monohydrate, epichlorohydrin (ECH), $NaNO_2$ were purchased from Aldrich Chemical Co. and used as received. All other solvents and reagents were purchased commercially and used without further purification.

2.2. Measurements

IR spectra were recorded with a Perkin-Elmer 1000 FT-IR spectrophotometer on KBr pellets. ^{1}H NMR spectra were recorded by using a Varian Mercury 300 (300 MHz) NMR spectrometer. Differential scanning calorimetric measurements were performed using a TA instrument 910S DSC apparatus under dry nitrogen flow at the scanning rate of 10 °C/min. The transition temperatures were taken at the maximum point of the peaks for each sample. The transition enthalpies were evaluated from the integrated area of the endothermic peaks using a reference indium sample as the standard. Optical microscopy observation was carried out using a Nikon Labophot-2 polarizing microscope fitted with a RTC-1 temperature controller (Instec Inc., Broomfield, Co.) and a Mettler FP-82HT hot stage.

2.3. Synthesis of dimesogens

The $2A_n$ dimesogens were prepared as illustrated in Scheme 1. $2A_n$ were synthesized according to the method described in the literature [5–7]. Final products and intermediates were structurally characterized by IR, ^{1}H NMR and elemental analysis (CE instruments, Flash EA 1112 Series).

2.3.1. 4-Pentyloxy-4′-hydroxyazobenzene (A_5)

Brown solid (50%, mp. 104 °C). IR (KBr, cm^{-1}): 3315 (stretch, *OH*), 1580 (stretch, N=N). ^{1}H NMR ($CDCl_3$, ppm): δ 0.91 (t, 3H, CH_3), 1.20–1.47 (m, 4H, $(CH_2)_2$), 1.80 (m, 2H, CH_2CH_2O), 4.01 (t, 2H, CH_2CH_2O), 5.40 (s, 1H, *OH*), 6.93–7.90 (m, 4H, Ar–H). Elemental analysis: calcd for $C_{17}H_{20}N_2O_2$, C 71.81, H 7.09, N 9.85; found C 71.78, H 7.01, N 9.89%.

2.3.2. 4-Heptyloxy-4′-hydroxyazobenzene (A_7)

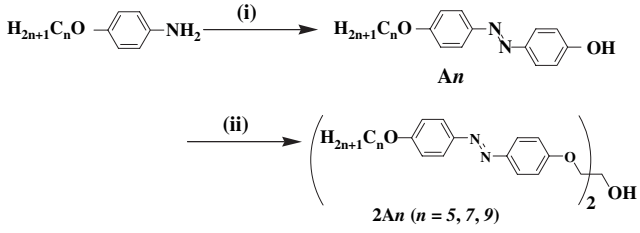
Brown solid (65%, mp. 102.3 °C). IR (KBr, cm^{-1}): 3305 (stretch, *OH*), 1575 (stretch, N=N). ^{1}H NMR ($CDCl_3$, ppm): δ 0.92 (t, 3H, CH_3), 1.21–1.52 (m, 8H, $(CH_2)_4$), 1.85 (m, 2H, CH_2CH_2O), 4.02 (t, 2H, CH_2CH_2O), 5.29 (s, 1H, OH), 6.95–7.94 (m, 4H, Ar–H). Elemental analysis: calcd for $C_{19}H_{24}N_2O_2$, C 73.05, H 7.74, N 8.97; found C 73.01, H 7.69, N 9.01%.

2.3.3. 4-Nonyloxy-4′-hydroxyazobenzene (A_9)

Brown solid (70%, mp. 108.2 °C). IR (KBr, cm^{-1}): 3320 (stretch, *OH*), 1575 (stretch, N=N). ^{1}H NMR ($CDCl_3$, ppm): δ 0.93 (t, 3H, CH_3), 1.29–1.61 (m, 12H, $(CH_2)_6$), 1.89 (m, 2H, CH_2CH_2O), 4.00 (t, 2H, CH_2CH_2O), 5.33 (s, 1H, OH), 6.99–7.90 (m, 4H, Ar–H). Elemental analysis: calcd for $C_{21}H_{28}N_2O_2$, C 74.08, H 8.29, N 8.23; found C 74.02, H 8.32, N 8.29%.

2.3.4. 1,3-Bis-(4-(4-pentyloxyphenylazo) phenoxy)propan-2-ol ($2A_5$)

Yellow solid (34%). IR (KBr, cm^{-1}): 3482 (stretch, *OH*), 1595 (stretch, N=N). ^{1}H NMR ($CDCl_3$, ppm):



Scheme 1. Synthesis of dimesogens. (i) PhOH, $NaNO_2$, HCl; (ii) ECH, K_2CO_3, EtOH.

δ 0.95 (t, 6H, CH_3), 1.29–1.61 (m, 8H, $(CH_2)_2$), 1.89 (m, 4H, CH_2CH_2O), 2.77 (broad, 1H, $OCH_2CH(OH)CH_2O$), 4.00 (t, 4H, CH_2CH_2O), 4.11 (d, 4H, $OCH_2CH(OH)CH_2O$), 4.35 (m, 1H, $OCH_2CH(OH)CH_2O$), 7.05 (dd, 8H, Ar–H), 7.85 (d, 8H, Ar–H). Elemental analysis: calcd for $C_{37}H_{44}N_4O_5$, C 71.13, H 7.10, N 8.97; found C 71.07, H 7.15, N 8.90%.

2.3.5. 1,3-Bis-(4-(4-heptyloxyphenylazo) phenoxy)propan-2-ol ($2A_7$)

Yellow solid (53%). IR (KBr, cm^{-1}): 3495 (stretch, *OH*), 1600 (stretch, N=N). ^1H NMR ($CDCl_3$, ppm): δ 0.92 (t, 6H, CH_3), 1.29–1.58 (m, 16H, $(CH_2)_4$), 1.86 (m, 4H, CH_2CH_2O), 2.70 (broad, 1H, $OCH_2CH(OH)CH_2O$), 4.02 (t, 4H, CH_2CH_2O), 4.08 (d, 4H, $OCH_2CH(OH)CH_2O$), 4.25 (m, 1H, $OCH_2CH(OH)CH_2O$), 7.03 (dd, 8H, Ar–H), 7.84 (d, 8H, Ar–H). Elemental analysis: calcd for $C_{41}H_{52}N_4O_5$, C 72.32, H 7.70, N 8.23; found C 72.29, H 7.69, N 8.20%.

2.3.6. 1,3-Bis-(4-(4-nonyloxyphenylazo) phenoxy)propan-2-ol ($2A_9$)

Yellow solid (50%). IR (KBr, cm^{-1}): 3494 (stretch, *OH*), 1597 (stretch, N=N). ^1H NMR ($CDCl_3$, ppm): δ 0.93 (t, 6H, CH_3), 1.25–1.68 (m, 24H, $(CH_2)_6$), 1.85 (m, 4H, CH_2CH_2O), 2.75 (broad, 1H, $OCH_2CH(OH)CH_2O$), 4.00 (t, 4H, CH_2CH_2O), 4.18 (d, 4H, $OCH_2CH(OH)CH_2O$), 4.32 (m, 1H, $OCH_2CH(OH)CH_2O$), 7.02 (dd, 8H, Ar–H), 7.86 (d, 8H, Ar–H). Elemental analysis: calcd for $C_{45}H_{60}N_4O_5$, C 73.34, H 8.21, N 7.60; found C 73.30, H 8.19, N 7.55%.

3. Results and discussion

The synthetic route used for the preparation of dimesogens ($2A_n$) is outlined in Scheme 1. The mesomorphic properties for the series of dimesogens were determined by means of differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). Table 1 summarizes the thermal transitions and thermodynamic parameters of $2A_n$ dimesogens. Fig. 2 presents the DSC heating and cooling traces of dimesogens ($2A_5$, $2A_7$ and $2A_9$). In the heating scans, only the compound with the longest terminal chains ($n = 9$) in this series shows a crystal to smectic C phase transition at 163 °C and a smectic C to isotropic phase transition at 168 °C. In contrast, the compounds of relatively shorter terminal chains ($n = 5$ and 7) do not show liquid crystalline phase. In the cooling scans, however, the smectic mesophase emerges for the compounds of $n = 7$ and 9, but not for the $n = 5$ compound. Optical micrographs obtained during the cooling cycle are shown in Fig. 3(a) and (b). The micrographs exhibit schlieren textures of the smectic C phase for the $2A_7$ and $2A_9$. Results of the thermal transitions and texture analysis for $2A_n$ series with azobenzene mesogens suggest that the compound of $n = 9$ forms an enantiotropic liquid crystal of SmC phase with the schlieren texture, and $n = 7$ a monotropic liquid crystal of SmC phase with the schlieren or broken-fan texture. The compound having the shortest terminal chains ($n = 5$), on the other hand, does not show liquid crystal phase.

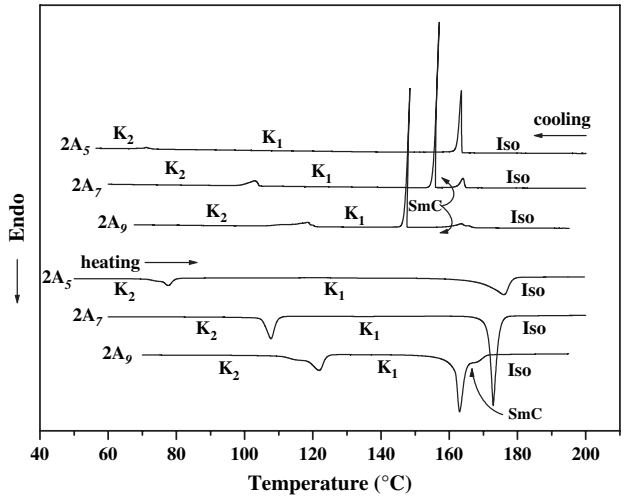


Fig. 2. Differential scanning calorimetric curves for $2A_5$, $2A_7$ and $2A_9$ (10 °C/min).

In Fig. 4, the dependence of the transition temperatures on the terminal chain length n for all $2A_n$ series including even-numbered compounds [5,6] and odd-numbered terminal chains (this work) are compared. Since the molecules are bent-shaped dimers with two

Table 1
Thermal transition behaviors and thermodynamic data for $2A_n$ dimesogens

n	Phase transitions (°C)[a]	ΔH_{K_1-S} (kJ/mol)	ΔH_{S-I} (kJ/mol)	ΔS_{K_1-S} (J/K mol)	ΔS_{S-I} (J/K mol)	Ref.
10	K_2 122.6, K_1 150.3, SmC 173.0 I	52.6	12.1	124.2	27.1	[6]
9	K_2 118.2, K_1 146.2, SmC 164.1 I	24.2	10.0	57.8	22.9	This work
8	K_2 105.5, K_1 155.2, SmC 170.5 I	44.1	8.7	102.9	19.5	[6]
7	K_2 102.9, K_1 153.4, SmC 163.0 I	48.0	4.1	112.6	9.3	This work
6	K_2 83.3, K_1 164.0 I	68.3	–	156.3	–	[6]
5	K_2 71.3, K_1 162.3 I	40.4	–	92.7	–	This work
4	K_2 77.2, K_1 182.4 I	62.7	–	137.5	–	[8]

[a] K_1 and K_2 = crystalline states, SmC = smectic C phase, I = isotropic state, all data are obtained from 2nd cooling scan at 10 °C/min.

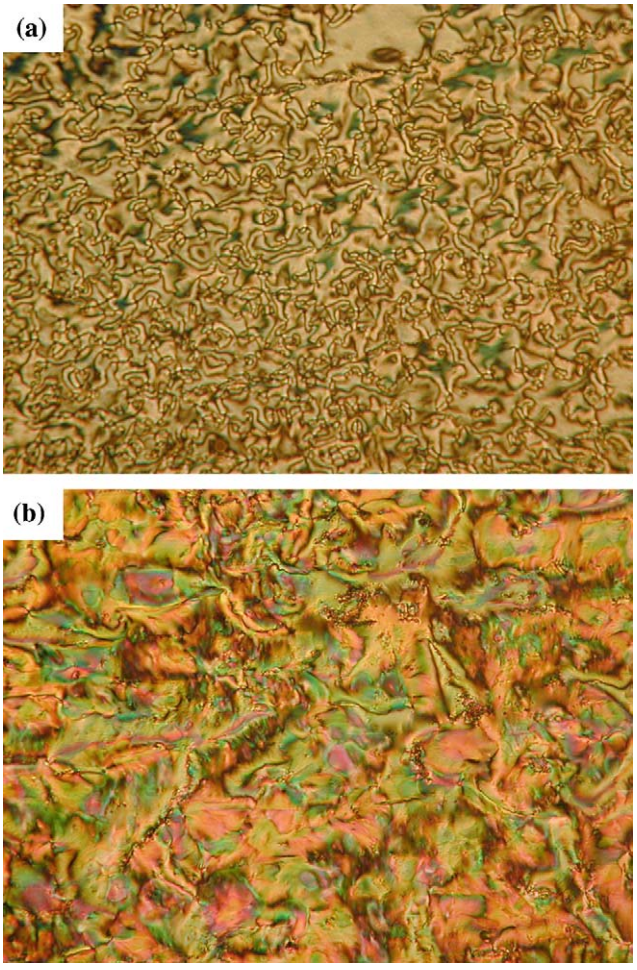


Fig. 3. Optical micrographs of (a) Schlieren texture (160 °C, $2A_7$); (b) Schlieren texture (160.2 °C, $2A_9$) (×100).

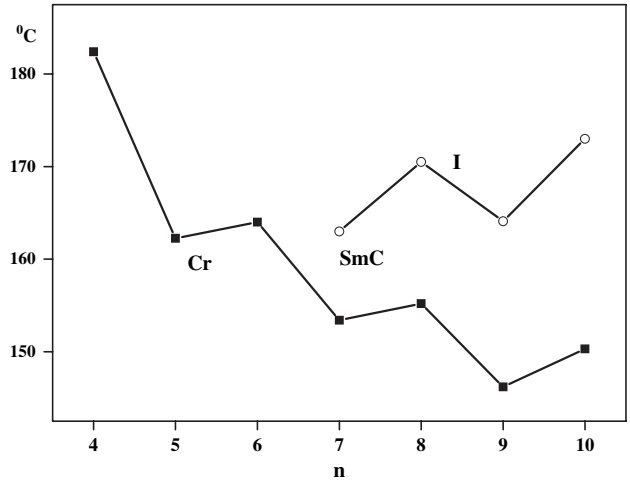


Fig. 4. The dependence of the transition temperatures on the number of carbons, n, in the terminal chain for $2A_n$ series. ■ indicates crystallization points and ○ isotropic–smectic C transitions. The transition temperatures are based on DSC cooling data.

terminal chains, increasing the terminal chain length is anticipated to increase significantly the length-to-breadth ratio resulting in liquid crystal phases, and particularly smectic phases, being stabilized at higher temperatures for higher homologues. In the figure, the compounds of short terminal changes only show isotropic to crystal transition without liquid crystallinity, but those of longer terminal chains ($n \geq 7$) show emergence of the smectic mesophase. We also note that the temperature range of the smectic mesophase increases with the terminal chain length. The compounds of $n = 10$ show the largest temperature interval extending to 23 °C. Also the entropy changes for the clearing to smectic transitions continue to increase with increasing n. These results demonstrate that the tendency toward smectic mesomorphism and the thermal stability of tilted smectic phase increases with increasing terminal alkoxy chain length. This may be the result of the terminal alkoxy chains lying at an angle to the long molecular axis inducing the molecular tilt between neighboring molecules. And an even–odd alternation effect noted in this series as a function of the parity of the terminal chains has often been observed in the recrystallization and isotropic–smectic transition temperatures of the compounds containing mesogens. The effects of the terminal chain length on the transition temperatures and phases behavior observed in this series are in accord with those observed for conventional low molar mass mesogens.

4. Conclusion

We synthesized homologous azo-typed dimers ($2A_n$) consisting of two azobenzene mesogenic units with odd-numbered terminal alkoxy chains ($n = 5$, 7 and 9). Their mesomorphic properties were examined in conjuction with the even-numbered homologues reported previously [5,6]. The tendency toward smectic mesomorphism increased with the increase of the terminal alkoxy chain length. The compound of $n = 7$ and 9 showed monotropic SmC phase and enantiotropic SmC phase, respectively. But the compound of $n = 5$ did not show liquid crystal phase. The thermal stability of tilted smectic phase also increased with increasing the terminal alkoxy chain length. Combining the results of those with even-numbered alkoxy chains [5,6], the system showed an even–odd effect in the phase transition temperatures.

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