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Synthesis and transition properties of novel dimesogenic compounds possessing *cis*-1, 4-dioxa-2-butene as a linking group

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We have designed novel liquid crystalline compounds in which two mesogenic units are connected via *cis*-2-buten-1,4-diol. We prepared *cis*-4-{6-[4-(4-cyanophenyl)phenyloxy]-hexyloxy}-1-{6-[4-(4-methyloxy)phenyloxy]hexyloxy}-2-butene (6OCMBCB), *cis*-1,4-bis{6-[4-(4-cyanophenyl)phenyloxy]hexyloxy}-2-butene (6OCCBCB) and *cis*-1,4-bis{6-[4-(4-methyloxy)-phenyloxy]hexyloxy}-2-butene (6OMMBCB), and investigated their transition properties. 6OCMBCB and 6OCCBCB exhibited nematic phases whereas 6OMMBCB showed no liquid crystalline phase. We discuss the effects of the mesogenic structure and linkage group on the transition behaviour of the dimesogenic compounds.

1. Introduction

The driving force of mesophase formation is a fundamental topic of study in molecular assembly. A primary factor in the formation of thermotropic liquid crystal phases is the gross molecular shape of a compound [1, 2]. Well designed intermolecular interactions, viz. metal-containing systems [3, 4], charge-transfer systems [5] and hydrogen-bonded systems [6], have been much investigated. Recently, molecular topology [1] and microsegregation [7] have attracted much attention as the basis for producing novel self-organizing systems. Supramolecular assemblies composed of supermolecules [8], i.e. dimeric and oligomeric liquid crystals, and dendrimers [9–11], have been investigated extensively. Dimeric liquid crystals are attractive because they exhibit different properties from the corresponding low molar mass mesogens [12]. For example, the transition properties of dimeric liquid crystals are known to depend critically on the length and parity of the flexible spacer. Many kinds of dimeric and trimeric mesogenic molecules have been reported [13, 14]. We have reported novel liquid crystal oligomers; U-shaped molecules [15], V-shaped molecules [16], binaphthyl derivatives [17], λ–shaped molecules [18] and chiral T-shaped molecule [19]. The liquid crystal oligomers were found to induce various frustrated phases in the supramolecular liquid crystalline phase.

Recently, Luckhurst *et al.* reported that experiments on dielectric relaxation in symmetric and non-symmetric bimesogns have been successfully explained in terms of a temperature-dependent equilibrium between extended and bent conformations [20]. We have therefore designed a new liquid crystal oligomer in which a mesogenic unit with an electron-accepting group and one with an electron-donating group are connected via *cis*-2-buten-1,4-diol. Two main conformers, the linear-extended and U-shaped configurations, are thought to exist as shown in figure 1. The equilibrium between them can depend on several factors, e.g. space filling considerations, intermolecular interactions and intramolecular interactions. We have investigated the effects of the mesogenic unit and linkage group on the phase transition properties of the liquid crystal oligomer.

2. Experimental

2.1. *Spectroscopic analysis*

Purification of final products was carried out using column chromatography over silica gel (63–210 µm) (Kanto Chemical Co., Inc.) using dichloromethane or a dichloromethane/ethyl acetate mixture as the eluant, followed by recrystallization from ethanol. The purities of final compounds were checked by thin layer chromatography (TLC, aluminum sheets, silica gel 60 F254, Merck); dichloromethane was used as the solvent, and products were detected by UV irradiation (λ=254 and 365 nm).

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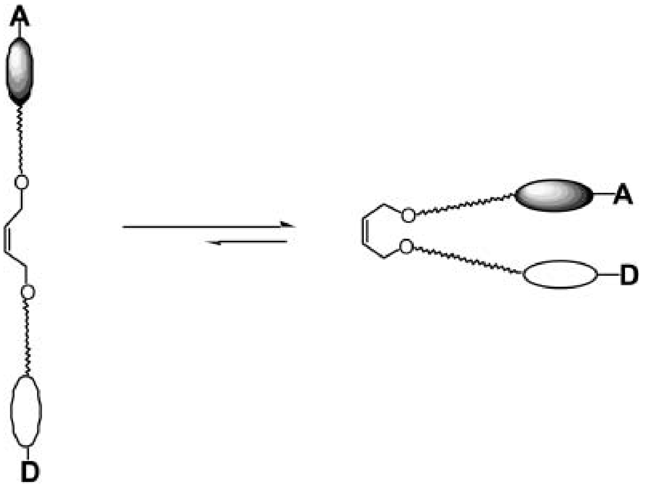


Figure 1. Equilibrium between extended and bent conformations in a dimesogen possessing *cis*-1,4-dioxa-2-butene as a linking unit.

The structures of the final products were elucidated by infrared (IR) spectroscopy (BIORAD FTS-30) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy (JEOL JNM-GX270).

2.2. *Preparation of materials*

2.2.1. *cis*-4-{6-[4-(4-Cyanophenyl)phenyloxy]hexyloxy}-1-{6-[4-(4-methyloxy)phenyloxy]hexyloxy}-2-butene, 6OCMBCB. Potassium carbonate (709 mg, 5.1 mmol) was added to a solution of 4-cyano-4′-hydroxybiphenyl (983 mg, 5.0 mmol) and 1, 6-dibromohexane (1.83 g, 7.5 mmol) in cyclohexanone (20 ml). The reaction mixture was stirred at 70°C for 7 h. After filtration of the precipitate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with toluene. 4-Cyano-4′-(6-bromohexyloxy)-biphenyl (**1**) was obtained; yield 982 mg (2.7 mmol, 55%). Formation of the disubstituted compound was estimated to be less than 10%, suppressed by the low reaction temperature.

Potassium carbonate (1.73 g, 13 mmol) was added to a solution of 4-methoxy-4′-hydroxybiphenyl (2.00 g, 10 mmol) and 1, 6-dibromohexane (3.66 g, 15 mmol) in cyclohexanone (30 ml). The reaction mixture was stirred at 70°C for 8 h. After filtration of the precipitate, the solvent was removed by evaporation. The residue was purified by washing with chloroform and ethanol to give 4-methoxy-4′-(6-bromohexyloxy)biphenyl (**2**); yield 2.09 g (5.8 mmol, 58%). Formation of the disubstituted compound was estimated to be less than 5%.

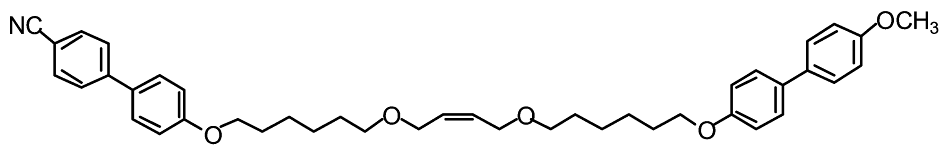
To a solution of *cis*-2-buten-1,4-diol (480 mg, 5.5 mmol) and compound **2** (493 mg, 1.4 mmol) in dimethylformamide (30 ml) was added potassium hydroxide (100 mg, 1.8 mmol). The reaction mixture was stirred at room temperature for 20 h. The solvent was removed by evaporation and the residue dissolved in dichloromethane. After filtration of particulates, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with a dichloromethane/ethylacetate (3/1) mixture to give *cis*-4-[6-(4′-methoxybiphenyl-4-yloxy)hexyloxy]-2-buten-1-ol (**3**); yield 261 mg (0.70 mmol, 43%).

To a solution of compound **3** (265 mg, 0.72 mmol) and compound **1** (512 mg, 1.4 mmol) in dimethylformamide (30 ml) was added potassium hydroxide (70 mg, 1.2 mmol). The reaction mixture was stirred at room temperature for 40 h. The solvent was removed by evaporation and the residue dissolved into dichloromethane. After filtration of solids, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with a dichloromethane/ethyl acetate (40/1) mixture and recrystallized from an ethanol/ethyl acetate (4/1) mixture to give 6OCMBCB; yield 87 mg (0.13 mmol, 19%). One reason for the low yield is thought to be loss of the desired compound during the purification. ^{1}H NMR (270 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 7.69–7.60 (m, 4H, Ar–**H**), 7.52–7.43 (m, 6H, Ar–**H**), 6.99–6.91 (m, 6H, Ar–**H**), 5.72–5.70 (m, 2H, –**HC**=**CH**–), 4.04 (d, 4H, –O–CH_2–, J=4.9 Hz), 4.02–3.96 (m, 4H, –O–CH_2–), 3.83 (s, 3H, –OCH_3), 3.43 (t, 4H, –O–CH_2–, J=6.5 Hz), 1.81–1.47 (m, 16H, aliphatic–**H**). IR (KBr) ν_{max}/cm^{-1}: 2939, 2864, 2227, 1607, 1500.

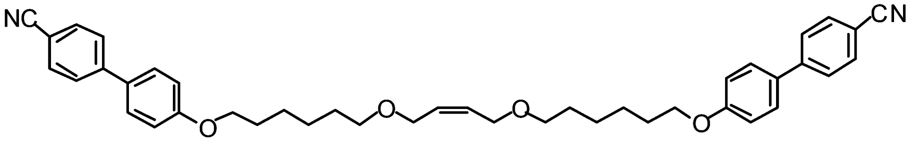
The other compounds were obtained using a similar method to that for 6OCMBCB.

2.2.2. *cis*-1,4-Bis{6-[4-(4-cyanophenyl)phenyloxy]hexyloxy}-2-butene, 6OCCBCB. ^{1}H NMR (270 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 7.70–7.61 (m, 8H, Ar–**H**), 7.51 (d, 4H, Ar–**H**, J=8.9 Hz), 6.98 (d, 4H, Ar–**H**, J=8.9 Hz), 5.72–5.70 (m, 2H, –**HC**=**CH**–), 4.04 (d, 4H, –O–CH_2–, J=4.9 Hz), 4.00 (t, 4H, –O–CH_2–, J=6.5 Hz), 3.43 (t, 4H, –O–CH_2–, J=6.5 Hz), 1.86–1.42 (m, 16H, aliphatic–**H**). IR (KBr) ν_{max}/cm^{-1}: 2937, 2862, 2229, 1603, 1496.

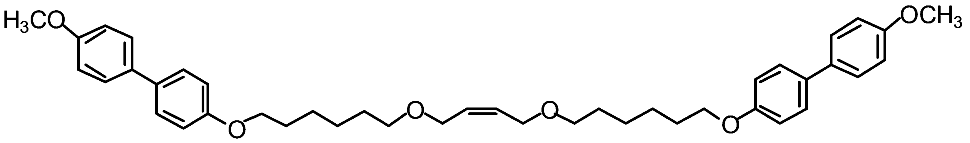
2.2.3. *cis*-1,4-Bis{6-[4-(4-methyloxy)phenyloxy]hexyloxy}-2-butene, 6OMMBCB. ^{1}H NMR (270 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 7.48–7.43 (m, 8H, Ar–**H**), 6.96–6.91 (m, 8H, Ar–**H**), 5.72–5.70 (m, 2H, –**HC**=**CH**–), 4.04 (d, 4H, –O–CH_2–, J=4.9 Hz), 3.98 (t, 4H, –O–CH_2–, J=6.5 Hz), 3.83 (s, 3H, –OCH_3), 3.43 (t, 4H, –O–CH_2–, J=6.5 Hz), 1.83–1.43 (m, 16H, aliphatic–**H**). IR (KBr) ν_{max}/cm^{-1}: 2939, 2864, 1607, 1500.



6OCMBCB



6OCCBCB



6OMMBCB

Figure 2. Molecular structures of mesogeneic compounds containing *cis*-1,4-dioxa-2-butene.

2.3. *Liquid crystalline properties*

The initial assignments and corresponding transition temperatures for the final products were determined by thermal optical microscopy using a Nikon Optiphoto POL polarizing microscope equipped with a Mettler FP82 microfurnance and FP80 control unit. The heating and cooling rates were 5°C min^{-1}. Temperatures and enthalpies of transition were investigated by differential scanning calorimetry (DSC) using a Seiko DSC 6200.

3. Results and discussion

We prepared the non-symmetric dimer 6OCMBCB in which 4-cyanobiphenyl and 4-methoxybiphenyl units are connected via *cis*-2-buten-1,4-diol. We also prepared the corresponding symmetric dimers 6OCCBCB and 6OMMBCB. Molecular structures of those compounds are shown in figure 2. Transition temperatures and enthalpies of transition for the novel oligomeric compounds are listed in table 1.

Both 6OCMBCB and 6OCCBCB exhibited enantiotropic nematic phases whereas 6OMMBCB showed no liquid crystalline phase. The isotropic–nematic transition entropies ($\Delta S/R$) of 6OCMBCB and 6OCCBCB are 0.99 and 1.12, respectively. There is no marked difference in the transition entropy between them. To determine the virtual T_{IN} of 6OMMBCB, we performed miscibility studies between 6OCCBCB and 6OMMBCB; figure 3 shows their binary phase diagram. The virtual T_{IN} of 6OMMBCB is estimated to be 378 K from the data in figure 3, by extrapolating the virtual T_{IN} measured for the binary mixtures to 100% of 6OMMBCB. Thus the I–N transition temperatures for 6OCMBCB, 6OCCBCB and 6OMMBCB are 386, 380 and 378 K, respectively.

From these results it can be seen that the nature of the *p*-substituent in the biphenyl groups does not change

Table 1. Transition temperatures (K) and enthalpies (kJ mol^{-1}, in brackets) of transition for the novel oligomeric compounds.

Compound	Cr	N	I	m.p.
6OCMBCB	• 372 (12.2)	• 386 (3.19)	•	374 (13.0)
6OCCBCB	• 342 (48.5)	• 380 (3.54)	•	348 (48.4)
6OMMBCB	• 395 (62.8)		•	415 (78.4)

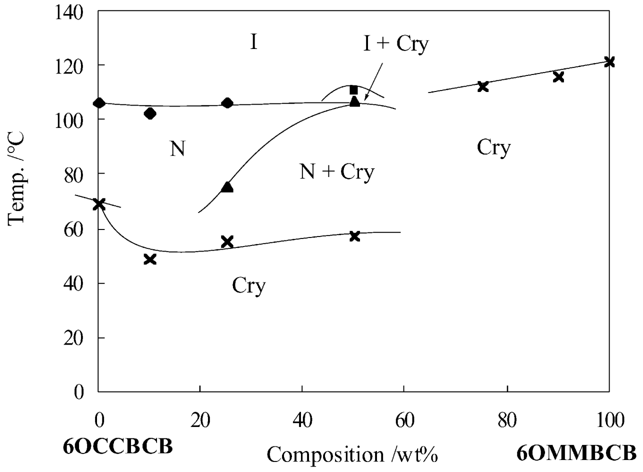
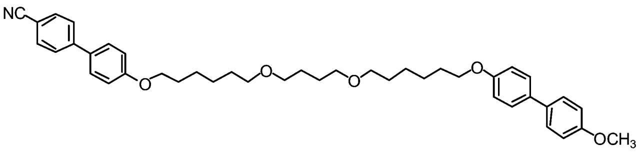


Figure 3. Binary phase diagram for 6OCCBCB and 6OMMBCB.

the T_{IN} to any significant extent. Therefore, specific interactions between the unlike mesogenic groups do not stabilize the nematic phase of the non-symmetric dimer 6OCMBCB. As shown in figure 3, the addition of 6OMMBCB to 6OCCBCB did not change the T_{IN} of 6OCCBCB, indicating that intermolecular interactions between 4-cyanobiphenyl and 4-methoxybiphenyl groups do not affect stabilization of the nematic phase of the symmetric dimer 6OCCBCB.

In order to investigate the effect of the linking group, we prepared a non-symmetric dimer containing 1,4-dioxa-*n*-butane (6OCMBNB). The molecular structure and transition properties of 6OCMBNB are shown in figure 4. T_{IN} at 381 K for 6OCMBNB is essentially unchanged from that for 6OCMBCB containing the ethylenic bond. The transition entropy ($\Delta S/R$) of 6OCMBNB is 0.91, which is the same magnitude as that of 6OCMBCB. The similarity in transition properties between 6OCMBCB and 6OCMBNB suggests that the U-shaped conformation organized by intramolecular core–core interactions makes an insignificant contribution to the properties of 6OCMBCB. Therefore, space filling of the linear-extended molecules plays an important role in the transition properties of 6OCMBCB.

Let us consider the transition properties of the present dimesogenic compounds in comparison with those of some symmetric dimers possessing a polymethylene spacer. Luckhurst has recently reported the transition properties of a homologous series of α, ω-bis(4-cyanobiphenyl-4′-yloxy)alkanes with a spacer containing from 3 to 24 methylene groups [21]. There is a dramatic odd–even effect for the nematic–isotropic transition entropy. The symmetric cyanobiphenyl dimer containing 20 methylene groups, which replaces the *cis*-1,4-dioxa-2-butene of 6OCCBCB by methylene groups, shows a T_{NI} of 417 K and $\Delta S/R$ of 2.18. The marked difference in T_{NI} between 6OCCBCB and the symmetric dimer with the polymethylene spacer is not surprising. It is known that replacing the ether links by methylene groups in a dimer can alter T_{IN} by a significant amount because the angle between the mesogenic groups is decreased [22]. The C–O–C bond angle would be 120° whereas the C–C–C bond angle should be 109°. The higher entropy change of the symmetric dimer with the polymethylene spacer is typical of dimeric compounds with an even-numbered spacer. Nematic–isotropic transition entropies of the cyanobipheny dimer containing 19 methylene groups and that containing 21 groups, are 1.23 and 1.34, respectively. On the other hand, the entropy change of 6OCCBCB is 1.12.



6OCMBNB: Cry 376 (18.3) N 381 (2.87) Iso mp 392 (103)

Figure 4. Molecular structure, transition temperatures (K) and enthalpies (kJ mol^{-1}) of transition of the dimesogenic compound containing 1,4-dioxa-*n*-butane.

The transition properties of 6OCCBCB are similar to those of the α, ω-bis(4-cyanobiphenyl-4′-yloxy)alkanes with an odd-numbered spacer, indicating that the two mesogenic uints of 6OCCBCB are inclined with respect to each other, because of the *cis*-butene unit. Furthermore, both 6OCMBCB and 6OCMBNB show lower entropy changes, indicating that the central oxygen atoms have a greater influence on transition properties than does the *cis*-butene unit. The smaller entropy change at T_{IN} for the mesogenic compounds possessing the central oxygen atoms may be related to the shapes of the ground state conformations. The similarity in isotropic–nematic transition entropy between 6OCMBCB and 6OCMBNB allows us to say that the central oxygen atoms can induce a *gauche* conformation in the spacer of 6OCMBNB.

4. Conclusion

We have prepared several dimesogenic compounds containing *cis*-1,4-dioxa-2-butene as a linking group. A comparison of transition properties between the non-symmetric and symmetric compounds indicates that there are no specific interactions between the unlike mesogenic groups to stabilize the nematic phase. The central oxygen atoms were found to have a greater influence on the transition properties than did the *cis*-butene unit. The driving force for mesogen formation might be space filling of the linear-extended molecule in which two mesogenic units are inclined with respect to each other.

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