Importance of Molecular Geometry in Liquid Crystal Formation—Incapability of Mesophase-Formation by Bent Dimesogenic and Star-Shaped Trimesogenic Compounds

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A series of compounds were synthesized that contain varying number of mesogenic units, 4-*n*-butylazobenzene moiety, attached to the central benzene ring through ester bond. These compounds were subjected to thermal analysis on a differential scanning calorimeter (DSC) and also on a polarizing microscope. It was found from this study that the presence of mesogenic units in a multi-mesogenic compound does not guarantee for the compound to become mesomorphic and that the linear molecular shape is conducive to form a liquid crystalline phase.

Introduction

Structure and properties of many organic liquid crystalline compounds are thoroughly documented in a handbook[1], many monographs[2,3] and review articles.[4-6] There are still, however, many questions yet to be answered on the structural characteristics of di- and multimesogenic liquid crystalline compounds and molecular order they exhibit in mesophases. Most of the liquid crystalline compounds so far studied are monomesogenic, in other words, contain only one mesogenic group. And the properties of the compounds containing more than one mesogenic groups did not attract much interest up until recent time.[7-11] Dimesogenic compounds were found to be the excellent models for the main chain liquid crystalline polymers with polymethylene spacers.[12]

While we were trying to estabilish structure–property relationships of liquid crystalline polyesters, we became interested in the mesomorphic properties of such dimesogenic compounds, and they are the subjects of a series of research reports by us.[8,10,13-15] All of these compound have a common structural feature as shown below:

flexible spacer
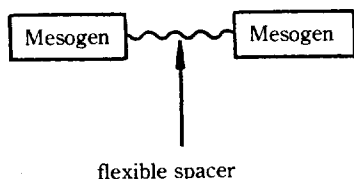
As a part of our continuing effort to delineate structure–properties relationships of mesogen containing compounds, a trimesogenic compound and their monomesogenic and dimesogenic counterparts were synthesized and their liquid crystallinities were compared. The structure of the compounds are as shown below:
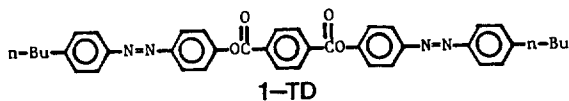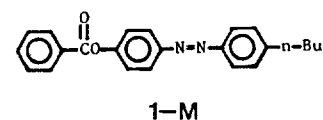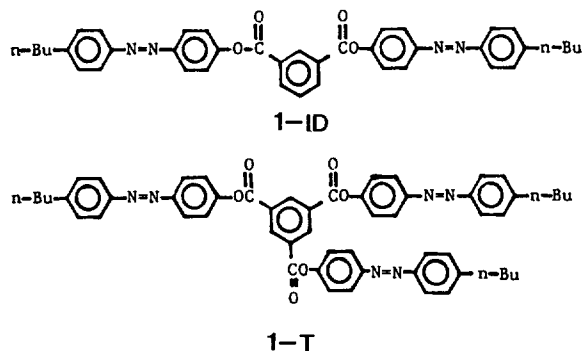

1—M

1—TD

Table 1. Thermal and Liquid Crystalline Properties

Compounds	T_m, °C[a]	ΔH_m, kJ/mole	T_i, °C[b]	ΔH_i, kJ/mole	LC[c]
1—1	78.4	5.25			no
1—M	108	6.2	100	0.20	nematic
1—TD	215	11.2	>300[d]		nematic
1—ID	196	16.0			no
1—T	190	11.3			no

[a] Melting temperature. [b] Isotropization or clearing temperature. [c] Liquid crystallinity. [d] Decomposed before reaching T_i.

1—ID

1—T

These compounds contain the same mesogenic units, 4-*n*-butylazobenzene moieties attached through ester bonds to the central benzene ring. Structural confirmation of the compounds were made by their elemental, IR and NMR spectral analyses. Their thermal and liquid crystalline properties were investigated on a differential scanning calorimeter (DSC) and on a polarizing microscope equipped with a hot-stage.

Experimental
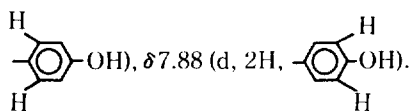
Synthesis of the Compounds

4-*n*-Butyl-4′-hydroxyazobenzene(1-1). *n*-Butylaniline (11.9 g; 8.0 × 10⁻² mole) and 12 m*l* of concentrated HCl were dissolved in 110 m*l* of distilled water. To the solution was added slowly NaNO₂ (5.52 g; 8.0 × 10⁻² mole) solution in 30 m*l* of distilled water. The temperature of the mixture was maintained at 0–5 °C in an ice bath. As the NaNO₂ solution was added, precipitate was formed. Reaction was allowed to continue further for 30 min, after which the precipitate was collected on

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a filter and was dissolved in 250 m*l* of ethanol. The ethanol solution was dropwise added to a 200 m*l* of aqueous solution of phenol (7.5 g; 8.0×10^{-2} mole) and CH$_3$COONa (13.1 g; 16×10^{-2} mole) over a period of one hour. Again the temperature of the reaction mixture was maintained between 0° and 5 °C. The mixture was stirred one more hour and the reddish purple precipitate was collected on a filter and dried in a vacuum oven. The product was recrystallized from a H$_2$O/CH$_3$OH (v/v = 3/2) mixture. Yield(18.7 g) was 92%; m.p. 78.4 °C.

Anal. Found C 75.49, H 7.57, N 10.73; Calcd. C 75.59, H 7.09, N 11.02%.

^{1}H-NMR spectrum (acetone-d$_6$/TMS); δ 0.95 (t, 3H, CH$_3$), δ 1.38 (sex., 2H, CH$_2$), δ 1.60 (quin., 2H, CH$_2$), δ 2.68 (t,

2H, -⬡-CH$_2$-), δ 7.02 (d, 2H, -⬡-*n*-Bu), δ 7.82 (d, 2H,

-⬡-OH), δ 7.88 (d, 2H, -⬡-OH).

IR-spectrum (KBr); O-H stretching at 3500 cm^{-1}, aliphatic C-H stretching at 2950 cm^{-1}, aromatic >C = C<stretching at 1610 cm^{-1} and -N = N- stretching at 1450 and 1395 cm^{-1}.

4-Benzoyloxy-4′-*n*-butylazobenzene (1-M). Benzoyl chloride (0.675 g; 4.8×10^{-3} mole) was dissolved in a mixture of 10 m*l* of dichloroethane and 5 m*l* of pyridine. To this solution was slowly added 10 m*l* of dichloroethane solution containing 1.22 g (4.8×10^{-3} mole) of 4-*n*-butyl-4′-hydroxyazobenzene (1-1) prepared above. The mixture was stirred at room temperature for 12 hours and then was heated to and maintained at 60 °C for 1 hour. Solvents were removed by a rotatory evaporator and the solid residue was washed with 0.5M-NaOH, 0.5M-HCl and finally with distilled water. The crude product was recrystallized from 95% ethanol. Yield (1.48g) was 86%; m.p. 108 °C. This compound was thermotropic (T_m : 108 °C) and exhibited clearing transition at 110 °C.

Anal. Found C 77.18, H 6.24, N 7.34; Calcd. C 77.09, H 6.15, N 7.82%

^{1}H-NMR spectrum (acetone-d$_6$/TMS); δ 2.68 (t, 2H, -⬡-CH$_2$-), 7.32-8.31 (m, 13H, Ar).

IR-spectrum (KBr); >C = O stretching at 1750 cm^{-1}, -N = N- stretching 1450, 1390 cm^{-1}.

Bis(4-*n*-butyl-4′-diazophenyl) terephthalate (1-TD). Terephthaloyl chloride (1.83 g; 9.0×10^{-3} mole) was dissolved in a mixture of 10 m*l* of dichloroethane and 5 m*l* of pyridine. This solution was cooled to 5 °C in an ice-bath. To this mixture was slowly added 4-*n*-butyl-4′-hydroxyazobenzene (4.58 g; 1.8×10^{-2} mole) dissolved in 20 m*l* of pyridine. The mixture was stirred at room temperature for 12 hours and then at 60 °C for one hour. Solvent was evaporated using a rotatory evaporator. The residue was washed with 0.5M-NaOH, 0.5M-HCl and finally with distilled water. The crude product was recrystallized from DMF. Yield (4.60 g) was 80%, m.p. 215 °C.

Anal. Found C 75.30, H 5.92, N 10.12; Calcd. C 75.14, H 5.95, N 10.02%.

^{1}H-NMR spectrum (CF$_3$COOD/TMS); δ 2.78 (t, 2H, -⬡-CH$_2$-), δ 7.54-8.52 (m, 20H, Ar).

IR-spectrum (KBr); >C = O stretching at 1750 cm^{-1}, -N = N- stretching at 1455, 1390 and C-O stretching at 1250 cm^{-1}.

Bis(4-*n*-butyl-1′-diazophenyl) isophthalate (1-ID). This compound was synthesized from isophthaloyl chloride and 4-*n*-butyl-4′-hydroxylazobenzene using the exact same procedure as employed in the synthesis of the previous compound, 1-TD. Yield was 81.5%, m.p. 196 °C.

Anal. Found C 75.82, H 6.01, N 9.89; Clacd. C 75.14, H 5.95, N 10.02%.

^{1}H-NMR(CF$_3$COOD/TMS); δ 2.78(t, 2H, -⬡-CH$_2$), δ 7.54 -8.62(m, 19H, Ar), δ 9.11(s, 1H, -O-C(=O)-⬡-C(=O)-O-).
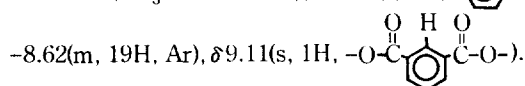
IR-spectrum (KBr); >C = O stretching at 1750 cm^{31}, - N = N-stretching at 1450 and 1359 cm^{-1}, and C-O stretching at 1250 cm.

1,3,5-Tris(4-*n*-butyl-4′-diazophenyl) benzenetricarboxylate (1-T). This compound was synthesized from 1,3,5-benzenetricarboxylic acid chloride (1.0g; 3.8×10^{-3} mole) using the same reaction procedure as employed in the synthesis of 1-TD and 1-ID. The only difference lies in the fact that reaction was conducted at 50 °C for 10 hours and then 70 °C for 2 hours. The crude product was recrystallized from acetone. Yield (0.8g) was 46.5%, m.p. 190 °C.

Anal. Found C 74.73, H 6.04, N 8.86; Calcd. C 74.48, H 5.89, N 9.16%.

^{1}H-NMR spectrum (CF$_3$COOD/TMS); δ 2.88 (t, 2H, -⬡-CH$_2$), δ 7.52 - 8.49 (m, 24H, Ar), δ 9.52 (s, 3H, -C(=O)-⬡-C(=O)-). O=C-
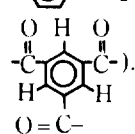
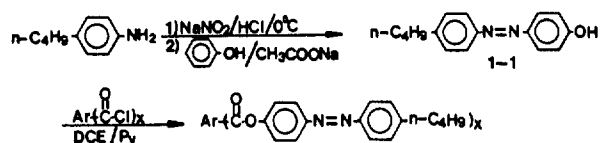IR-spectrum (KBr); >C = O stretching at 1760 cm^{-1}, -N = N- stretching at 1430 and 1390 cm^{-1}.

Thermal and Microscopic Characterization

Thermal behavior of the compounds was studied on a differential scanning calorimeter (DSC; Mettler TA 3000) and on a polarizing microscope (Leitz, Ortholux) equipped with a hot-stage (Mettler FP-2). Heating and cooling rates were maintained at 10 °C/min. Thermodynamic parameters for thermal transitions were obtained from the area of the peaks that was calibrated against indium reference. Optical texture of the melts were observed with the polarizers crossed and the magnification was 200×. Elemental analysis was performed by the Analytical Department of the Korea Research Institute of Chemical Technology.

Results and Discussion

The compounds prepared in this study, as shown in Introduction, contain two or three 4-*n*-butylazobenzene residues linked to each other through the central benzene ring. The connecting links between the mesogenic units and the central ring are ester bonds. The synthetic steps taken for their preparation are as follows:
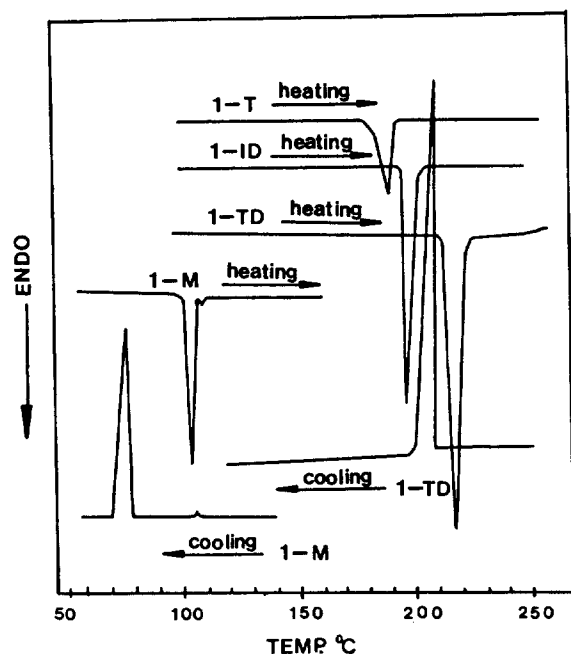
n-C$_4$H$_9$-⬡-NH$_2$ →(1)NaNO$_2$/HCl/0°C →(2)⬡-OH/CH$_3$COONa → *n*-C$_4$H$_9$-⬡-N=N-⬡-OH
1-1

Ar(-CO-Cl)$_x$ →(DCE/Py) Ar(-CO-O-⬡-N=N-⬡-*n*-C$_4$H$_9$)$_x$

Figure 1. DSC Thermograms of the compounds (N_2 atomosphere, heating rate; 10 °C/min).
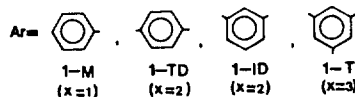

Figure 1 compares thermal behavior of the compounds as illustrated by their DSC thermograms. The thermogram of the linear compound, 1-M, shows two endothermic transitions. The lower temperature one corresponds to crystal-to-mesophase transition and the higher temperature one to mesophase-to-isotropic phase transition. These transitions occurred reversibly indicating that the compound is enantiotropically thermotropic. The mesophase it formed was nematic as judged by its optical texture observed through a microscope (Figure 2).

In contrast to 1-M, the rest compounds exhibited only one transitions on heating (Figure 1) as well as on cooling but observation of optical textures of the melts during heating and cooling leads to the conclusion that 1-TD also is mesomorphic (Figure 2). In other words, the compound 1-TD melts into a nematic melt at 215 °C. The other two compounds, 1-ID and 1-T, however, are not liquid crystalline. Their solids melt directly into isotropic liquids at T_ms.

All of the present compounds contain the same mesogenic units, but their number and the way by which they are interconnected are different. The compound 1-M is monomesogenic and, as expected, enantiotropic. The dimesogenic compounds 1-TD and 1-ID differ in that in the former the two mesogens are connected through the linear terephthaloyl moiety, whereas in the latter they are connected through the bent isophthaloyl moiety. Such a bent connection seems to be enough to make 1-ID nonliquid crystalline in spite of the presence of mesogenic moieties. Linear connection of the two mesogenic units in 1-TD certainly favors the enantiotropic formation of the nematic phase.

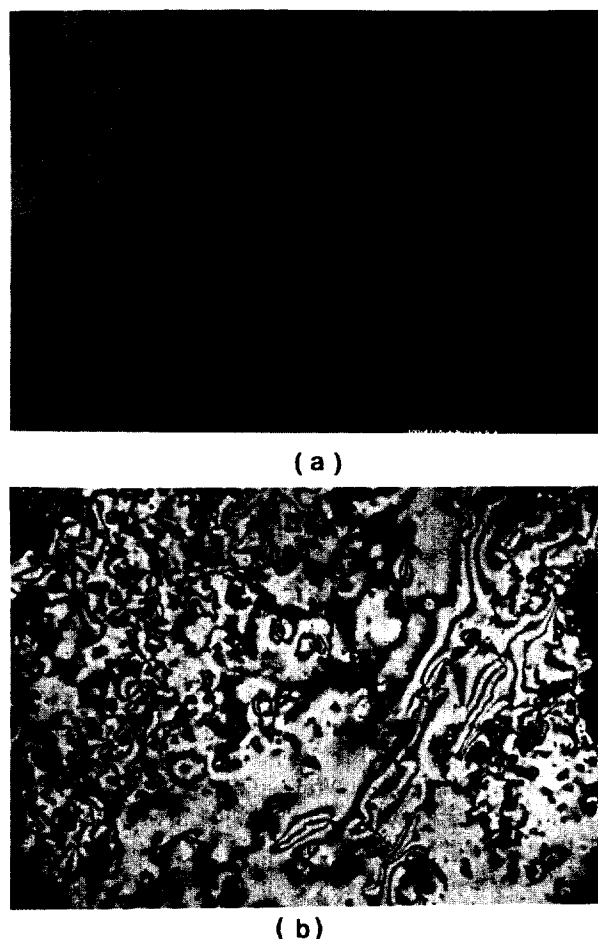The tri-branched shape of 1-T does not allow the mesogens or the molecule to form ordered alignment in melt.

Figure 2. Photomicrographs of (a) 1-M and (b) 1-TD taken at 112 °C and 280 °C, respectively (Magnification 200×).

Competitive attractive interaction among the three mesogens directed angled and broadening the molecular shape act unfavorably on the molecule's ability to form a mesophase in melt. Of course, it may be possible to obtain discotic liquid crystals when the *n*-butyl group in 1-T is displaced with much longer alkyl or alkoxy group. Huang *et al.*[16] recently reported that 1,3,5-tris(4-benzylidene oxy-4'-hexylaniline)triazine and 1,3,5-tris(4-benzylidene oxy-4'-decylaniline)triazine are able to form a discotic liquid crystalline phase. These compounds also are star-shaped trimesogenic compounds, but with longer alkyl substituent than 1-T having *n*-butyl substituent.

The melting point of linear 1-TD, 215 °C, is significantly higher than that (196 °C) of the corresponding bent compound, 1-ID. Surprisingly, 1-T, in spite of its much higher molecular weight, melts at a lower temperature, 190 °C. The monomeric 1-M's melting point, 108 °C, was the lowest as expected. The mesophase temperature range of 1-M was very narrow, only 2 °C on heating at a 10 °C/min heating rate. However, the range broadened to 31 °C (109 °C-78 °C) on cooling its isotropic melt at a 10 °C/min cooling rate. The nematic mesophase formed by 1-TD was very stable and persisted to thermal decomposition temperature (>300 °C).

The magnitude of isotropization enthalpy ΔH_i of 1-M is very low (0.20 kJ/mole) when compared with that (6.2 kJ/mole) of its ΔH_m, suggesting that much less thermal energy

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is necessary to disrupt the liquid crystalline order than to destroy crystalline order in the solid state. The corresponding value of 1-TD could not be obtained by DSC analysis due to thermal decomposition before reaching isotropization temperature.

Conclusion

Following conclusions can be drawn from the results of the present study:

1) The presence of mesogenic unit in a molecule does not guarantee for the compound to become liquid crystalline.
2) When a compound is dimesogenic, *i.e.*, contains two mesogenic units, linear molecular shape is prerequisite to be mesomorphic.
3) A trimesogenic and star–shaped compound is not able to form a mesophase when the mesogenic units are connected directly to the central core.

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Dichloro and Ethylenediamine Rhodium(III) Complexes of Ethylenediamine–N,N'–di–α–butyric Acid

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Dichloro and ethylenediamine rhodium(III) complexes of a flexible N_2O_2-type tetradentate ligand, ethylenediamine-N, N'-di- -butyric acid(eddb), have been prepared. Both *s–cis–* and *uns–cis* geometrical isomers have been yielded in the [Rh(eddb)Cl$_2$]$^-$ and [Rh(eddb)(en)]$^+$ complexes. Ir, pmr, and electronic absorption spectra are used to characterize the complexes obtained in this work.

Introduction

A linear flexible N_2O_2-type tetradentate ligand such as edda (ethylenediamine-N,N'-diacetic acid, $HOOCCH_2$ $NHCH_2CH_2NHCH_2COOH$) can occupy four coordination sites in an octahedral complex with three geometrical isomers possible *s–cis* (symmetric *cis*), *uns–cis* (unsymmetric *cis*), and *trans* (Figure 1). A good number of N_2O_2-type ligands and the cobalt(III) complexes of these ligands have been prepared.[1-3] While no *trans* isomers have so far been observed, *s–cis* and/or *uns–cis* isomers have been yielded in the cobalt (III) complexes of the N_2O_2-type ligands, [Co(N_2O_2 ligand) L]$^{n+}$ depending upon the nature of the N_2O_2-type ligand and the ligand L which occupy the remaining two sites in an octahedral complex. Only a few such works have been reported

on the complexes of metal ions other than the cobalt (III) ion. Liu *et al.*[4] reported the synthesis of the *s–cis* and *uns–cis* isomers of the rhodium(III) complexes of the ethylenediamine-N,N'-di-S-α-propionic acid (SS-eddp). Recently we have prepared the rhodium(III) complexes of N,N'-dimethylethylenediamine-N,N'-diacetic acid (dmedda), in which both the *s–cis* and *uns–cis* isomers have been yielded.[5]

Recently we reported the synthesis of a flexible N_2O_2-type ligand, ethylenediamine-N,N'-di-α-butyric acid, $HOOCCH(C_2H_5)NHCH_2CH_2NHCH(C_2H_5)COOH$(eddb).[6] The cobalt(III) complexes of [Co(eddb)L]$^{n+}$ (L = Cl$_2$, (H$_2$O)$_2$ClH$_2$O, CO$_3$) have yielded the *s–cis* isomer only. The present work involves the rhodium (III) complexes of the eddb ligand. It is of interest to observe what isomers are obtained upon coordination of the eddb ligand to the rhodium (III) ion. It will be