behavior associated with the ionic conductivity.

Comparing the specific conductivity found for $Li^+$ and $Na^+$ ions in PEO-intercalated silicates, it appears that sodium ions exhibit higher conductivity than lithium ions ($10^{-4}$ vs $10^{-5}$ S/cm). Similar behaviors are reported for $\beta$-alumina[44] and for some PEO-salt complexes.[1] In our case, this can be accounted for by the ability of lithium ions to move from the interlayer region to vacancy sites located in the octahedral silicate layers. This property, called the "Hoffman-Klemem effect",[45] takes place upon thermal treatment of some $Li^+$-exchanged dioctahedral phyllosilicates, as is the case with our montmorillonite samples. A consequence of this, is the immobilization of a fraction of charge carriers ($Li^+$) in the core of the silicate.

## Conclusions

Many authors devoted much work to improve electrical properties of PEO-salt complexes acting as solid polyelectrolytes.[4,5] So, mixtures of PEO with various electrolytes have been investigated in order to reduce crystallinity, increase flexibility of the polymer chains, and increase the number of charge carriers. Enhancement of conductivity is produced when plasticizer molecules are added to the system, but these molecules are susceptible to leakage. Incorporation of ceramic additives such as alumina increases the amorphous phase ratio of PEO, favoring ion transport.[7-9] Thus, the great relevance of the PEO aggregation state is apparent, the intercalation being an alternative way to break the crystalline state of the polymer. PEO-silicate compounds show conductivity values lower than conventional PEO-salt complexes, although they present better thermal stability and reach good ion conductivity over a broader temperature range. In PEO intercalation materials only the cations are able to move, avoiding problems of formation of ion pairs, and consequently transport number is equal to one ($t_+ = 1$), which is of interest in the study of ion-transport phenomena in polymer electrolyte systems. Finally, intercalation of PEO in layered solids opens the way to new polyelectrolyte materials using host lattices with electronic conductivity, giving solids exhibiting mixed ionic electronic conductivity. Following this approach, PEO intercalations in hydrated vanadium pentoxide have been recently reported.[46,47]

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**Registry No.** PEO, 25322-68-3; $Li^+$, 17341-24-1; $Na^+$, 17341-25-2; $K^+$, 24203-36-9; $NH_4^+$, 14798-03-9; $Ca^{2+}$, 14127-61-8; $Ba^{2+}$, 22541-12-4; $Al^{3+}$, 22537-23-1; $Cr^{3+}$, 16065-83-1; $CH_3CH_2CH_2NH_3^+$, 17033-39-5; $H_2O$, 7732-18-5; MeOH, 67-56-1; montmorillonite, 1318-93-0; hectorite, 12173-47-6; acetonitrile, 75-05-8; ethanol, 64-17-5; dimethyl sulfoxide, 67-68-5.

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# Dimesogenic Compounds Consisting of Two Aromatic Ester or Amide Type Mesogenic Units Having Trifluoromethyl Substituents at Terminal Phenylene Rings and a Central Dimethylenetetramethyldisiloxyl Spacer

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A series of new dimesogenic compounds whose mesogens are diad or triad aromatic ester or amide or esteramide types having trifluoromethyl substituents at the para position of terminal phenylene rings were synthesized. The two mesogenic units are interconnected through the central spacer of 1,3-dimethylenetetramethyldisiloxyl ($-CH_2Si(CH_3)_2-O-Si(CH_3)_2CH_2-$) structure. Their liquid-crystalline properties were studied by differential scanning calorimetry (DSC) and on a cross-polarizing microscope. The compounds having diad aromatic ester or amide type mesogens are monotropically mesomorphic, whereas those having triad mesogens are enantiotropically mesomorphic. All of the compounds form the $S_A$ phase according to their observed optical textures. The $CF_3$ terminal substituent in the mesogenic units together with the disiloxyl spacer appears to favor the formation of a smectic phase.

## Introduction

Thermotropic compounds having two identical mesogenic units attached to both ends of a central flexible spacer are interesting not only as a new class of liquid-crystalline compositions[1-13] but also as models[14-16] for main-chain liquid-crystalline polymers (LCP)[17-20] which

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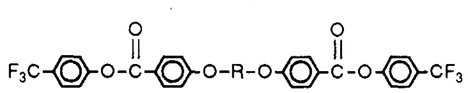
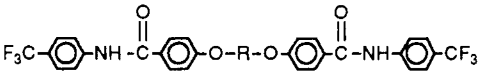
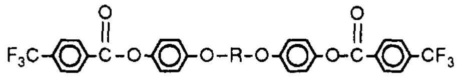
**Chart I**[a]



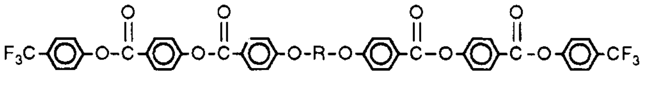
1,3-bis[4-(*p*-(trifluoromethyl)phenoxycarbonyl)phenoxymethyl] tetramethyldisiloxane, Ia



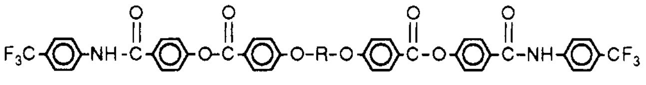
1,3-bis[4-(*p*-(trifluoromethyl)phenyliminocarbonyl)phenoxymethyl] tetramethyldisiloxane, Ib



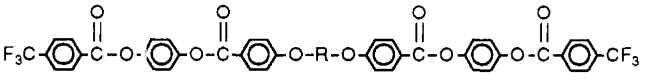
1,3-bis[4-(*p*-(trifluoromethyl)benzoyloxy)phenoxymethyl] tetramethyldisiloxane, Ic



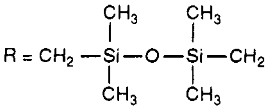
1,3-bis[4-{4'-(*p*-(trifluoromethyl)phenoxycarbonyl)phenoxymethyl} phenoxymethyl]tetramethyldisiloxane, IIa



1,3-bis[4-{4'-(*p*-(trifluoromethyl)phenyliminocarbonyl)phenoxycarbonyl} phenoxymethyl]tetramethyldisiloxane, IIb

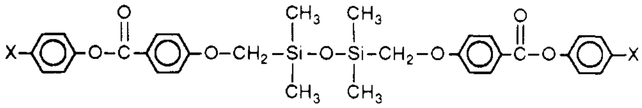


1,3-bis[4-{4'-(*p*-(trifluoromethyl)benzoyloxy)phenoxycarbonyl} phenoxymethyl]tetramethyldisiloxane, IIc



$$R = \mathrm{CH_2}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{CH_2}$$

contain mesogenic units interconnected through flexible spacers. Many series of these compounds with a variety of structures were reported earlier by us[1-5] and others.[6-13] One of our earlier papers describes liquid-crystalline properties of the following compounds:[3]



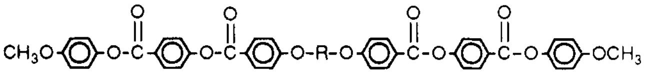
X = H, $CH_3$, $OCH_3$, Cl, CN, $NO_2$, and $C_6H_5$

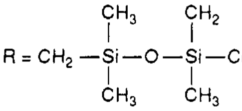
These compounds have a similar structure to Ia shown in Chart I, but they have different terminal substituents. All of the compounds are enantiotropically thermotropic, forming the $S_B$ phase in the melt. The compound with the $NO_2$ substituent, however, is different and forms the $S_A$ phase. This observation is very much in contrast with the fact that similar dimesogenic compounds containing a pentamethylene central spacer instead of dimethylenetetramethyldisiloxane exhibit only the nematic phase.[21,22] Although the reason the disiloxyl spacer promotes the formation of a smectic phase is not yet clear, we can make a conjecture that the very low rotational energy barrier[23-25] of the –Si–O– bond facilitates the occurrence of a more highly ordered state by the mesogenic units. On the contrary, the conformation of polymethylene spacers connected to mesogens is known to be rather restricted.[26-28]

As a part of our continuing efforts to delinate the structure–property relationship of liquid-crystalline compounds of this type, we synthesized a series of new compounds that have two identical rigid units having trifluoromethyl terminal groups interconnected through the central, flexible dimethylenetetramethyldisiloxyl group, and their thermal properties and liquid crystallinity were investigated. The structures and designation of the compounds are given in Chart I.

Compounds I contain diad aromatic ester or amide type mesogens and the central spacer, whereas compounds II contain triad ester or amide or esteramide type mesogenic groups. In each group of the compounds, a systematic structural change was made in the nature of linking groups and bonding direction of bridging ester groups in the mesogenic units.

For the purpose of comparison the following compound was also prepared and characterized. This compound has the same structure as IIa with the only difference being in the nature of terminal substituents:





$$R = \mathrm{CH_2}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_2}}{\mathrm{Si}}}-\mathrm{CH_2}$$

1,2-bis[4-{4'-(*p*-methoxyphenoxycarbonyl)phenoxycarbonyl} phenoxymethyl]tetramethyldisiloxane, III

Our previous paper[29] describes the mesomorphic properties of the compounds that have the same structures as those of series I and II but contained decamethylene spacer in place of dimethylenetetramethyldisiloxyl group of the

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present compounds. We learned from the previous study that CF$_3$ terminal group tends to induce the formation of a smectic phase.

## Experimental Section

**Characterization.** IR spectra in the 5000–400-cm$^{-1}$ region were recorded on Shimadzu IR-440 spectrometer. $^1$H NMR spectra were taken on a Bruker FT-80 SY spectrometer with Me$_4$Si as an internal standard. Elemental analyses were performed by the Microanalytical Laboratory at the University of Massachusetts. The transition temperatures and the enthalpy changes were measured by differential scanning calorimetry (Mettler DSC 30) at a heating/cooling rate of 10 °C/min. Calibrations of temperature and entropy changes were carried out using indium, tin, and zinc as references. The texture of the mesophases were observed on a Leitz Ortholux polarizing microscope equipped with a Mettler FP-5 hot stage.

**Synthesis of Ia and Ib.** For the synthesis of these compounds, 1,3-bis(*p*-carboxyphenoxymethyl)tetramethyldisiloxane, **1**, first was reacted either with *p*-(trifluoromethyl)phenol (for compound Ia) or with *p*-(trifluoromethyl)aniline (for compound Ib). Compound **1** was prepared following the literature method[30] from 1,3-bis(bromomethyl)tetramethyldisiloxane and ethyl *p*-hydroxybenzoate. Compound **1** (1.0 g 2.29 mmol) was dissolved in 25 mL of thionyl chloride, and the mixture was refluxed for 4 h. Excess thionyl chloride was then removed by vacuum distillation. 1,3-Bis(*p*-(chloroformyl)phenoxymethyl)tetramethyldisiloxane, **2**, thus obtained was dissolved in 2 mL of pyridine. To this solution was added a solution of 0.774 g (4.58 mmol) of 4-(trifluoromethyl)phenol in 2 mL of pyridine at room temperature under N$_2$ atmosphere. The mixture was stirred at 60 °C for 5 h under N$_2$ atmosphere. The precipitate formed by pouring the mixture into excess water was washed with water and methanol. The crude product was recrystallized from acetone. Yield of the product, 1,3-bis[4-(*p*-trifluoromethylphenoxycarbonyl)phenoxymethyl]tetramethyldisiloxane (Ia), was 1.5 g (90.5%), mp 138.3 °C. $^1$H NMR (acetone-$d_6$) $\delta$ 6.42–7.81 (m, 16 H, Ar), 3.59 (s, 4 H, CH$_2$), 0.27 (s, 12 H, CH$_3$). IR (KBr) 3050 (Ar =C—H str), 2940 (aliphatic C-H str), 1730 (C=O str), 1058 (Si-O str), and 1330 cm$^{-1}$ (C–F str). Anal. Found: C 55.95, H 4.58, F 15.42, Si 7.69%. Calcd: C 56.49, H 4.47, F 15.77, Si 7.77%.

Compound Ib, 1,3-bis[4-(*p*-(trifluoromethyl)phenyliminocarbonyl)phenoxymethyl]tetramethyldisiloxane, was prepared by the same procedure using 4-(trifluoromethyl)aniline in place of 4-(trifluoromethyl)phenol. The crude product was recrystallized from acetone. Yield was 2.0 g (91%), mp 288.5 °C. $^1$H NMR (acetone-$d_6$) $\delta$ 6.9–8.3 (m, 16 H, Ar), 9.7 (s, 2 H, -NH-), 3.8 (s, 4 H, CH$_2$), 0.3 (s, 12 H, CH$_3$). IR (KBr); 3350 (N-H str), 3000 (Ar =C—H str), 2920 (aliphatic C-H str), 1650 (C=O str), 1410 (C–N bending), 1330 (C–F str) and 1080 cm$^{-1}$ (Si-O str). Anal. Found: C 56.49, H 4.85, F 15.95, N 3.83, S 7.75%. Calcd: C 56.65, H 4.76, F 15.81, N 3.89, Si 7.79%.

**Synthesis of Ic.** Compound Ic, 1,3-bis[4-(*p*-(trifluoromethyl)benzoyloxy)phenoxymethyl]tetramethyldisiloxane, was prepared from 1,3-bis(*p*-(hydroxyphenoxy)methyl)tetramethydisiloxane, **3**, and *p*-(trifluoromethyl)benzoic acid. Preparation method of compound **3** was reported earlier by us.[30]

*p*-(Trifluoromethyl)benzoic acid (1.0 g, 5.25 mmol) was first converted to *p*-(trifluoromethyl)benzoyl chloride by reacting with thionyl chloride. And this acid chloride was dissolved in 1.5 mL of pyridine and was mixed with compound **3** (1.0 g, 2.63 mmol) dissolved in 2 mL of pyridine. This solution was stirred at 60 °C under N$_2$ atmosphere for 5 h. The mixture was poured into excess water, and then the precipitate was washed with water and methanol. The crude product was recrystallized from acetone, mp 96.8 °C; yield 1.7 g (89%). IR (KBr) 3050 (Ar =C—H str), 2950 (aliphatic C-H str), 1730 (C=O str), 1060 (Si-O str), and 1320 cm$^{-1}$ (C–F str). $^1$H NMR (CDCl$_3$) $\delta$ 6.38–7.93 (m, 16 H, Ar), 3.59 (s, 4 H, CH$_2$), 0.27 (s, 12 H, CH$_3$). Anal. Found: C 56.59, H 4.54, F 16.02%. Calcd: C 56.49, H 4.47, F 16.02%.

**Synthesis of IIa, IIb, and III.** These compounds were prepared by reacting compound **2** with either 4′-(trifluoromethyl)phenyl 4-hydroxybenzoate, **4** (for IIa), or 4-hydroxybenz-4′-(trifluoromethyl)anilide, **5** (for IIb), or 4′-methoxyphenyl 4-hydroxybenzoate (for III) in the presence of pyridine. For example, to prepare IIa, compound **4** (1.30 g, 4.58 mmol) dissolved in 2.5 mL of pyridine was mixed with pyridine solution (2 mL) containing 2.2 mmol of compound **2**. The mixture was stirred at 60 °C for 5 h under N$_2$ atmosphere. The precipitate was collected on a filter and washed with distilled water and methanol. The crude product IIa was recrystallized from acetone; mp 166.6 °C; yield 2.0 g (91%). $^1$H NMR (CF$_3$COOD) $\delta$ 6.9–8.6 (m, 24 H, Ar), 4.1 (d, 4 H, CH$_2$), 0.67 (S, 12 H, CH$_3$). IR (KBr) 3050 (Ar C=C str) 2900 (aliphatic C–H str), 1730 (C=O str), 1048 (Si–O str), 1322 (C–F str), and 1205 and 1060 cm$^{-1}$ (C-O str). Anal. Found: C 59.05, H 4.31, F 12.07, Si 5.93%. Calcd: C 59.86, H 4.20, F 11.86, Si 5.83%.

Compound IIb was prepared via the exact same procedure as the one used in the preparation of IIa using compound **5** in place of compound **4**, mp 288.5 °C; yield 2.0 g (91%). $^1$H NMR (CD$_3$COOD) $\delta$ 7.1–8.3 (m, 24 H, Ar), 9.9 (s, 2 H, -NH-), 4.1 (d, 4 H, CH$_2$), 0.66 (s, 12 H, -CH$_3$). IR (KBr) 3350 (N–H str), 2980 (aliphatic C–H str), 1730 (ester C=O str), 1650 (amide C=O str), 1330 (C-F str) and 1060 cm$^{-1}$ (Si-O str). Anal. Found: C 59.24, H 4.60, F 12.09, N 3.02, Si 5.92%. Calcd: C 59.38, H 4.41, F 11.86, N 2.92, Si 5.84%.

Compound III was synthesized via the same procedure as that used in the preparation of IIa and IIb by the reaction between compounds **2** and **6**. Crude product was recrystallized from acetone; mp 146 °C; yield 1.9 g (92%). $^1$H NMR (CF$_3$COOD) $\delta$ 7.0–8.6 (m, 24 H, Ar), 4.12 (s, 4 H, CH$_3$), 4.06 (s, 6 H, OCH$_3$), 0.67 (s, 12 H, Si–CH$_3$). IR (KBr) 2960 (aliphatic C–H str), 1730 (C=O str), 1600 and 1504 (Ar C=C str) 1245 (CH$_3$–O str). Anal. Found: C 64.21, H 5.39, Si 6.95. Calcd: C 64.98, H 5.24, Si 6.33%.

**Synthesis of IIc.** Compound **2** prepared from 2.0 g (4.58 mmol) of compound **1** and thionyl chloride was dissolved in a mixed solvent of 3.0 mL of pyridine and 3.5 mL of *N,N*-dimethylformamide. To this solution added was 2.53 g (23.0 mmol) of hydroquinone dissolved in a mixture of 3.0 mL of pyridine and 4.0 mL of *N,N*-dimethylacetamide. The mixture was stirred at 60 °C for 5 h under N$_2$ atmosphere and then was poured into excess distilled water to precipitate the product. The precipitate was washed with cold water and recyrstallized from *N,N*-dimethylformamide.

The yield of 1,3-bis[4-(*p*-hydroxyphenoxycarbonyl)phenoxymethyl]tetramethyldisiloxane, **7**, thus prepared was 4.0 g (93%), mp 158 °C. IR (KBr) 3400 (O–H str), 2980 (aliphatic C–H str) 1700 (C=O str) and 1070 cm$^{-1}$ (Si–O str). Compound **7** (1.63 g, 2.63 mmol) dissolved in 2 mL of pyridine was mixed with a pyridine (1.5 mL) solution of 4-(trifluoromethyl)benzoyl chloride prepared from 1.0 g (5.25 mmole) of 4-(trifluoromethyl)benzoic acid and thionyl chloride. The mixture was stirred at 60 °C for 5 h under N$_2$ atmosphere and then was poured into excess distilled water to precipitate compound IIc.

The precipitate, after being washed with distilled water and methanol, was recrystallized from acetone, mp, 222.6 °C; yield of compound IIc 2.3 g (92%). $^1$H NMR (CF$_3$COOD + CDCl$_3$) $\delta$ 7.0–8.6 (m, 24 H, Ar), 4.1 (s, 4 H, CH$_2$), 0.67 (s, 12 H, CH$_3$). IR (KBr) 3050 (Ar C–H str), 2900 (aliphatic C–H str), 1720 (C=O str) 1060 (Si–O str) and 1320 cm$^{-1}$ (C–F str). Anal. Found: C 60.04, H 4.28, F 11.85%. Calcd: C 59.86, H 4.20, F 11.86%.

## Results and Discussion

**Synthesis.** Synthetic routes used in the preparation of the present compounds consist of rather well-known simple reactions given in Chart II.

The final synthetic steps involve a relatively simple condensation reaction between an acid chloride and a phenolic compound. This type of reaction is known to proceed almost quantitatively even at room temperature in the presence of an HCl acceptor. Indeed, we could obtain the final products in high yields ranging from 89 to 92%. All of them were purified through recrystallization. The chemical structures of the compounds were identified by elemental analyses and IR and NMR spectroscopy. TLC was employed to confirm the purity of the compounds.

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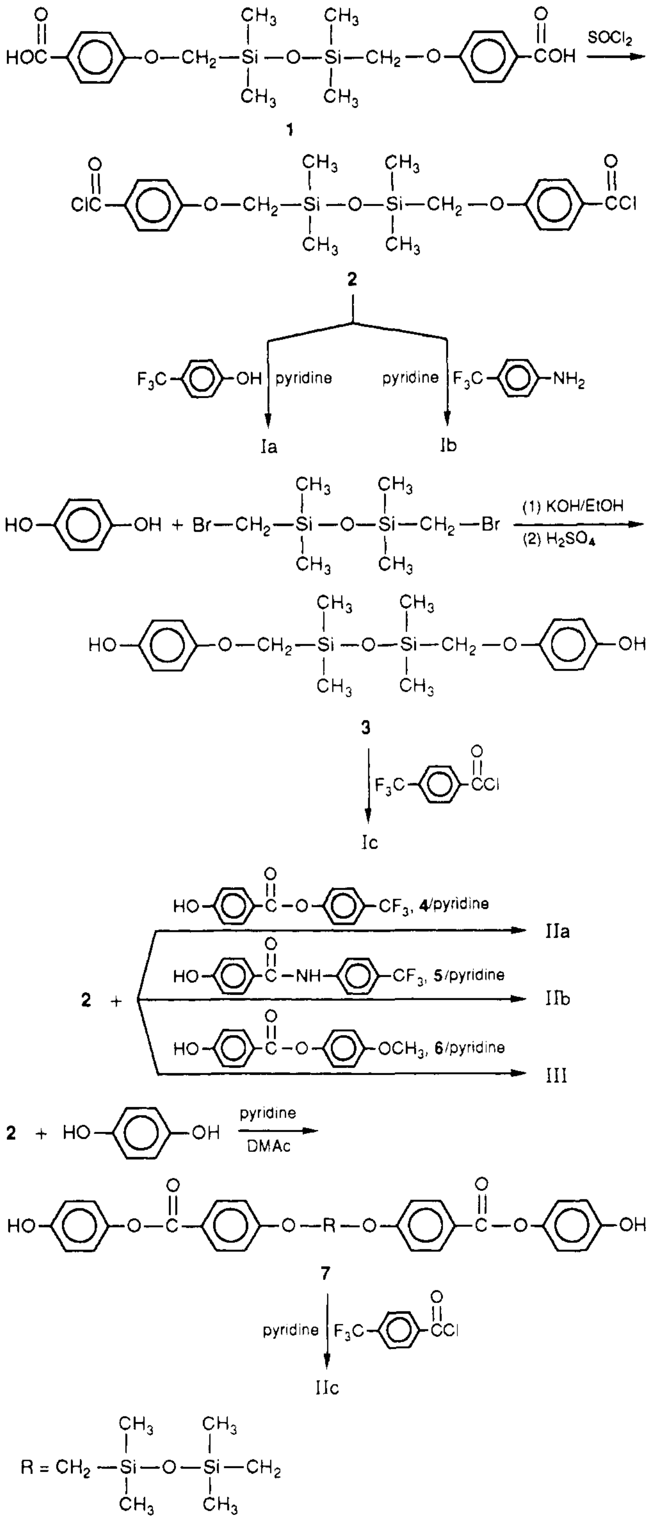
[30] Jo, B.-W.; Jin, J. I.; Lenz, R. W. *Eur. Polym. J.* **1982**, *18*, 233.

**Chart II**[a]



**Thermal Transition.** Figure 1 shows DSC thermograms obtained for compounds Ia, Ib, and Ic under $N_2$ atmosphere. The three compounds commonly exhibit only one endothermic transition peak on heating, whereas their cooling thermograms show two exothermic peaks. The endothermic peak for each compounds on the heating DSC curves corresponds to crystalline melting. The melting temperature, $T_m$, of Ib, 211 °C, is the highest among the three. This can be ascribed to the fact that, differently from the other two, this compound contains amide bonds, which are known to be more rigid than ester bonds, and promote intermolecular hydrogen bond. Compound Ia and Ic have isomeric structures; their only difference is the reverse linking order of the ester bonds. It is very interesting to note that such a minor structural modification leads to a significant difference in $T_m$; 145 °C for Ia vs 97 °C for Ic.

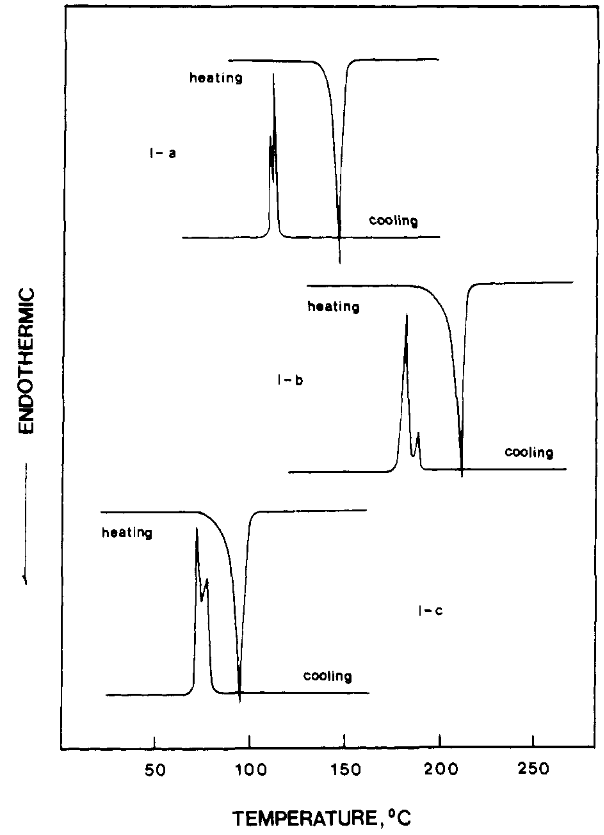
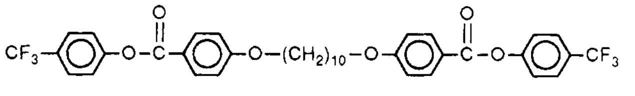


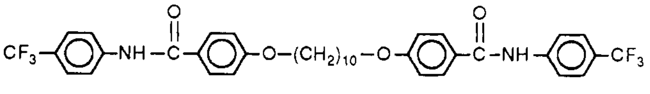
**Figure 1.** DSC thermograms of compounds I under $N_2$ atmosphere at the heating/cooling rate of 10 °C/min.

When we observed the thermal behavior of the three compounds on a polarizing microscope equipped with a hot stage, the solid melted directly into an isotropic liquid. However, cooling the isotropic liquid leads to the appearance of a mesophase over a rather narrow temperature range before final solidification into solid. This observation agrees with the two exothermic peaks appearing on the cooling DSC thermograms; the high-temperature exotherm corresponds to a isotropic-to-mesophase transition and the lower-temperature one to mesophase-to-crystal conversion. In other words, all of the series I compounds are monotropic. The isotropic-to-mesophase transition temperature is the highest (190.7 °C) for Ib followed by those for Ia (116.5 °C) and Ic (76 °C). It is noted that mesophase temperature range (1.5–4.5 °C) for the compounds is rather narrow.

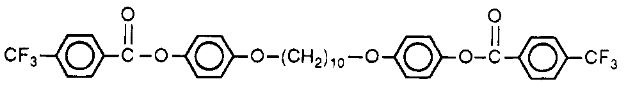
It was reported previously by us[29] that the dimesogenic compounds having similar structure are not mesomorphic when the central spacer is a decamethylene group. This comparison demonstrates the importance of the structure of the spacer in rendering a twin compound mesomorphic. This difference in the LC behavior of the siloxane-containing compounds versus the decamethylene-containing compounds is difficult to explain. A simple analysis of their expected permanent dipole directions and moments does not readily provide us with any definite ground to reason out the answer to the question. Further knowledge on the molecular motions and intermolecular attractions is deemed necessary. We, however, should discern the fact that the siloxane-containing compounds go through much higher degree of supercooling before solidification than the decamethylene-containing compounds, when their isotropic melts were cooled down; When their isotropic melts were cooled at the rate of 10 °C/min, the former compounds crystallize about 25–30 °C below their melting points (Figure 1), whereas the latter compounds crystallize only about 8–10 °C below their $T_m$'s.[29] This implies that the crystallization of siloxane compounds is significantly slower than that of the decamethylene compounds and, thus, they have a greater opportunity to form mesophases in the supercooled state before solidification. It is speculated that this difference comes from a combination of the low rotational energy barrier of the Si–O–Si bond and bulky nature of the disiloxyl group, both of which hinder molecular packing of the siloxane compounds into the three dimensionally ordered states of a crystalline solid:



nonmesomorphic, mp 147 °C

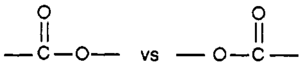


nonmesomorphic, mp 234.5 °C



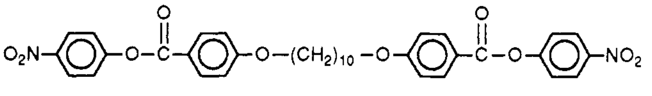
nonmesomorphic, mp 159 °C

It was pointed out above that the isotropic-to-mesophase transition temperature of Ia was much higher than that of Ic, although their structural difference lies only in the reverse order of the ester linkage, i.e.

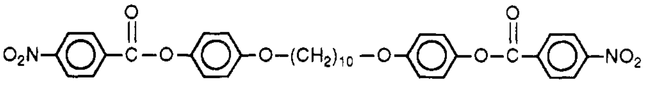


$$-\overset{O}{\overset{\|}{C}}-O- \quad \text{vs} \quad -O-\overset{O}{\overset{\|}{C}}-$$

Earlier we[21,31] observed an even more dramatic dependence of mesophase forming ability of dimesogenic compounds on such structural variations as



enantiotropic, K144 N160 I (on heating)



monotropic, K148 N153 I (on cooling)

These two compounds have the exactly same structure as Ia and Ib, respectively, with the exception that the terminal substituents are $NO_2$ groups in place of $CF_3$ groups of the latter. The first compound is enantiotropically nematic, while the second is only monotropically nematic. Main-chain thermotropic polyesters having flexible spacers also exhibit a delicate dependence of their mesophase and transition behavior on their microchemical structure.[32,33]

DSC thermograms (Figure 2) of the series II compounds all show two endotherms on heating cycle. The lower-temperature one corresponds to melting, and the higher-temperature one to isotropic phase transition. Only IIc reveals narrowly spaced, two sharp endothermic transitions in the melting point region. A careful examination of a sample on a microscope reveals that it melts only at the temperature where the second peak appears. Therefore, there are two possibilities: the first peak corresponds to a solid-to-solid transition or the sample contains two different crystal structures whose melting points are very closely positioned. Further study such as X-ray diffraction is required before one can draw a concrete conclusion. The melting and isotropization transitions were reversibly observed on DSC analysis, suggesting that the compounds are enantiotropically mesomorphic. Their observation on a polarizing microscope also confirmed this behavior. The presence of longer mesogenic units in these compounds certainly favors the formation of the liquid-crystalline state. As a result, the compounds of series II are enantiotropic whereas those of series I containing shorter mesogenic units are monotropic.

Comparing the melting temperatures of the compounds, we realize that compound IIb that contains amide linkages, again has the higher $T_m$ like Ib in series I. And all of $T_m$'s of the series II compounds are quite higher than those of series I, which coincides with what is expected. Compound III contains two methoxy terminal groups in place of trifluoromethyl substituents in compound IIa. This structural change brings about a reduction in the melting point as well as in the isotropization temperature.

Comparison of the magnitude of enthalpy changes ($\Delta H_m$) for melting estimated from DSC thermograms (Table I) provides us with a thermodynamic explanation on the question why the compounds of series II are enantiotropically thermotropic while those of series I are only monotropic. The $\Delta H_m$ values for series I are much greater than those for series II; this means that the series I compounds require much higher thermal energy than those of series II in order to transform solid into liquid. If the $\Delta H_m$ value for a compound is too high, thermal motion of the molecules at its melting point will be too vibrant for them to form an ordered state, i.e., a liquid-crystalline phase.[34] In other words, the packing energy in the crystalline state of series I is much greater than that of series II. Similar phenomenon has been observed earlier by us[21,29,31] for other series of compounds. In fact, so-called group efficiency of a substituent in the ability to induce the mesophase formation appears very often directly related to how it influences the melting thermodynamics of a compound.

Table I carries the data on the heat of isotropization ($\Delta H_i$) for each compound. It is rather difficult to make any correlation between the magnitude of $\Delta H_i$ and the structure of compounds. It is clear that, for all of the compounds in series I and II, the ratios of $\Delta H_i$ to $\Delta H_m$ are extraordinarily high, ranging from 0.13 to 1.2, when compared with those of other dimesogenic compounds.[1-5,21,22] The similar trend also was earlier observed by us[3] in another series of dimesogenic compounds containing disiloxyl spacer. Unfortunately, the reason is not yet clear. Probably, further knowledge on the crystal lattice energy and intermolecular interactions in the liquid-crystalline state is prerequisite to the understanding of this difference. This ratios[35] for other dimesogenic compounds with

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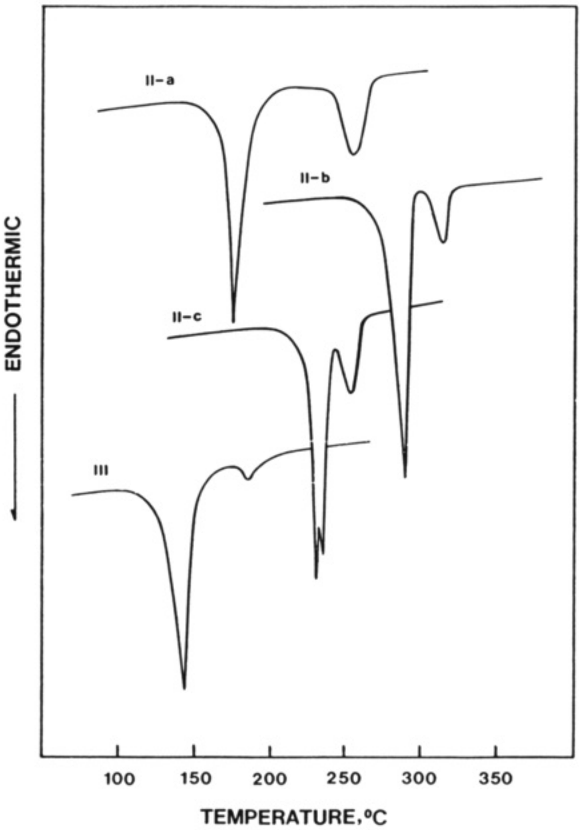


**Figure 2.** DSC thermograms of compounds II and III under $N_2$ atmosphere at the heating rate of 10 °C/min.

**Table I. Thermal Properties of Compounds**[a]

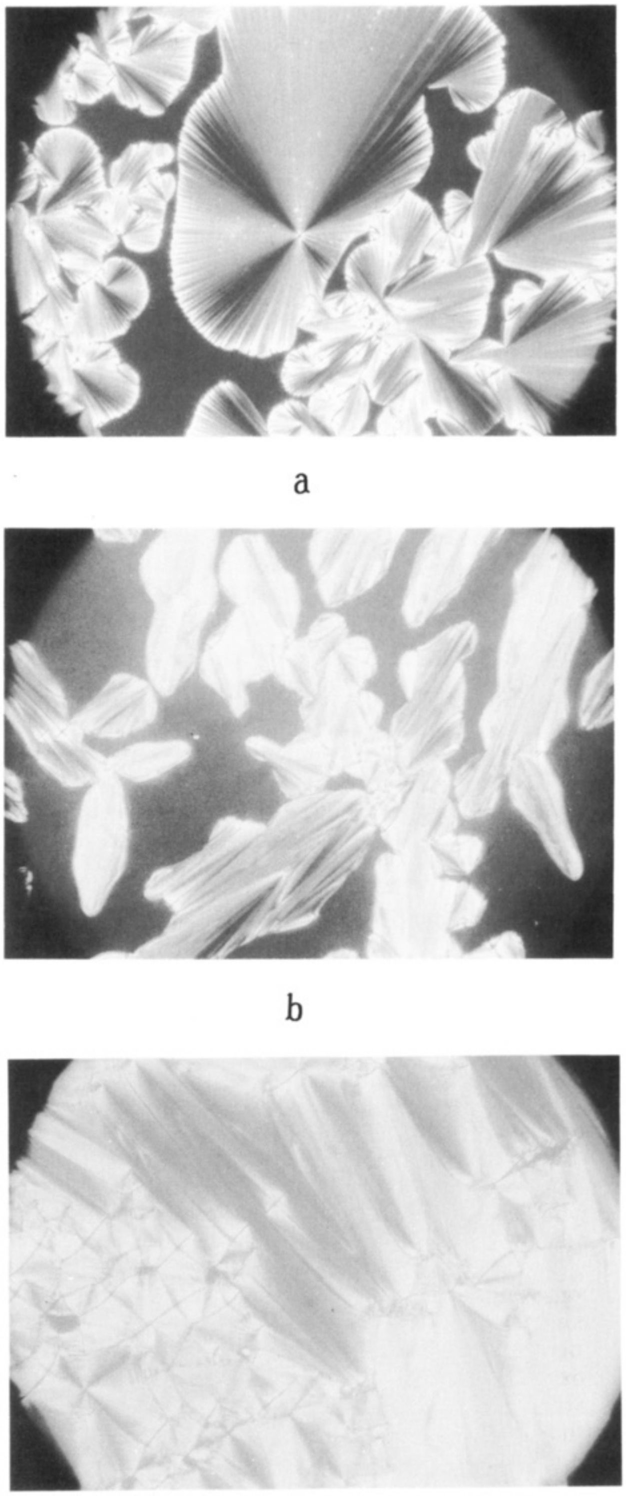
| compd | $T_m$, °C | $\Delta H_m$, J/g | $T_i$, °C | $\Delta H_i$/(J/g) |
|---|---|---|---|---|
| Ia | 145 (115) | 66.9 (21.9) | (116.5) | (38.5) |
| Ib | 211.3 (186.2) | 85.6 (58.3) | (190.7) | (7.97) |
| Ic | 96.8 (73) | 62.2 (34.1) | (76) | (28.1) |
| IIa | 172.7 | 38.6 | 253.2 | 18.1 |
| IIb | 287.9 | 70.5 | 313.6 | 9.38 |
| IIc | 230.3 | 44.9 | 252.2 | 11.7 |
| III | 146 | 33.8 | 181.6 | 1.60 |

[a] Values in the parentheses are those obtained from the cooling DSC thermograms.

polymethylene spacers are in the range 0.1–0.2, although the value appears to be a little higher for the compounds having $CF_3$ terminal groups.

**Nature of Mesophase.** The three compounds of series I showed monotropic behavior and exhibited $S_A$ textures in supercooled state (Figure 3ac for Ia, Ib, and Ic, respectively). Figure 3a shows the separation of the $S_A$ phase in the form of the focal-conic fan texture,[36] whereas Figure 3b shows the formation of $S_A$ phase in the form of batonnets[36] from isotropic liquid. Compound 3c exhibits a fan texture[36] typical for the $S_A$ phase.

According to the optical textures shown in Figure 4ac, all of the series II compounds also adopt the $S_A$ phase in melt. Figure 4a shows the typical broken-fan texture. We observe the distinct focal-conic and polygonal textures respectively for IIb (Figure 4b) and IIc (Figure 4c). In contrast, compound III is found to be a nematic compound as shown by its optical texture in Figure 4d. Compound III has the same chemical structure as IIa with only the difference lying in the character of the terminal substituents. The $CF_3$ group in IIa is known to be very strong electron-attracting group, whereas the $CH_3O$ group is a relatively strong electron-donating group. The present observations combined with our previous results[29] strongly suggest that $CF_3$ terminal group is a strong smectic phase promoter. In connection with our observations, others[37–39]


a

b

c

**Figure 3.** Photomicrographs (a, b, and c) of the mesophases formed respectively by Ia (116 °C), Ib (189 °C), and Ic (74 °C) on cooling isotropic phase (magnification 200×).

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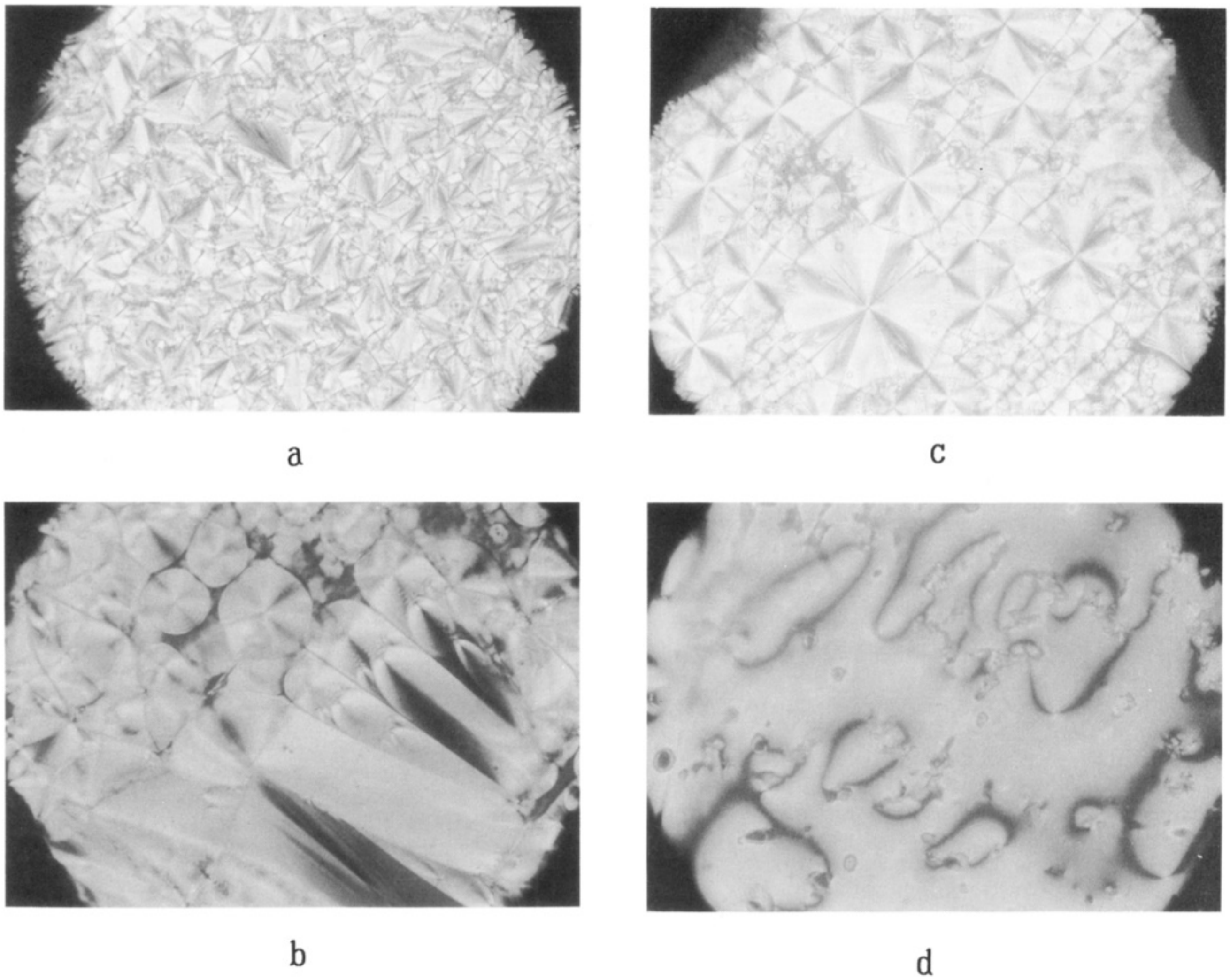

**Figure 4.** Photomicrographs (a, b, c, and d) of the mesophases formed respectively by IIa (202 °C), IIb (290 °C), IIc (240 °C), and III (166 °C) (magnification 200×).

earlier reported that the 4′-(trifluoromethyl)biphenyl esters of 4-alkoxybenzoic acids, 4′-(alkoxybenzylidene)-4-(trifluoromethyl)anilines, and 4′-[(trifluoromethyl)-benzylidene]-4-alkylalkoxyaniline are smectic compounds.

## Conclusion

From the present investigation we can draw the following conclusions;

A new series of dimesogenic compounds consisting of a disiloxyl-containing spacer and two terminal mesogenic units of diad or triad aromatic ester or amide or esteramide type having $CF_3$ substituents on the last phenylene rings could be readily synthesized.

The $CF_3$ terminal substituent in the mesogenic structure together with disiloxyl group in the spacer appears to induce the formation of smectic A phase.

The compounds of lower heat of melting ($\Delta H_m$) values tend to favor the formation of mesophases. The molar mass of series II compounds are much higher than that of series I compounds, but the magnitude of $\Delta H_m$ is reversed. As a result, series II are enantiotropically liquid crystalline, whereas series I are monotropic.

The relative magnitude of heat of isotropization ($\Delta H_i$) to $\Delta H_m$ of the present compounds is much higher than those of polymethylene spacer containing compounds. The similar observation was made for other series of dimesogenic compounds containing a disiloxyl spacer.

**Acknowledgment.** We thank the Korea Research Foundation and the Ministry of Education, Republic of Korea, for the support of this research in the fiscal year of 1992 through the Basic Sciences Research Center of Korea University.

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