mic molecule in terms of the 16 Jordan-Schwinger generators $G_i = \{a^+{}_m a_n; m,n = 1,2,3,4\}$ of the group $U(4)$.

$$H=\Sigma a_i G_i+\Sigma a_{ik} G_{ik}+\cdots \tag{11}$$

It is assumed that H conserves the total vibron number $N = (a^+ \bullet a)$ and is invariant under rotations of the subgroup $O(3) \subset U(4)$. For a given total vibron number N, the states span the totally symmetric irreducible representations of $U(4)$. Under the Jordan-Schwinger generators J_1, J_2, J_3 of $O(3)$,

$$J_i= - i(a_j^+ a_k - a_k^+ a_j)\ ;\ i, j, k=1, 2, 3 \text{ cyclic} \tag{12}$$

$\pi-(a_1, a_2, a_3)$ and $\pi^+=(a^+{}_1, a^+{}_2, a^+{}_3)$ transform as vectors while $\sigma=a_4$ and $\sigma^+ = a^+{}_4$ transform as scalars. Consequently, one can construct three more scalar products

$$\pi^{+2}= (\pi^+ \cdot \pi^+),\ \pi^2= (\pi \cdot \pi),\ n_\pi= (\pi^+ \cdot \pi). \tag{13}$$

which are consistent with Eq. (8). There exist, however, only three elementary hermitian scalars which conserve the vibron number $\hat{N}$,

$$A= n_\pi,\ B=\pi^{+2}\pi^2,\ C=\pi^{+2}\sigma^2+\sigma^{+2}\pi^2. \tag{14}$$

Note that $n_\sigma= \sigma^+\sigma$ is given by $N-n_\pi$.

Now one can write down the most general Hamiltonian, which is a hermitian scalar and conserves N, in the form

$$H=H_0+H_1+H_2+\cdots, \tag{15}$$

where H_n is a linear combination of the symmetrized scalars contained in the set S_n,

$$S_n= \{[A^{n-2k}B^{k-p}C^p]\}\ ;\ n=0, 1, \cdots,$$

$$k=0, 1, \cdots, [n/2],\ p=0, 1, \cdots, k, \tag{16}$$

where $[n/2]$ is the integral part of $n/2$. The set S_n contains the n-th order symmetrized scalars with respect to the generators of $U(4)$ and its order $|S_n|$ is given by

$$|S_n| = ([n/2]+1)([n/2]+2). \tag{17}$$

It can be shown[3] that the operators A, B and C can be expressed in terms of the Casimir operators belonging to two different group chains. This helps the actual calculation of the spectra. A detailed calculation based on the most general Hamiltonian given in Eq. (15) will be given in a forthcoming paper.

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Synthesis and Liquid Crystalline Properties of Dimesogenic Compounds Containing Trifluoromethyl Substituents at Terminal Phenylene Rings and Central Decamethylene Spacer

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A series of new dimensogenic compounds whose mesogens are of aromatic ester or amide type having a trifluoromethyl (CF_3) substituent at the para-position of each terminal phenolic rings were prepared and their liquid crystalline properties were studied by differential scanning calorimetry (DSC) and on a cross-polarizing microscope. The compounds have two identical mesogenic units bracketing a central decamethylene spacer. Trifluoromethyl group appears to favor the formation of smectic phases when it is attached to a phenoxy or anilide terminal. Its group efficiency for mesophase formation seems to be inferior to other common substituents. A thermodynamic analysis of the phase transitions was made and the results were explained in relation to the structures of the compounds.

Introduction

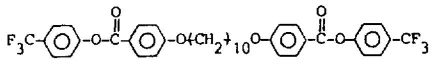
Thermotropic behavior of various dimesogenic compounds that consist of two identical mesogenic units bracketing a central spacer has been a subject of our previous reports.[1-6] These compounds exhibits very interesting properties such as odd-even effect in melting (T_m) and isotropization temperatures (T_i) when the spacer is polymethylene,[7] a zig-zag odd-even effect in the entropy change for isotropization, greater values in thermodynamic parameters of ΔH_m,

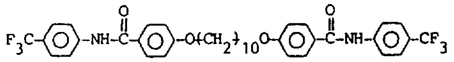
ΔH_i and ΔS_i than the corresponding monomesogenic compounds, and similar nematic or smectic group efficiency for various substituents as those observed in monomesogenic systems.

In addition, we recently observed that dimesogenic compounds are more prone to be enantiotropically thermotropic than monomesogenic compounds, indicating a higher degree of molecular orders for the formers than latters in the melt.[8] It also was found earlier that these dimesogenic compounds are excellent model compounds for main chain thermotropic polyesters that contain similar mesogenic units interconnected through the same flexible spacers.[9]

When the two terminal mesogenic units are not identical, the mesophases observed are not the same as those observed separately for the two monomesogenic compounds containing only one type of mesogenic structure.[10] This phenomenon is a result of cooperating molecular interactions of constituting structures. The importance of linear molecular geometry in the ability for a compound to be mesomorphic also was clearly demonstrated recently by us.[11] When the two mesogenic structures are linked para to each other through the central phenylene ring maintaining a linear molecular shape as a whole, the compound is liquid crystalline. On the other hand, when they are attached to the central ring meta to each other, the resulting molecule acquires a bent molecular shape and is found to be unable to form a mesophase in the melt.

As a part of our continued efforts to delineate the structure-properties relationship of dimesogenic compounds, we prepared the following series of compounds, and their thermal properties and liquid crystallinity were studied:


I - 1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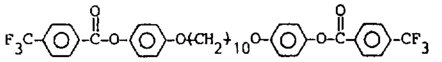
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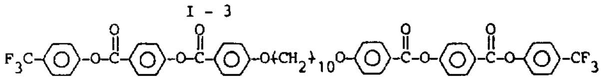
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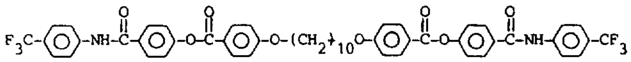
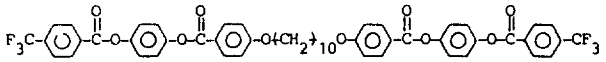
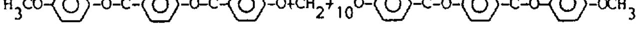

II - 2


II - 3

All of the compounds contain the decamethylene spacer and trifluoromethyl group as a substitutent at the terminal phenylene rings of mesogenic structures. The compounds I consist of dyad aromatic ester or amide type mesogenic units and the central spacer, whereas the compounds II have triad aromatic ester or amide type mesogens. And in each group of compounds made was a systematic structural change. For a comparison purpose, the following compound was also synthesized and its properties were examined:



Experimental

Synthesis of Compounds I-1 and I-2. These compounds were prepared by reacting 1,10-bis(4-carboxyphenoxy)decane **1** either with *p*-trifluoromethylphenol or with *p*-trifluoromethylaniline. The former was prepared via the literature method from ethyl *p*-hydroxybenzoate and 1,10-dibromodecane.[12] The compound **1** (1.0 g; 2.4 m mol) was dissolved in 20 m*l* of $SOCl_2$ and the mixture was refluxed for 4 h. The excess $SOCl_2$ was then removed by distillation under a reduced pressure. 1,10-Bis(4-chloroformylphenoxy)decane prepared was dissolved in 3 m*l* of 1:1 (v/v) mixture of pyridine and N,N-dimethylformamide(DMF). To this solution added at room temperature under a N_2 atmosphere was a solution of 0.78 g (4.8 m mol) of 4-trifluoromethylphenol dissolved in 2 m*l* of pyridine. The mixture was stirred at 60 °C under a N_2 atmosphere for 5 h. And then the mixture was poured into excess water. The precipitate formed was washed with water and methanol. The crude product was recrystallized from DMF. The yield of the product, 1,10-bis[4-(*p*-trifluoromethylphenoxycarbonyl)phenoxy]decane (I-1), was 1.5 g(94%). m.p., 146.7 °C. ^{1}H-NMR (CF_3COOD); 7.1-8.3 (m, 16H, Ar.), 4.25 (t, 4H, $-OCH_2-$), 1.25-2.1 (m, 16H, $-CH_2-$). IR (KBr); 3050 cm^{-1} (Ar. = C-H str.), 2930 (aliphatic C-H str.), 1730 (-C = O str.), 1605 (Ar. C = C str.), 1260 and 1055 cm^{-1} (C-O str.), and 1330 cm^{-1} (C-F str.).

The compound I-2, 1,10-bis[4-(*p*-trifluoromethylphenyliminocarbonyl)phenoxy]decane, was prepared by the same procedure using 4-trifluoromethylaniline in place of 4-trifluoromethylphenol. Finally, the product was recrystallized from acetone. The yield was 90%. m.p., 234.5 °C, ^{1}H-NMR (CF_3COOD); δ 7.0-8.1 (m, 16H, Ar.), 4.25 (t, 4H, $-OCH_2-$), 1.3-2.1 (m, 16H, $-CH_2-$). IR (KBr); 3340 (-N-H str.), 3050 (Ar. = C-H str.), 2940 (aliphatic C-H str.), 1660 (-C = O str.), 1605 and 1505 (Ar. C = C str.), 1410 (C-N bending), 1330 (C-F str.), and 1255 and 1065 cm^{-1} (C-O str.).

Synthesis of Compound I-3. The compound I-3,1,10-bis[4-(*p*-trifluoromethylbenzoyloxy)phenoxy]decane, was prepared from 1,10-bis(*p*-hydroxyphenoxy)decane **3**[12] and *p*-trifluoromethylbenzoic acid. *P*-Trifluoromethylbenzoic acid (1.0 g; 5.25 m mol) was first converted to *p*-trifluoromethylbenzoyl chloride by reacting with $SOCl_2$. And *p*-trifluoromethylbenzoyl chloride thus prepared was dissolved in 1.5 m*l* of pyridine. This solution was mixed at room temperature with a solution of compound **3** (0.95 g; 2.63 m mol) dissolved in 2 m*l* of pyridine. The solution was stirred at 60 °C under a N_2 atmosphere for 5 h. The mixture was poured into excess water. The precipitate was washed with water and methanol. The product was recrystallized from acetone. The yield was 1.6 g(89%). m.p., 159.4 °C. IR (KBr); 3060 (Ar. = C-H str.), 2920 (aliphatic C-H str.), 1740 (-C = O str.), 1600 and 1502 (Ar. C = C str.), 1475 (aliphatic C-H bending), 1270, 1245 and 1075 cm^{-1} (C-O str.).

Synthesis of Compounds II-1, II-2, and III. These compounds were prepared by reacting compound **1** with either 4′-trifluoromethylphenyl 4-hydroxy or 4-aminobenzoate or 4′-methoxyphenyl 4-hydroxybenzoate. The latters were prepared from *p*-hydroxybenzoic acid and 4-trifluoromethylphenol or 4-trifluoromethylaniline or methoxyphenol.

For the preparation of compound II-1, 1,10-bis[4-(*p*-trifluoromethylphenoxycarbonyl)phenoxycarbonylphenoxy]decane, 4′-trifluoromethylphenyl 4-hydroxybenzoate **7** was first synthesized. Ethyl-4-chloroformylphenyl carbonate **5** (0.024 mol) prepared from 4-carboxyphenylethyl carbonate 4(5.0 g; 0.024 mol)[13,14] and $SOCl_2$ was dissolved in 10 m*l* of pyridine. To this solution added dropwised was a solution of 4-trifluoromethylphenol (3.85 g; 0.024 mol) dissolved in 5 m*l* of pyridine. The mixture was stirred at 60 °C under a N_2 atmosphere for 5 h. The reaction mixture then was poured into excess water. The precipitate was thoroughly washed with water. The product was recrystallized from acetone. The yield of the product, ethyl 4-(4-trifluoromethyl)phenoxycarbonylphenyl carbonate **6**, was 7.9 g (93%). m.p., 118 °C.

The carbonate **6** (7.5 g; 0.022 mol) was hydrolyzed to 4′-trifluoromethylphenyl 4-hydroxybenzoate **7** by refluxing in 40 m*l* of ethanolic KOH solution for 2h.[15] The solution was acdified with acetic acid to pH 4. The solution was poured into excess water and the precipitate was collected on a filter. The precipitate was thoroughly washed with water. The yield was 3.8 g (61%). m.p., 142 °C. This product was found to be pure enough by TLC, and IR and NMR spectroscopy to be used in the next step without further purification.

1,10-Bis(4-chloroformylphenoxy)decane **2** prepared from 1.0 g (2.4 m mol) of 1,10-bis(4-carboxyphenoxy)decane **1** and $SOCl_2$ was dissolved in 3 m*l* of a 1:1 (v/v) mixture of pyridine and DMF. To this solution added dropwise was a solution of compound **7** (1.36 g; 4.8 m mol) dissolved in 2 m*l* of pyridine. The mixture was stirred at 60 °C under a N_2 atmosphere for 5h. The precipitate was collected on a filter and washed with distilled water and methanol. The product II-1 was recrystallized from acetone. The yield was 2.1 g(91%). m.p., 235.3 °C. ^{1}G-NMR (CF_3COOD); δ 6.9-8.6 (m, 24H, $-C_6H_4-$), 4.25 (t, 4H, $-OCH_2-$), 1.2-2.3 (m, 16H, $-CH_2-$). IR (KBr); 3050 (Ar. =C-H str.), 2900 (aliphatic C-H str.), 1735 (-C=O str.), 1600 and 1505 (Ar. C=C str.), 1335 (C-F str.), and 1205 and 1050 cm^{-1} (C-O str.).

The compound II-2, 1,10-bis[4-(*p*-trifluoromethylphenyliminocarbonyl)phenoxycarbonylphenoxyl]decane, was prepared *via* the exact same proceudre as used in the synthesis of II-1. The carbonate 8, ethyl-4-(4-trifluoromethylphenyliminocarbonyl)phenyl carbonate, derived from ethyl-4-chloroformylphenyl carbonate 5 and *p*-trifluoromethylaniline had a m.p. of 197.8 °C. 4′-Trifluoromethylanilide **9** was obtained by the hydrolysis of the corresponding carbonate in an alcoholic KOH with the yield of 62%. (m.p. 199 °C). IR (KBr); 3450 (N-H str.), 3070 (Ar. =C-H str.), 2920 (aliphatic C-H str.), 1730 and 1662 (-C=O str.), 1600 and 1510 (Ar. C=C str.), 1325 (C-F str.), and 1255 and 1060 cm^{-1} (C-O str.).

The compound III, 1,10-bis[4-(*p*-methoxyphenoxycarbonyl)phenoxycarbonylphenoxy]decane, was prepared *via* the same procedure as used in the synthesis of II-1, by reacting compound 2 and 4′-methoxyphenyl 4-hydroxybenzoate **11** (m.p. 196 °C) that was obtained by the hydrolysis of the ethyl carbonate of *p*-methoxyphenoxycarbonylphenol **10** (m.p. 87 °C). The latter compound was synthesized from ethyl carbonate of *p*-chloroformylphenol 5 and *p*-methoxyphenol. The crude compound III was recrystallized from acetone. The yield was 91%. m.p., 179.4 °C, IR (KBr); 2800-2900 (aliphatic C-H str.), 1730 (C=O str.), 1330 cm^{-1} (C-F str.).

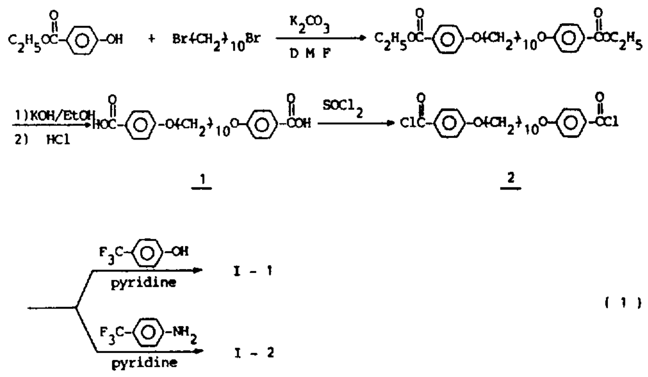
Synthesis of Compound II-3. 1,10-Bis(4-chloroformylphenoxy)decane 2 prepared from 2.0 g(4.8 m mol) of **1** and $SOCl_2$ was dissolved in a mixture of 2 m*l* of pyridine and 2.5 m*l* of DMF. To this solution added was a solution of hydroquinone (2.66 g; 0.024 mol) dissolved in a mixture of 3 m*l* of pyridine and 3.5 m*l* of N,N-dimethylacetamide. The solution was stirred at 60 °C under a N_2 atmosphere for 5 h. The mixture was poured into excess water. The precipitate was collected and washed with distilled water. The precipitate was recrystallized from DMF. The yield of 1,10-bis [4-(*p*-hydroxyphenoxycarbonyl)phenoxy]decane **12** thus obtained was 2.6 g (90.5%). m.p., 205 °C. IR(KBr); 3350 (O-H str.), 2900 (aliphatic C-H str.) and 1720 cm^{-1} (C=O str.). NMR (CF_3COOD); 7.0-8.5 (m, 24H, Ar.), 4.25 (t, 4H, $-CH_2O-$), 1.2-2.15 (m, 16H, $-CH_2-$).

The above compound **12** (1.57 g; 2.63 m mol) dissolved in 2 m*l* of pyridine was mixed with a pyridine (1.5 m*l*) solution of trifluoromethylbenzoyl chloride prepared from 1.0 g(5.25 m mol) of trifluoromethylbenzoic acid and $SOCl_2$. The mixture was stirred at 60 °C under a N_2 atmosphere for 5 h. The mixture then was poured into excess distilled water. The precipitate, after being washed with distilled water and methanol, was recrystallized from acetone. The yield of the compound II-3, 1, 10-bis-[4-{*p*-(4-trifluoromethylbenzoyloxy)phenoxycarbonyl}phenoxy] decane, was 2.3 g (91%). m.p., 221.8 °C. IR (KBr); 3050 (Ar. C-H str.), 2900 (aliphatic C-H str.), 1720 (-C=O str.) and 1320 cm^{-1} (C-F str.).

Characterization of Compounds. Elemental analyses were performed by the Microanalytical Laboratory at the University of Massachusetts, U.S.A.. IR and NMR spectra were recorded on a Shimadzu IR-440 and an FT-NMR 80 Sy of Bruker, respectively. Thermal properties were studied on a Fisher-Johns melting point apparatus and also on a differential scanning calorimetry (DSC-Mettler DSC 30) at a heating rate of 10 °C/min. Calibrations of temperature and entropy changes were conducted using indium, tin and zinc as references. Thermal and liquid crystalline properties were studied also on a polarizing microscope (Leitz, Ortholux) equipped with a hot stage (Mettler FP-5).

Results and Discussion

Synthesis of Compounds. Synthetic routes employed for the synthesis of the present compounds consist of rather well known simple reactions (eqs. 1-4), although they are of multi-steps. The structures of the intermediates and final compounds were confirmed by elemental analyses (Table 1), and IR and NMR spectra. Purity of the final compounds were checked by TLC and found to be very pure.

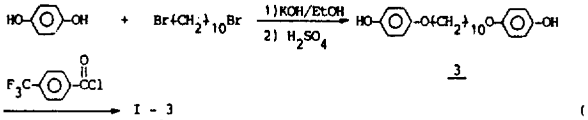


(1)

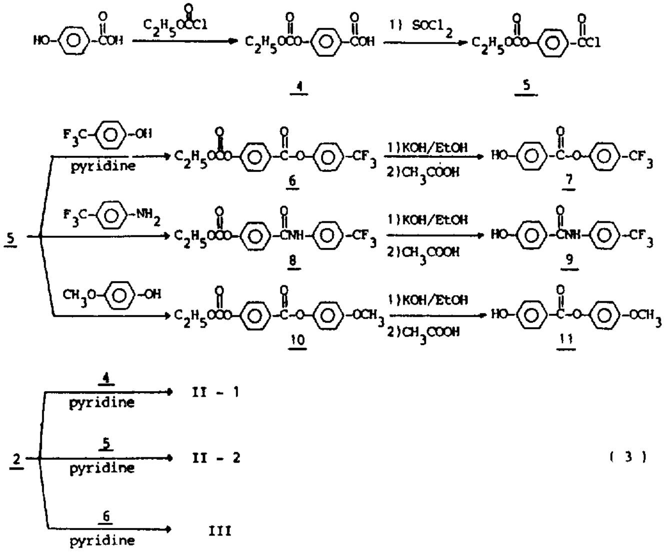
Table 1. The Results of Elemental Analyses#

Compound	Elemental Contents, Wt. %			
	C	H	F	N
I-1	64.89(64.94)	5.18(5.17)	15.95(16.22)	
I-2	65.10(65.12)	5.48(5.48)	15.98(16.27)	3.95(4.00)
I-3	64.95(64.94)	5.14(5.17)	15.98(16.22)	
II-1	66.18(66.23)	4.77(4.71)	12.02(12.07)	
II-2	66.35(66.37)	4.96(4.94)	12.12(12.11)	3.01(2.98)
II-3	65.98(66.23)	4.72(4.71)	12.08(12.09)	
III	71.95(72.03)	5.84(5.82)		

#The values in the parentheses are the calculated ones for the molecular formulas.



(2)



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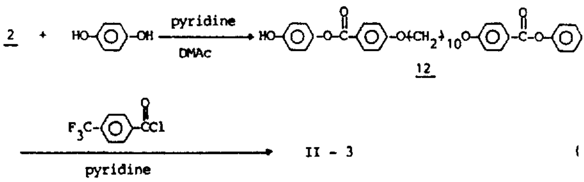


(4)

The final synthetic steps for all of the compounds involve relatively simple reactions between an aromatic acid chloride and a phenol. This type of reactions is known to proceed almost quantitatively even at room temperature in the presence of an HCl acceptor. The only special strategy we had to utilize was to protect hydroxyl group of *p*-hydroxybenzoic acid in the synthesis of the compounds **7-9** and **11**.[13,14] The carbonate-protecting group could be selectively removed by hydrolysis with alcoholic KOH.[15] Since a part of the ester or amide bonds was also attacked by the base, the yields for the deprotection reactions were not too high.

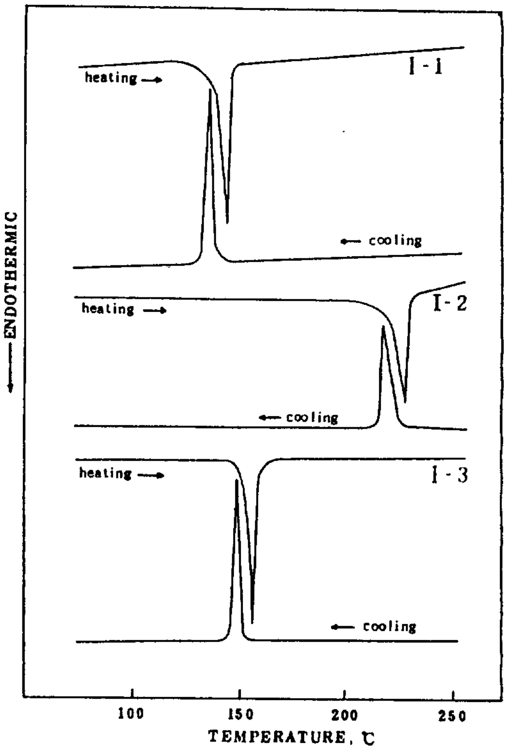


Figure 1. DSC thermograms of series I compounds.

Thermal Transition Properties. Each of three compounds of series I exhibited only a single endothermic transition peak on heating the solid and a single exothermic transition peak on cooling the liquid (Fig. 1). The transition corresponds to melting or crystallization. The melting point (234.5 °C) of compound (I-2) is much higher than those (146.7 and 159.4 °C, respectively) for I-1 and I-3. The presence of amide groups in I-2 certainly promotes intermolecular hydrogen bonds in solid and increase the melting point. When their thermal behavior was observed on a polarizing microscopy, they were transformed directly from the solid state to isotropic liquid. In other words, they are not able to form mesophases, i.e., they are not liquid crystalline. This is rather surprising in light of our earlier observations[6] that the similar compounds having a wide variety of substituents such as H, CH_3, Cl, CH = O, NO_2, CN and C_6H_5 in place of CF_3 form nematic phases in the melts. Such a comparison indicates that the trifluoromethyl substituent somehow has a very poor group efficiency in promoting mesophase formation by the compounds having the structural feature we are concerned with. A thermodynamic reason for this will be discussed later.

In contrast, the monomesogenic compounds of 4′-trifluoromethylbiphenyl esters of 4-alkoxybenzoic acids were reported recently by Du Bois *et al.*[16] to be smectic compounds. Biphenyl structure certainly is much more efficient in induction of mesophase-formation than phenyl unit. 4′-Alkoxybenzylidene-4-trifluoromethyl anilines and 4′-trifluoromethylbenzylidene-4-alkyl or alkoxyanilines having long alkyl groups are known to be smectic compounds.[17,18] Schiff bases are certainly more prone to be liquid crystalline when compared with the corresponding esters.

The structure of compound I-3 is slightly different from that of compound I-1. The ester bonds in the mesogenic groups are reversed from oxycarbonyl $(\text{-O-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-})$ to carboxy $(\text{-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-O-})$ linkages. This change did not bring about meso-

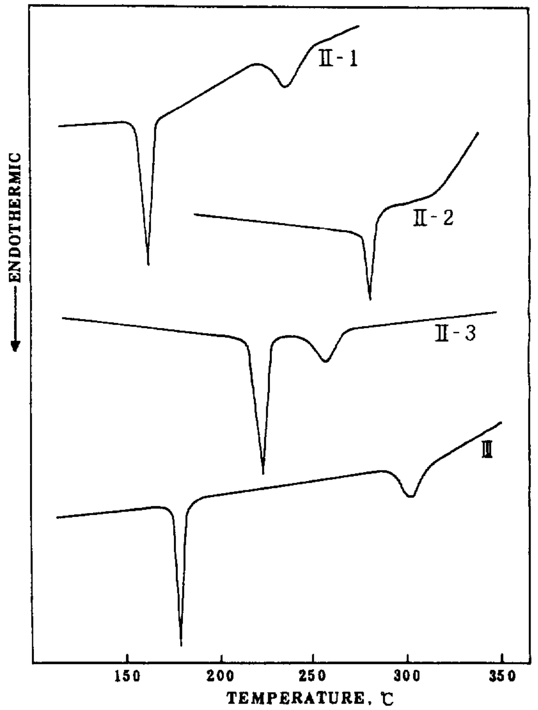
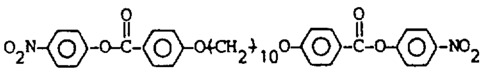
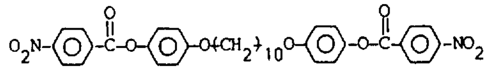


Figure 2. DSC thermograms on heating cycles of series II compounds and compound III.

phase-forming capability. In fact, we earlier observed that such a change reduces the mesophase-forming tendency as shown below:[5,6]


$O_2N-C_6H_4-O-C(=O)-C_6H_4-O(CH_2)_{10}O-C_6H_4-C(=O)-O-C_6H_4-NO_2$

enantiotropically liquid crystalline, K 144 N 160 I (on heating)


$O_2N-C_6H_4-C(=O)-O-C_6H_4-O(CH_2)_{10}O-C_6H_4-O-C(=O)-C_6H_4-NO_2$

monotropically liquid crystalline, I 158 N 148 K (on cooling)

As far as thermal transitions of the compounds of series II and compound III are concerned, they were very much different from those of series I. DSC thermograms of compounds II-1, II-3 and III (Fig. 2) exhibit two endothermic peaks when the solids are heated. The lower temperature peaks correspond to melting, whereas the higher temperature ones to liquid crystal-to-isotropic phase transition, *i.e.*, isotropization. These transitions were reversibly observed on cooling the isotropic liquids. In other words, these compounds are enantiotropically mesomorphic. The compound II-2, however, underwent thermal decomposition before reaching isotropization temperature T_i. Therefore, a DSC thermogram of this compound shows only a melting endotherm at 284 °C. The microscopic observation on a hot stage also confirmed this compound to be liquid crystalline and melts at 284 °C.

The melting point (284 °C) of compound II-2 that contains amide bonds is significantly higher than those (160 °C and 222 °C, respectively) for compounds II-1 and II-3 having only ester groups. The similar phenomenon was described above for the compounds of series I. Such a difference is rather general for other simple esters and amides. The same trend is also observed for the isotropization temperatures, T_i's. The T_i values are in the order of II-2 (>350 °C)>II-3 (255 °C)>II-1 (235 °C). This signifies that the amides bond stabilize mesophases much more efficiently than the ester bonds.

When the thermal properties of the compounds of series I were discussed above, it was mentioned that CF_3 group is a poorer mesophase inducer than other substituents such as CH_3 and OCH_3 groups. Comparison of T_i (235 °C) for compound II-1 with that (303 °C) for compound III leads to the same conclusion. The lower T_i of compound II-1 indicates that its mesophase is less thermally stable than the other which has the CH_3O substituents in place of CF_3 groups.

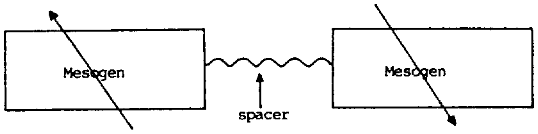
Nature of Mesophases Formed By Series II Compounds. Phase transition behavior of the compounds described above was confirmed by observing the samples through a polarizing microscope equipped with a hot-stage whose temperature was automatically controlled. In addition, from the optical textures (Fig. 3) observed for the mesomorphic compounds, we could identify the nature of the mesophases that each compound formed in the melts. According to the textures, compound II-1 and II-2 form a smectic-A phase, whereas compound II-3 forms a nematic phase. Although its optical texture is not included here, compound III also was found to be nematic. A qualitative consideration of the geometrical structures and bond dipoles of compound II-1 and II-2 indicates that their total dipole directors of mesogenic units direct substantially angled from the long molecular axis as depicted below;


(a) (b) (c)

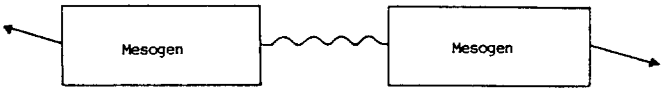
Figure 3. Optical textures of series II compounds: (a) optical texture of II-1 taken at 220 °C on heating, (b) of II-2 taken at 273 °C on cooling and (c) of II-3 taken at 224 °C on cooling.

Table 2. Thermal and Liquid Crystalline Properties of the Compounds

Compound	T_m, °C	T_i, °C	ΔH_m, J/g	LC phase
I-1	146.7		65.1	non-LC
I-2	234.5		38.4	non-LC
I-3	159.4		112.2	non-LC
II-1	159.7	235.3	13.3	smectic A
II-2	284.1		36.6	smectic A
II-3	221.8	254.5	32.7	nematic
III	179.4	302.7	55.2	nematic



This implies that a lateral intermolecular attraction is very strong when compared with end-wise interactions. Such a structural characteristics is known to favor the formation of smectic phases.[19,20] On the other hand dipoles of the mesogenic units in compound II-3 direct toward opposite directions more or less parallel to the molecular axis;



When molecular interactions along the molecular axis direction are comparable to lateral interaction, the compounds tend to form nematic phase instead of smectic phase.[19] The exactly same reasoning can be applied in order to understand why compound III forms a nematic phase in spite of its same skeletal structure as in compound II-1. This difference results from the electron donating nature of the CH_3O group in comparison to the strong electron withdrawing character of the CF_3 group. Therefore, we can conclude that the characteristics of chemical bonds in linking groups, in our case, ester groups, and the electronic effect of the terminal substituents are extremely important in controlling the nature of mesophases formed.

Enthalpy Changes for Melting. Enthalpy changes for melting (ΔH_m) were estimated from DSC analyses and the values are included in Table 1. The magnitudes of ΔH_m bear out a very important point that provides us with some or at least a partial answer on the question why the compounds of series II are liquid crystalline whereas those of series I are not. The ΔH_m values are much greater for the series I compounds than for the series II, especially for those of wholly aromatic ester type. For example, ΔH_m of compound I-1 is 65.1 J/g, which is about 5 times as large as ΔH_m(13.3 J/g) of compound II-1. This means that I-1 requires much greater thermal energy to transform the solid into liquid than the other compound does. This amount of thermal energy must be more than enough to convert the solid of I-1 directly into an isotropic liquid without going through a mesophase. If heat of melting for the crystals are too high, thermal motion will prevent the existence of an ordered liquid crystal after melting occurs.[21]

As mentioned earlier, the compounds are liquid crystalline that have the exact same structures as I-1 but have different substituents such as CH_3, Cl, and so on in place of CF_3.[6] These compounds were reported to have much lower ΔH_m (about one half to one fourth) when compared with the value for compound I-1. This again tells us that ΔH_m value for I-1 is extraordinarily high, which must be at least one of the reasons why this compound is not able to form a mesophase. A similar explanation can be given for the observation that neither compounds I-2 nor I-3 is liquid crystalline. It is evident that the presence of the terminal CF_3 in series I results in very high lattice energy in the solid state.

Conclusion

The following conclusion can be drawn from the present investigation:

1. All of the compounds of series I are not liquid crystalline although the similar compounds having other substituents in place of trifluoromethyl group are known to be enantiotropically mesomorphic. The trifluoromethyl group does not appear to be effective mesophase inducer, at least, for the present compounds.
2. In contrast, all of three compounds of series II reversibly form a liquid crystalline phase in melt. The nature of mesophases that they form depends greatly on their detailed structures, which, in turn, govern the intermolecular attractions. Compounds II-1 and II-2 are smectogens, whereas compound II-3 is a nematogen. The formers form a S_A phase in the melts.
3. The enthalpy changes, ΔH_m, for melting are much greater for the series I compounds than for the series II. This is taken as one of the major reasons why the series I compounds are not mesomorphic, whereas, the series II are liquid crystalline.

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Oxygen Interstitial Defects and Ion Hopping Conduction of X ThO_2 + (1 – X) Gd_2O_3 Solid Solutions: $0.08 \leq X \leq 0.12$

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Gd_2O_3-ThO_2 solid solutions containing 8, 10 and 12 mol % ThO_2 were synthesized with spectroscopically pure Gd_2O_3 and ThO_2 polycrystalline powders. X-ray diffraction revealed that all synthesized specimens have the modified fluorite structure, and the lattice parameter of Gd_2O_3 is nearly unchanged with increasing ThO_2 mol %. Both *ac* and *dc* conductivities were measured in the temperature range 500–1100 °C under Po_2's from 10^{-6} to 10^{-1} atm. The *dc* conductivities are nearly independent of Po_2, and agree with the *ac* values. This implies that the solid solutions are ionic conductors. The conductivity increases with increasing ThO_2 mol % with an average activation energy of 1.23 eV. An oxygen interstitial defect and ionic hopping conduction are suggested.

Introduction

Gd_2O_3 is one of the lanthanide oxides and is known to have cubic C-type structure with lattice constant 10.813 Å at temperatures up to 1200 °C. There are 24 Gd^{3+} ions on sites with two-fold rotational symmetry (C_2), 8 Gd^{3+} ions on sites with three-fold rotatory inversion symmetry (C_3), the 48 rotatory O^{2-} ions at general positions, and 16 interstitial sites in the unit cell of C-Gd_2O_3. Gd_2O_3 has p-type characteristics in the high oxygen partial pressure region[2]. Tare and Schmalzried[3] reported through an emf study that Gd_2O_3 is essentially an ionic semiconductor under oxygen partial pressures of between 10^{-2} and 10^{-1} atm. An activation energy of 1.57 eV was observed by Subbarao *et al.*[4]. Gd_2O_3 is capable of dissolving considerable amounts of tetravalent and higher valence cations and apparently produces interstitial O^{2-} ions which are mobile[5]. Diness and Roy[6] reported that a Gd_2O_3-ThO_2 solid solution having the cubic C-type structure was easily formed at a low sintering temperature, 800 °C.

The additions of lower valence cations such as Y_2O_3 to ThO_2[7], Gd_2O_3 to ThO_2[8] and Y_2O_3 to ZrO_2[9] have been reported to produce mobile O^{2-} ions due to their interstitial sites in the cubic C-type structure. The aim of this work is to characterize the influence of the ThO_2 dopant on the electrical behavior of X ThO_2+(1-X) Gd_2O_3 solid solutions. These solid solutions were chosen because Gd_2O_3 has a high activation energy for electrical conduction, ThO_2 is easily soluble up to 16 mol% in Gd_2O_3 at low temperature, 800 °C, and both oxides have good thermal stability and stoichiometric composition[6].

Experimental

Sample Preparation. C-Gd_2O_3(5N) and ThO_2(5N) polycrystallines obtained from the Rare Metallic Company were used as the starting powders. Specimens with grain size <1 μm were prepared by ultrasonic treatment. The mixed oxide was calcined at 680 °C for 10 h in air. The powder mixture was stirred for 12 h in ethyl alcohol, and then dried. The dried powder was hydrostatically pressed at 1×10^9 Pa into a pellet, presintered at 880 °C for 96 h, and then slowly cooled to room temperature. The surfaces of the presintered pellets were etched by $(NH_4)_2S_2O_8$ and H_3PO_4 solutions, respectively. The phases of the presintered pellets were investigated by X-ray diffraction technique. The X-ray patterns showed that all pellets formed cubic C-type solid solutions. The presintered specimens were reground in an agate mortar, stirred in ethyl alcohol for 24 h, and then dried. The powders were re-pelletized, resintered at 1330 °C for 40 h, and annealed at 1130 °C for 30 h to reduce the grain boundary effect. X-ray analysis results for these resintered specimens are listed in Table 1. As shown in Table 1, the specimens are all cubic C-type solid solutions.

Analysis. DTA and TGA measurements were carried