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Smectic Mesophase Properties of Dimeric Compounds. 2. Distinct Formation of Smectic Structures with Antiferroelectric Ordering and Frustration

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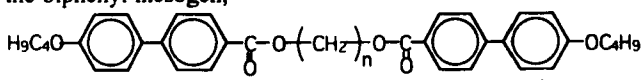
We have prepared two series of dimeric compounds, which comprise the schiff's base mesogen, alkyl spacer with the carbon number of 5 and alkyl or alkoxy tail with the carbon number of m = 4~16. In these compounds, we observed three types of smectic liquid crystals, the single layer phase with the tail group randomly mixing with the spacer, the bilayer phase in which the segregation of the spacer and tail groups takes place and so two mesogenic layers are included within a repeat unit, the frustrated smectic phase in which the density modulation appears along the layer as well as the layer normal. The bilayer phase was found to be antiferroelectric and the frustrated smectic phase was considered to result from the two dimensional escape from the dipolar interaction. The phase behaviour with m and the structure and properties of each phase will be described in detail.

Keywords: dimer; smectic liquid crystal; antiferroelectric liquid crystal; conformation; frustrated smectic phase

1. Introduction

During a course of the studies on main-chain type of polymers,[1] the studies were extended to the dimeric compounds, di-BB-n, with the biphenyl mesogen,[2]



In this series of dimers, we have found that two different phases are formed depending on the number of intervening methylene units, n. From di-BB-n with even n, a S_A phase is formed in which the axes of both the molecule and mesogenic group lie perpendicular to the layers. In contrast, di-BB-n with odd n formed a S_{CA} where the molecular axes lie perpendicular to the layer but the mesogenic groups are tilted to the layer normal. The distinct structural feature in the S_{CA} phase is that the tilt direction of the mesogenic groups is opposite in

two neighboring layers.[1] Such an odd-even effect on the smectic structures has been explained as resulting from a conformational constraint whereby the spatial arrangement of mesogenic groups within a molecule is strongly confined by the conformation of intervening alkylene spacer.[1] The molecules with odd n tend to assume the conformation with two successive mesogenic groups tilted toward each other, while the mesogenic groups in molecules of even n lie parallel to each other.

In addition to the conformational constraint, another interesting effect can be considered in a smectic structure of the twin dimer. Twin dimer has three different units, alkyl tail, mesogenic group and alkylene spacer. In order to give a more detailed picture of the smectic layer structure, we have to understand how the alkyl tail and spacer groups are being accommodated into a smectic layer.[3-6] In the dimeric di-BB-n, the smectic layer spacings have been observed to be half a molecular length.[2] This means that each mesogenic biphenyl group participates to form the basic layer with a random mixing of the spacer and tail groups. Such a random mixing can gain the entropy and so may be reasonable since two groups are not significantly different in length.

Here arises a simple question on how the smectic layer structure is constructed by dimeric compounds when the length of the alkyl tail is remarkably different from that of the alkyl spacer. If the two aliphatic groups are still randomly mixed with each other, the smectic layer structure would be significantly damaged or destabilized. On the other hand, if the molecules tend strongly to form the smectic phase, segregation of the spacer and tail alkyl groups may occur to result in the bilayer structure with two mesogenic layers included in a repeat unit because of a steric incompatibility of the two alkyl groups.Then, the bilayer smectic phase which may be formed from the dimers with

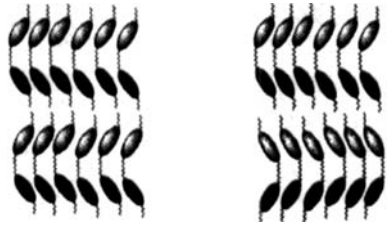
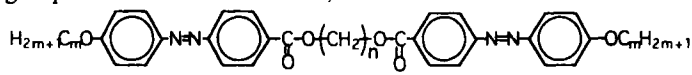


Figure 1. Two possible smectic structures with bilayer modification formed by twin dimers assuming a bent conformation, when the alkyl tail and spacer groups segregate from each other. (a) ferroelectric alignment and (b) antiferroelectric alignment.

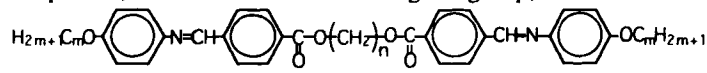
odd numbered spacer is especially interesting since it would be ferroelectric or antiferroelectric even in achiral system.[7-9] The basic structures are illustrated in Figure 1. The space groups are analogous to a crystallographic C_{2v} for ferroelectric phase of Figure 1a and D_2 for antiferroeletric phase of Figure 1b. In both phases, spontaneous polarization can be expected to arise along the tilt direction of molecule.

The previous study has been performed to clarify this point in the following dimeric compounds, mOAznAzOm, with the mesogenic group based on the azobenzene[6];

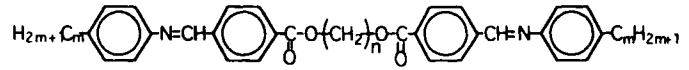


Effect of the length of the spacer was examined by preparing four series of the dimers in which the carbon number of the spacer, n, is varied from 3 to 9 while the carbon number of the terminal chain, m, is held constant at either 2,4,8 or 12. A marked odd-even effect due to n was observed as mentioned above, but all the smectic phases were found to be constructed by a random mixing of the two groups.

In this study, we have prepared another series of the dimeric compounds, with the Schiff's base mesogenic group,



These compounds are abbreviated here mOAMnAMOm where m and n indicate the carbon numbers of the alkyl tail and spacer, respectively. Here, the value of m is varied from 4 to 16 with the constant value of n = 5. Further, we have prepared a series of mAMnAMm

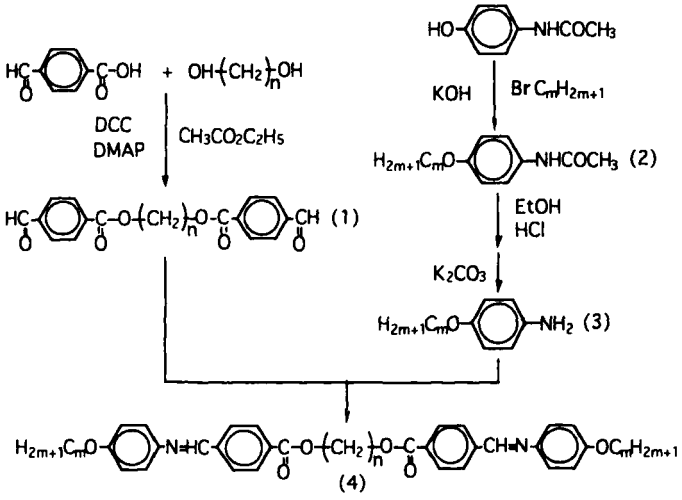


with n = 5 and m = 4~14. In these two systems, we have found three types of smectic phases, single-layer smectic phase, frustrated smectic phase and the antiferroelectric bilayer smectic phase. The phase behaviour as a function of m and the structure and properties of the phases will be reported.

2. Experimental

2.1. Materials

The mOAMnAMOm compounds were synthesized according to Scheme 1. Each procedure is described in detail below.



Scheme 1

α,ω-Bis(4-formyl-phenyl-4'-carbonyloxy)alkane (1) was prepared by direct esterification of 4-formyl-benzoic acid and corresponding diol using N,N'-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)-pyridine (DMAP) and purified by recrystallization from ethanol/water.

4-Alkoxyacetanilide (2): a mixture of 4-hydroxyacetanilide (0.1 mol), potassium hydroxide (0.1 mol) and n-alkylbromide (0.12 mol) in ethanol (200 ml) was refluxed for 16h. After reaction the precipitated KBr was filtered and solvent was cooled. Then the precipitates were filtered off (m=12 and 16) or the solvent was removed (m=4 and 8). The crude product was recrystallized from ethanol (m=12 and 16) or mixture of ethanol and water (m=4 and 8).

4-Alkoxyaniline (3): 4-alkoxyacetanilide was dissolved in ethanol and refluxed for 24h in the presence of hydrochloric acid. The cooled reaction mixture was evaporated under reduced pressure and residue was dissolved in chloroform. An aqueous potassium carbonate was added to this chloroform solution and organic layer was removed. The final compounds were purified by recrystallized from ethanol (m=12 and 16) or gel filtration (m=4 and 8).

α,ω-Bis(4-alkoxyanilinebenzylidene-4'-carbonyloxy)alkane (4): 0.01 mol of compound (1) and 0.02 mol of compound (3) were dissolved in anhydrous ethanol and refluxed for 3h. The mixture was cooled and then precipitates were filtered. The residue was

recrystallized from chloroform/ethanol, purified by column chromatography (alumina activated; chloroform as eluent), and finally recrystallized twice from chloroform/ethanol. All the synthesized compounds gave proton NMR spectra, which were consistent with their formulae.

The same procedure was applied for the synthesizing mAMnAMm by using alkylaniline as (3).

2.2. Methods

The calorimetric behaviour was investigated with a Perkin-Elmer DSC-II calorimeter at a scanning rate of 10°C/min. The textures of mesophase were studied using a polarizing microscope (an Olympus BH-2) equipped with a Mettler FP-80 hot stage. X-ray diffraction photographs were taken at different temperatures by using Ni-filtered CuKα radiation. The temperature was measured and regulated within an accuracy of 0.2°C by using a Mettler FP-80 heater. The film to specimen distance was determined by calibration with silicon powder. To examine the ferroelectric or antiferroelectric response, switching current was observed in a pseudo-planar cell, by means of triangular and rectangular wave methods, where the layer normal lies parallel to the glass surface but is randomly oriented between domains.

3. Results and Discussion

Figure 2a shows the phase behaviour of mOAM5AMOm with m = 4, 8, 10, 12, 16. The enantiotropic smectic phase was observed for all the materials. The thermodynamic data are given in Table I.

By a microscopy, the smectic phase appears from the isotropic melt in a similar way. The spherelike texture appears and coalesce to the fan shape texture. Shearing the sample between glasses results in the homeotropic alignment of molecules which shows a strong birefringence.[10] This indicates the smectic phase with the tilted association of the mesogenic groups.

Furthermore, the X-ray diffraction patterns show the layer reflections in a small-angle region and broad hallow in a wide-angle region, showing the smectic phase without lateral positional ordering. Spacings of the layer reflections are listed in the last column of Table I. It is interesting that the spacing of the first layer reflection is relatively changed from the sample to sample. The spacing is 19.3 Å for 4OAM5AMO4, which is roughly half a molecular length. On the other hand, 10OAM5AMO10, 12OAM5AMO12 and 16OAM5AMO16 show the spacings of 45.1Å, 49.8Å and 54.8Å, which are almost twice that of 4OAM5AMO4 and so correspond to the molecular length. Obviously, the former forms the single-layer phase, so called

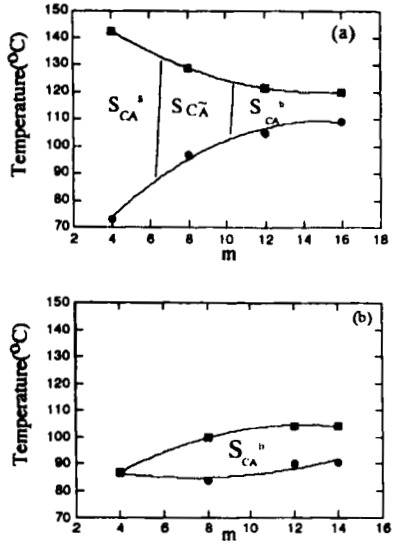


Figure 2. Phase behaviour as observed for (a) mOAM5AMOm and (b) mAM5AMm with a variation of m. Transition temperatures were collected from the DSC cooling curves.

Table I. Thermodynamic Data and layer spacings of mOAM5AMOm and mAM5AMm

mOAM5AMOm

n	Transition Temperature (°C)					ΔHm (kcal/mol)	ΔHi (kcal/mol)	ΔSm (cal/K·mol)	ΔSi (cal/K·mol)	Layer Spacings (Å)
	K	S_{CA}^{a}	$S_{C\tilde{A}}$	S_{CA}^{b}	I					
4	● 73.2	●		142.5	●	3.71	2.08	10.74	4.99	19.33
8	●	97.0	●	128.6	●	5.38	3.17	14.50	7.89	35.39, 22.67
10	●		99.1	● 121.4	●	8.99	3.42	24.18	8.67	45.07, 22.51
12	●		105.0	● 121.5	●	14.89	4.77	39.43	12.10	49.78, 24.92
16	●		109.2	● 120.0	●	20.07	5.53	52.51	14.07	54.76, 27.87

mAM5AMm

n	Transition Temperature (°C)				ΔHm (kcal/mol)	ΔHi (kcal/mol)	ΔSm (cal/K·mol)	ΔSi (cal/K·mol)	Layer Spacings (Å)
	K	S_{CA}^{b}		I					
4	●		143.0	●		7.74		21.48	
8	●	83.5	● 100.0	●	7.25	2.87	20.41	7.70	43.83, 22.24
12	●	89.9	● 104.0	●	15.79	4.65	43.65	12.33	51.47, 25.56
14	●	90.6	● 104.0	●	12.07	4.08	33.15	10.82	53.56

Thermodynamic data were collected from the DSC cooling curves.

S_{CA}^{a} phase, while the latters form the bilayer smectic phase, S_{CA}^{b} phase.

The intermediate 8OAM5AMO8 shows the interesting diffraction pattern. The observed inner reflections are not equally spaced (see Table I). This is an indication of the frustrated smectic phase.[7,11,12] The detailed description of the frustrated smectic phase can be made from the oriented pattern of Figure 3, which was taken for the homeotropically oriented specimen. The homeotropic alignment was obtained on the glass plate which was treated by silane coupling agent. As found in Figure 3, the most inner reflection is split from the

Figure 3. X-ray diffraction pattern observed for the frustrated smectic phase of 8OAM5AMO8. X-Ray was irradiated parallel to the smectic layer.

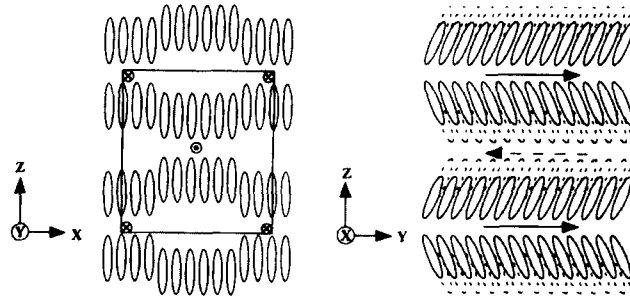


Figure 4. Schematic illustration of frustrated smectic strtucture with unusual density modulation along the layer. (a) and (b) illustrate the layer structure projected on a plane parallel and perpendicular to the tilt direction, respectively. Solid lines and arrows indicate the two-dimensional rectangular lattice and the spontaneous polarization, respectively. From the microbeam X-ray and birefringence measurements, it was confirmed that the frustration takes place in a diredtion perpendicular to the tilt direction of mesogens.[12]

meridian while the second reflection appears just on the meridian. This is a direct evidence of the frustrated smectic phase in which the density modulation appears along the layer as well as the layer normal. Thus, the smectic phase of 8OAM5AMO8 has the two dimensional lattice with a = 55.3Å (parallel to the layer) and c = 45.3Å (normal to the layer). Only the model shown in Figure 4 can explain such a lattice, in which the molecules are packed into a bilayer within a domain but domains are stacked in a zigzag manner. This frustrated structure was called here $S_{\tilde{C}A}$.

The phase behaviour of mAM5AMm with m = 4, 8, 10 and 14 is shown in Figure 2b. Thermodynamic and X-ray data are listed in Table I. In this system, all the smectic phase has a bilayer character, indicating that the segregation effect is stronger than that in mOAM5AMOm system.

As predicted in Introduction, the bilayer smectic phase should be ferroelectric or antiferroelectric liquid crystal. In fact, this was assured from the measurement of switching current.[9] Figure 5 shows a switching current curve obtained for S_{CA}^{b} phase of 12AM5AM12 by applying a triangular voltage wave of ±12 V/μm at a frequency of 1 Hz. With a change in the polarity of the electric field, two switching current peaks were clearly observed, confirming the antiferroelectric liquid crystal. The reversal of the spontaneous polarization was also observed by a rectangular wave field of ±12V/μm at a frequency of 1Hz (see Figure 6). In Figure 6a, a small and broad peak attributed to an ionic current is observed at t=0.75 msec. Figure 6b shows the expanded current profile in the vicinity of t=0 sec. In addition to the

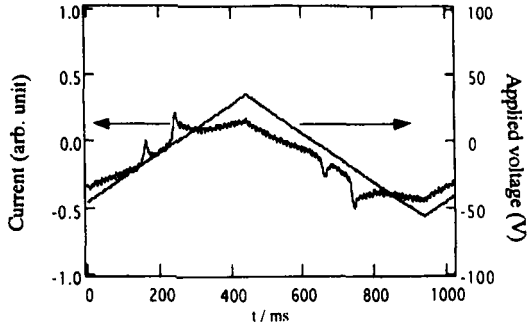


Fig. 5. Switching current curve obtained by applying a triangular voltage wave:(± 12 V/μm, 1 Hz).

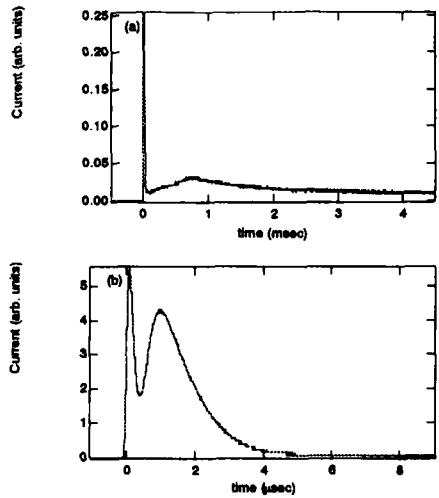


Figure 6. (a) Switching current profile obtained by a square wave field of ± 12 V/μm at a frequency of 1 Hz. (b) shows the expanded profile in the vicinity of t = 0 sec.

ionic peak, a single sharp peak is observed at t=1μsec. This fast response peak is surely caused by polarization switching, but not by the switching due to dielectric anisotropy. Spontaneous polarization was determined to 600nC/cm^2. It should be further noted that the two states under positive and negative maximum electric fields cannot be distinguished by a polarizing optical microscope. In contrast, the birefringence observed in the zero field is different from that in the maximum field. The structural change is proposed as illustrated in Figure 7. The bending direction of the molecule is initially parallel to the glass surface with the polarity of each layer directed in an alternate fashion (see Figure 7(b)). In the case of an applied field, it orients along the electric field and so is perpendicular to the glass surface (Figure 7(a)). On reversing the polarity of the field, it reverses the orientation throughout the original state on the way (Figure 7(c)). Similar antiferroelectric switching was observed for the $S_{CA}{}^b$ phases of 14AM5AM14 and 16OAM5AMO16.

We next refer to the frustrated smectic structure. In this phase, the bilayer is constructed in a small domain and the molecules in adjacent domain slide halfway along the layer normal. In addition to the sliding, the 180° rotation around the chain axis is required to maintain the tilted orientation of the mesogenic groups.[7,11] In other words, it can be described by a periodic structure of domain walls; in each domain the basic layer structure is the same as the bilayer structure of

Figure 1 and its spontaneous polarization is canceled between neighboring domains (see Figure 4).[7,11] Thus, the frustrated smectic phase is considered to result from the cancelation of polarization, that is a two-dimensional escape of spontaneous polarization. In the frustrated smectic phase, there is a significant overlapping of the aromatic mesogenic core and alkyl group, which may be energetically unfavourite. This energy cost is counterbalanced by the energy gain due to the cancelation of polarization. As the length of tail group increases, the overlapping becomes significant so that the energy cost overcomes the energy gain to result in the transformation to the antiferroelectric S_{CA}^{h} phase. This may be a reason why the frustrated smectic liquid crystal appears in the limited region between the single layer and bilayer mesophases.

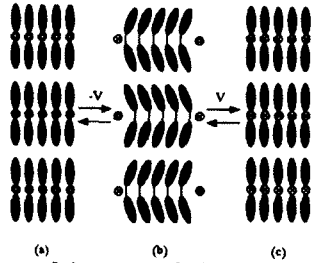


Figure 7. The occurrence of the structural change due to an applied field: (a) -20 V/μm; (b) 0 V/μm; (c) 20 V/μm.

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