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New Liquid Crystalline Homologous Series Exhibiting the Smectic C Phase

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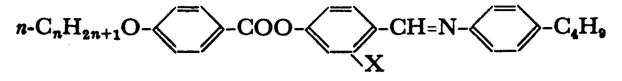
Synopsis. A liguid crystalline homologous series of *N*-[4-(4-alkoxybenzoyloxy)benzylidene]-4-butylanilines and their hydroxyl derivatives at the 2-position were synthesized, and then the liquid-crystalline-phase transitions were determined using a differential scanning calorimeter and a polarizing microscope. All of the members exhibit a nematic phase, and a smectic C phase can be observed for the homologues with a relatively long alkoxyl chain.

It is well-established that smectic liquid crystalline phases can be further subdivided into several modifications, denoted by the letters A through I.[1,2] Among these smectic modifications, the smectic C phase has recently attracted increasing attention because the chiral compound in the smectic C phase can exhibit a spontaneous polarization and because this phase is ferroelectric.[3] The most characteristic feature of the smectic C structure is that the long axes of the molecules are tilted with respect to the planes of the layer.

Much efforts have thus far been made in order to obtain new ferroelectric smectic liquid crystals.[4,7] Unfortunately, the definite relationship between the molecular structure and the smectic C liquid crystal formation has remained unknown, although certain guidelines exist regarding the features of the molecular structure that favor the smectic C-phase formation.[2] Therefore, it is of great importance to synthesize a new liquid crystalline homologous series which exhibits the smectic C phase in connection with an attempt to find a common structural feature for the smectic C formation. In this paper we wish to report two new liquid crystalline homologous series exhibiting the smectic C phase of *N*-[4-(4-alkoxybenzoyloxy)benzylidene]-4-butylanilines and their derivatives, which have a lateral hydroxylsubstituent.



(n=1—8, X=H or OH)

Experimental

Materials. 4-Alkoxybenzoic acids obtained commercially are converted to acid chlorides by treatment with thionyl chloride in a benzene solution as the solvent. After the completion of the reaction, the excess of thionyl chloride and the solvent were removed; then the residue was distilled under reduced pressure. These acid chlorides were esterified by a reaction with 4-hydroxybenzaldehyde(2,4-dihydroxybenzaldehyde) in an ether solution including triethylamine. After they had then stood overnight, the triethylamine hydrochloride formed was removed by filtration, the ether was evaporated, and the solid residue was recrystallized from hexane. Finally, the substituted benzaldehydes thus obtained were coupled with 4-butylaniline by refluxing in an ethanol solution. The crude liquid crystals were purified by successive recrystallizations from ethanol.

Measurements. The liquid crystalline textures and the phase-transition temperatures were determined by means of a Nikon polarizing microscope equipped with a Mettler FP 52 microfurnace for sample temperature control. Checks on the transition temperatures were made using a Rigaku differential scanning calorimeter. Each sample was heated and cooled under a flow of nitrogen gas to prevent the sample from decomposing.

Results and Discussion

The transition temperatures and the liquid crystalline phases of the compounds without the lateral substituent are summarized in Table 1. All the members of this homologous series exhibit a nematic liquid crystal phase. As the length of alkoxyl chain is increased, smectic phases appear. This characteristic that the smectic phase is observed only for the homologues with a relatively long alkoxyl chain is not surprising, for the appearance of the smectic phase is not unusual; it has frequently been observed as the alkoxyl chain length increases in other homologous series of liquid crystalline materials.[8] Furthermore, it is worthwhile to state that, irrespective of the monotropic or enantiotropic transitions, the liquid crystalline phase transitions can be clearly detected by means of both the microscopic texture change and the thermal analysis.

Under polarizing microscopic observation, the smectic I phase of this homologous series exhibits broken fan-shaped or broken polygonal textures when formed on cooling from the nematic phase. These textures can be changed to a smectic schlieren texture by cover-slip displacement. All of the microscopic textures observed in the smectic I phase have been frequently found in the smectic C phase of other liquid

Table 1. Transition Temperatures of Liquid Crystals Without Lateral Hydroxyl Substituent (°C)

n	Smectic II	Smectic I(C)	Nematic	Isotropic
1			110	252
2			128	253
3			125	238
4			116	231
5	(77)	(99)	111	220
6	(76)	93	116	215
7	(77)	86	128	208
8	70	76	141	205

The figures in parentheses show the monotropic transition.

Table 2. Transition Temperatures of Liquid Crystals with Lateral Hydroxyl Substituent (°C)

n	Smectic C	Nematic	Isotropic
1		98	259
2		99	260
3		93	246
4		89	242
5		81	232
6	(77)	80	227
7	76	95	218
8	100	104	214

The figures in parentheses show the monotropic transition.

crystalline compounds and are typical textures of the smectic C phase.[2,9] In addition, it should be stressed that a homeotropic alignment, one of the textures typical of the smectic A phase, can not be observed at all in the smectic I phase. From these characteristic textures, it seems likely that the smectic I phase of this homologous series is the smectic C. On cooling from the smectic I phase to the smectic II phase, the smectic schlieren texture of the smectic C phase distinctly changes to a mosaic texture. However, the exact classification of this smectic II phase remains unclear because several different smectic modifications can exhibit a similar mosaic texture.[9]

Table 2 shows the phase transitions of another homologous series with the lateral substituent of the hydroxyl group. It is evident that, in this series, there also exist liquid crystalline phase transitions quite similar to those described above in the previous series without the lateral hydroxyl substituent. However, it should be kept in mind that the smectic II phase disappears in this homologous series; thus, no smectic polymorphism exists. Furthermore, it should be noted that a longer alkoxyl chain(C_6) is necessary for the smectic C phase to be formed compared with the previous series without the lateral substituent. It is also apparent from a comparison between the Tables 1 and 2 that the lateral hydroxyl substituent lowers the smectic C– nematic transition temperatures. These results indicate that the introduction of the hydroxyl group at the 2-position is unfavorable for the smectic formation and that it thus decreases the smectic C thermal stability. It seems that this behavior can be understood without difficulty by taking account of the change in the molecular structure. In general, it is well recognized that the lateral substituent exerts a full molecular-broadening influence, reducing the lateral intermolecular forces of attraction and thus lowering the smectic thermal stability.[10]

In addition, it is interesting to note the difference in the nematic–isotropic transition temperatures between the two series. The members with the lateral hydroxyl group exhibit higher nematic–isotropic transition temperatures than those without the lateral substituent. This result is quite likely to be associated with the strong intramolecular hydrogen bonding which has been found to occur for certain Schiff bases.[5,11] Such a hydrogen bonding will lead to a reduction in the rotational motions within the molecules and to a decrease in the twist from the noncoplanarity of a skeleton of *N*-(2-hydroxybenzylidene)aniline.[12,13] These effects are obviously favorable for the formation of the nematic structure; thus, they combine to give increased nematic thermal stability, i.e., an enhanced nematic–isotropic transition temperature.

In conclusion, we wish to point out that both the homologous series can exhibit the smectic C phase if the end alkoxyl chain is increased to a certain appropriate length.

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