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Mesomorphic Properties of Bis(4-alkoxycarbonylphenyl)terephthalates

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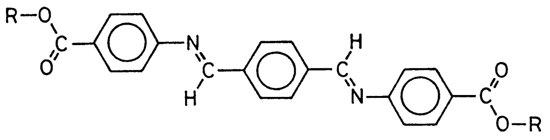
Synopsis. The mesomorphic behavior of fifteen bis(4-alkoxycarbonylphenyl)terephthalates has been examined in order to study the effects of branching of the ester alkyl groups. The 2-methylation of purely smectogenic butyl, pentyl, and hexyl esters gives rise to the appearance of nematic properties.

As part of investigations over the past several years on the effects of the branching of the ester alkyl chain on the liquid crystalline properties, we recently reported the behavior of dialkyl 4,4′-[1,4-phenylenebis(methylidynenitrilo)]bis[benzoates] (**1**).[1] Some branched alkyl esters were found to be more polymesomorphic than the unbranched ones. For example, the 3-methylpentyl ester exhibits smectic A, B, and G phases as well as the nematic phase, whereas the pentyl ester produces only the smectic A and nematic phases. Consequently, it seemed highly interesting to us to examine diesters in which only the linkage groups are different from compounds **1**. In this paper, we report on an extention of our study concerning diesters to a series of bis(4-alkoxycarbonylphenyl)terephthalates (**2**).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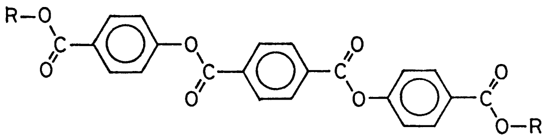
2

Experimental

Materials. Alkyl 4-hydroxybenzoates were prepared by the esterification of 4-hydroxybenzoic acid with alcohols in boiling benzene, employing sulfuric acid as a catalyst.[2] The reaction of terephthaloyl dichloride with alkyl 4-hydroxybenzoates yielded the desired compounds **2**.

Measurements. The mesophases were identified by an examination of their textures with the aid of a polarizing microscope in conjunction with a heated stage. The transition temperatures and associated enthalpy changes were determined by calorimetric curves recorded on a Rigaku Denki Thermoflex differential scanning calorimeter.

Results and Discussion

The thermal properties of the fifteen esters are summarized in Table 1. Here, K, S, N, and I stand for the crystalline, smectic, nematic, and isotropic liquid phases respectively. The ethyl ester was prepared by Dewar and Goldberg about twenty years ago as a part of their study on *p*- substituted phenyl esters of terephthalic acid, and was found to be mesogenic.[3] Furthermore, Chiellini and his co-workers examined fifteen esters consisting mostly the unbranched alkyl esters from the standpoint of possible model compounds of thermotropic polyesters.[4] The reported transition temperatures are in reasonable agreement with ours (see footnotes in Table 1).

While the methyl ester (No. 1) is purely nematogenic, the ethyl and propyl esters (Nos. 2 and 3) exhibit the smectic A phase as well as the nematic phase. The depression of clearing point by the lengthening the ester alkyl group is as large as 65 °C between the methyl and ethyl esters, but merely 19 °C between the ethyl and propyl esters. The smectic A behavior is slightly enhanced by the replacement of ethyl group with the propyl group. The mesophase is completely eliminated by the 1-methylation, whereas the effects of the 2-methylation of propyl group is rather small (see No. 4). The neopentyl ester (No. 5) still preserves a nematic phase, though it is metastable, in contrast to the absence of any mesophase in the corresponding member in series **1**.

The smectic A phase is the only mesophase displayed by the butyl ester (No. 6). The stable nematic phase and the metastable smectic C phase appear by 2-methylation (see No. 7). The emergence of the nematic phase by the introduction of a branching methyl group, specifically to the 2 position, has frequently been pointed out by the present authors for both monoesters and diesters.[1,5–7] The 3-methylbutyl ester (No. 8) exhibits the smectic C phase in addition to the smectic A phase, though no nematic phase is detectable. The thermal stabilities of these two smectic phases are higher than those given by the 2-methylbutyl ester.

The pentyl ester (No. 9) can produce only the smectic A phase. The additional mesophase appearing by chain branching is a nematic phase in the case of 2-methylation (see No. 10) and a smectic C phase in the case of 3-methylation (see No. 11). No extra mesophase is acquired by the 4-methylation of pentyl group (see No. 12). The smectic A phase in this ester is located below the melting point.

The 2-methylation of the purely smectogenic hexyl ester results in also the appearance of a nematic phase (compare Nos. 13 and 14). The heptyl ester (No. 15) is the only unbranched alkyl ester which exhibits the smectic C phase as well as the smectic A phase among those studied here.

In the present series too, the branched esters tend to be more polymesomorphic than the unbranched ones. However, it is evident from the foregoing presentation that alternation of the linkage from azomethine to

Table 1. Transition Temperatures (°C) and Enthalpy Changes (kJ mol^{-1}) of Compounds **2**[a]

No.	Alkyl group	K	Sc	SA	N	I
1	CH_3	. 247 (58)			. 301 (1.0)	.
2	CH_2CH_3[b]	. 193 (43)		. 204 (0.9)	. 236 (0.5)	.
3	$CH_2CH_2CH_3$[c]	. 130 (35)		. 207 (1.9)	. 217 (0.6)	.
4	$CH_2CH(CH_3)_2$	. 149 (35)		. 183 (0.4)	. 204 (0.5)	.
5	$CH_2C(CH_3)_3$	. 162 (42)			[. 159] (0.3)	.
6	$CH_2CH_2CH_2CH_3$[d]	. 137 (31)		. 182 (4.0)		.
7	$CH_2CH(CH_3)CH_2CH_3$	. 133 (35)	[. 115] (—)	. 153 (0.6)	. 165 (0.4)	.
8	$CH_2CH_2CH(CH_3)_2$	. 153 (47)	[. 139] (0.2)	. 167 (4.4)		.
9	$CH_2CH_2CH_2CH_2CH_3$[e]	. 145 (40)		. 190 (5.3)		.
10	$CH_2CH(CH_3)CH_2CH_2CH_3$	. 139 (49)		. 143 (0.3)	. 156 (0.4)	.
11	$CH_2CH_2CH(CH_3)CH_2CH_3$	. 143 (41)	[. 136] (0.2)	. 153 (3.9)		.
12	$CH_2CH_2CH_2CH(CH_3)_2$	. 169 (57)		[. 167] (4.3)		.
13	$CH_2CH_2CH_2CH_2CH_2CH_3$[f]	. 150 (41)		. 179 (5.6)		.
14	$CH_2CH(CH_3)CH_2CH_2CH_2CH_3$	. 133 (46)		. 134 (0.5)	. 141 (0.4)	.
15	$CH_2CH_2CH_2CH_2CH_2CH_2CH_3$[g]	. 145 (41)	[. 139] (—)	. 179 (6.3)		.

a) The latter quantities are in parentheses. The braced temperatures represent monotropic transitions. b) 191 (—) and 235 °C (—) by Dewar and Goldberg.[3] 192 (42), 205 (0.8), and 239 °C (0.3) by Galli et al.[4] c) 122 (30), 206 (1.5), and 219 °C (0.5) by Galli et al.[4] d) 133 (32) and 185 °C (4.1) by Galli et al.[4] e) 145 (21) and 188 °C (4.8) by Galli et al.[4] f) 146 (40) and 178 °C (5.5) by Galli et al.[4] g) 143 (40), 136 (—), and 173 °C (6.0) by Galli et al.[4]

ester groups significantly modifies the mesomorphic behavior of diesters. First, the nematic phase is more frequently observed in series **1**; namely, twelve esters in series **1** vs. eight esters in series **2** . Secondly, the smectic phases found with the present diesters are limited to the types A and C, whereas the smectic phases of the types B and G are also found with the 3-methylpentyl esters in series **1**. The smectic A phase is more predominant in the present series; that is, eight esters vs. thirteen esters. On the other hand, the smectic C phases exhibited by the four esters in series **1** are enantiotropic but those given by the four in this series are all monotropic.

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