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Study of New Liquid Crystal Materials (II): Synthesis and Mesomorphic Properties of Alkoxymethylene Substituted Phenyl Cyclohexanecarboxylates

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Study of New Liquid Crystal Materials (II): Synthesis and Mesomorphic Properties of Alkoxymethylene Substituted Phenyl Cyclohexanecarboxylates

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The properties of alkoxymethylene-substituted-phenyl alkylcyclohexanecarboxylates are described. Such phenyl cyclohexanecarboxylates exhibit either a monotropic or an enantiotropic nematic phase. Their clearing points were lower than those of alkoxy-substituted-phenyl alkylcyclohexanecarboxylates, an effect considered to be due to the flexibility of the alkoxymethylene groups.

Almost all nematic mesogens have a hard-rod core and two terminal groups.[1] We have described nematic mesogens which are alkoxy-methylene-substituted-phenyl alkylcyclohexanes (I).[2] These species exhibited monotropic nematic or smectic phases, and their clearing points were lower than those of alkoxy-substituted-phenyl cyclohexanes.[3] This indicated that introduction of alkoxymethylene groups into the mesogens had a remarkable influence on their properties. It is interesting at this point to investigate the properties of alkoxymethylene derivatives having another hard-rod core.

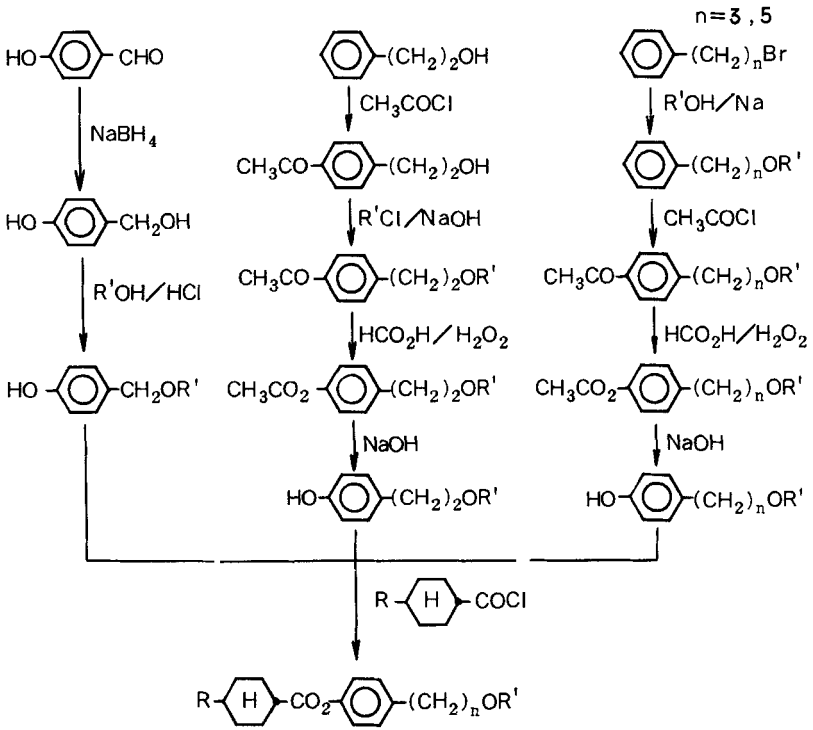
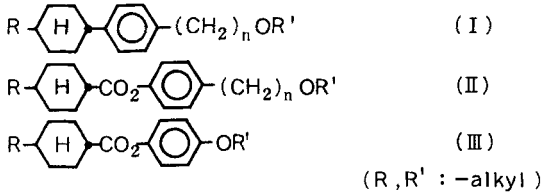


FIGURE 1 Synthetic route.

In this paper, we deal with alkoxymethylene-substituted-phenyl alkylcyclohexanecarbonxylates (II), and compare their properties with those of alkoxyl-substituted-phenyl alkylcyclohexanecarboxylates (III).[4]

The alkoxymethylene series (II) was prepared as shown in Figure 1. 4-Alkoxymethylphenols ($n = 1$) were prepared from 4-formylphenol; 4-alkoxyethylphenol ($n = 2$) was prepared from 2-phenylethanol. 4-Alkoxypropylphenol ($n = 3$) and 4-alkoxypentyl phenol ($n = 5$) were prepared from appropriate phenylalkyl bromides. These phenols were esterified with appropriate *trans*-4-alkylcyclohexane-1-carboxylic acids.[5] Details of the procedures will be reported elsewhere.



The transition temperatures of the alkoxymethylene series (II) are shown in Table I. These species exhibit either a monotropic or an enantiotropic nematic phase. Although the phenylcyclohexane series (I)[2] exhibited a smectic phase, in series (II), the smectic phase was not observed, even for long alkyl chains. The first enantiotropic transition was observed at $n = 5$ for this series (No. 18, 19). These are the first examples to exhibit enantiotropic transitions in alkoxymethylene substituted mesogens.

The members of series (II) generally show lower transition temperatures than the alkoxyphenyl esters (III), with clearing points below 40°C. In particular, the clearing points were below −10°C at $n = 1$. The examples shown in Figure 2 illustrate the magnitude of the effect of terminal groups on clearing points. The compounds are all similar in length, but the three alkoxymethylene species (series II) have lower

TABLE I

Transition Temperatures of

No.	n	x	y	Transition C−N/I	Temp.(℃) N−I
1	1	3	1	27	(18)
2	1	3	2	19	(−11)
3	1	3	3	4	(−15)
4	1	3	4	1	(−22)
5	1	3	5	4	(−15)
6	1	3	6	12	(−24)
7	1	3	7	13	(−12)
8	1	4	1	39	(−13)
9	1	5	1	53	(−34)
10	1	5	3	6	(4.5)
11	1	6	1	43	(29)
12	1	7	1	49	(34)
13	1	7	2	18	(19)
14	1	7	3	19	(14)
15	2	5	1	20	(11)
16	2	5	2	30	(15)
17	3	5	1	42	(32)
18	5	3	1	27	29
19	5	5	1	32	38

( ) : Monotropic Transition

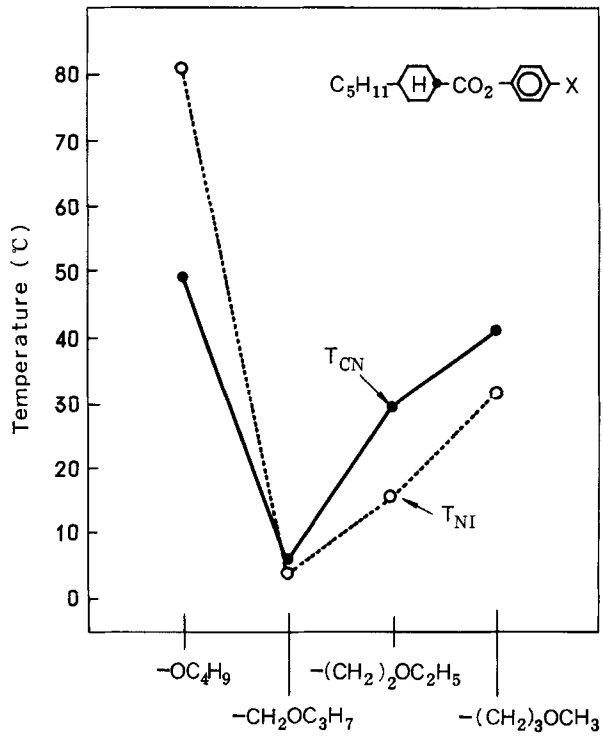


FIGURE 2 Transition temperatures vs terminal groups.

clearing points than the alkoxy species (series III). This result agrees approximately with that previously reported for the phenylcyclohexane series.[2]

Figure 3 shows a plot of the clearing points as a function of the length of the terminal chain. In the alkoxy series (III),[4] the relationship between clearing points and chain length had a pattern generally observed for nematic mesogens.[6] On the other hand, the alkoxymethylene series (II) did not show a similar behavior; the clearing points decreased steeply from $y = 1$ to $y = 2$ and then showed a general alternating but diverging pattern. These relationships illustrate the difference in behavior between alkoxymethylene groups and alkoxy groups in mesogenic molecules. One reason for this is attributed to the degree of flexibility in these groups. The flexibility of alkoxymethylene groups is considered to be larger than that of alkoxy groups because free rotation about the aliphatic C–O bond is easier than that about the C–C bond.[7] The alkoxymethylene group has two

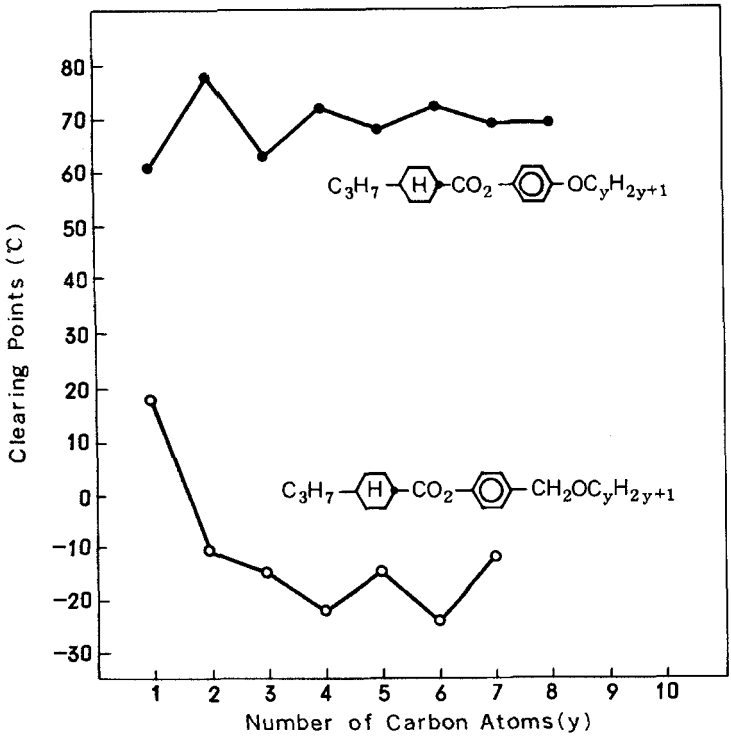
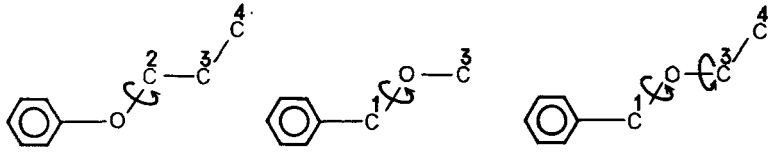


FIGURE 3 Clearing points vs y-number of terminal chain.

aliphatic C–O bonds and the alkoxy group has one. Conformational changes based on such free rotations are illustrated below.



The methoxymethyl group (b) has two C–O bonds, but rotation about O–C^3 does not affect the conformational situation. Therefore, the degree of conformational effect in (b) is the same as that in the alkoxy group (a). However, when the y-number is 2 or above, rotation of O–C^3 becomes significant as in (c), and the degree of conformational

effect becomes higher. Differences in the conformational possibilities such as those given above may explain the differences in behaviour shown in Figure 3.

From these results, it was concluded that the alkoxymethylene group has a remarkable influence on the mesomorphic properties, particularly the phase transition temperatures. Studies to examine the effects on other properties, including viscosity and birefringence, are now being carried out.

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