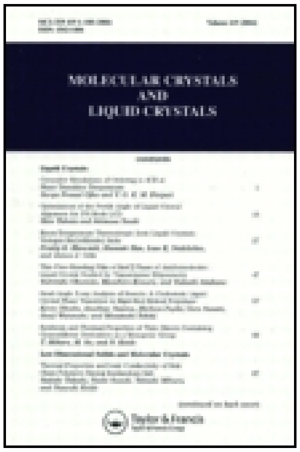

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Study of New Liquid Crystal Materials (I) Synthesis and Mesomorphic Properties of Alkoxymethylene Substituted Phenylcyclohexanes

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Study of New Liquid Crystal Materials (I) Synthesis and Mesomorphic Properties of Alkoxymethylene Substituted Phenylcyclohexanes

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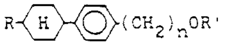
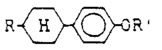
The synthesis of alkoxymethylene alkyl substituted phenylcyclohexanes is described. Such phenylcyclohexanes exhibited monotropic nematic and/or smectic phases. They also had lower clearing points and bulk viscosities than alkoxy alkyl substituted phenylcyclohexanes. This is apparently due to the high flexibility and low polarizability of the alkoxymethylene groups and their effects on the packing of the molecules.

Since the discovery of nematic mesogens, much attention has been given to the relations that hold between their properties and molecular structures. It is known that almost all of the nematic mesogens have a hard rod core and two terminal groups.[1] Various molecular structures have been proposed for the hard rod cores of nematic mesogens, and the influence of these on the properties of mesogens have been examined.[2-4] It has also been shown that the types of terminal group that nematic mesogens possess have a very large effect on their properties. Alkoxy groups are important for nematic mesogens, and such groups are widely used as terminal groups. In known mesogens,[2] alkoxy groups are attached to the benzene ring component of the hard rod core. We decided that it would be interesting to investigate the effect of the introduction of methylene groups, $(CH_2)_n$, between the alkoxy group and benzene ring. Therefore, we prepared alkoxymethylene alkyl substituted phenylcyclohexanes (I) and compared their mesomorphic properties with those of alkoxy alkyl substituted phenylcyclohexanes (II).[5,6]



(I)



(II) (R,R' : -alkyl)

The compounds (I) were prepared as shown in Figure 1. The synthesis started with the *trans*-alkylcyclohexyl benzene 1.[7-13]

The transition temperatures of the alkoxymethylene substituted phenylcyclohexanes (I) are shown in Table I. These compounds exhibit monotropic nematic and/or smectic phases. Although the values

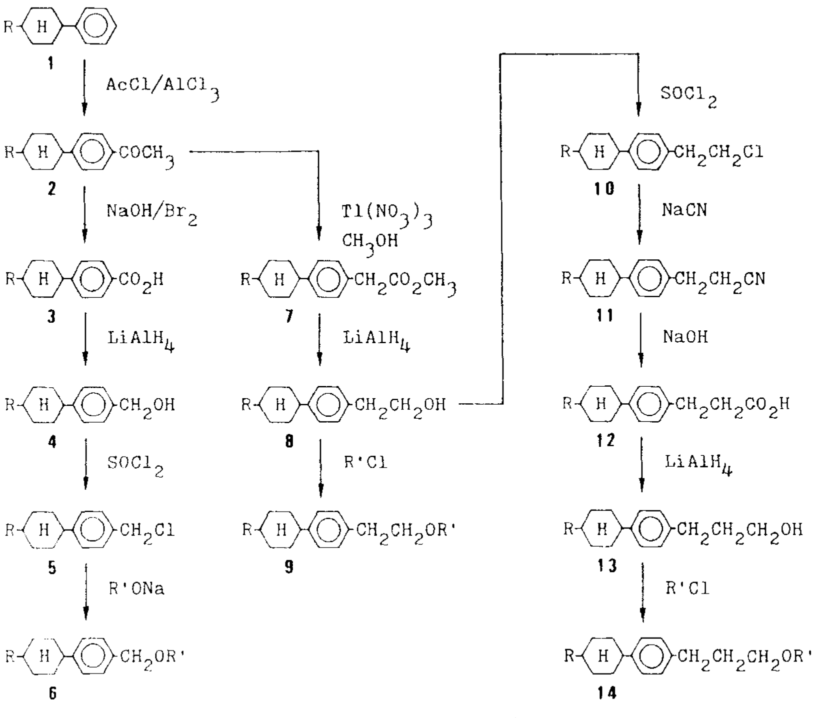
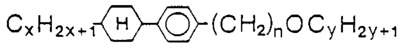


FIGURE 1 Route of synthesis.

TABLE I

Transition Temperatures of



Compound	n	x	y	Transition Temp. (°C) C–I	 S–N	 N–I
6a	1	5	1	9.5	—	(−9)
6b	1	5	3	25	—	(−38)
6c	1	6	1	12	—	(−10)
6d	1	6	3	5	(−35)	—
6e	1	7	1	18	(−1)	(7)
6f	1	7	2	9.5	(−11)	(−10)
6g	1	7	3	5	(−18)	—
9a	2	5	1	6	—	(−32)
9b	2	5	2	4	—	(−28)
14a	3	5	1	0	—	(−17)
14b	5	5	1	0	—	(−3)

( ); Monotropic transition.

for n, x and y (length of alkyl chain) were increased, these compounds did not exhibit enantiotropic mesophases. However, they did exhibit more pronounced smectic properties with increasing alkyl chain length x. Alkyl cyano[14] or alkyl alkoxy[5,6] substituted phenylcyclohexanes do not exhibit smectic phases even when they have a heptyl group. This indicates that a phenylcyclohexane hard rod core favors the nematic phase rather than the smectic phase. The alkoxymethylene substituted phenylcyclohexanes (I) must therefore exhibit smectic phases because the alkoxymethylene group favours this type of phase behaviour.

The members of series (I) generally showed lower transition temperatures, with the clearing points below 10 °C. The examples shown in Figure 2 illustrate the magnitude of the effect of the terminal groups on the clearing points. If the terminal groups are arranged in order of decreasing clearing points, the following relationships are obtained.

$$—OC_4H_9 > —(CH_2)_3OCH_3 > —(CH_2)_2OC_2H_5 > —CH_2OC_3H_7$$

These groups are of similar length, but the three alkoxymethylene series (I) have lower transition temperatures than the alkoxy series (II). In the three examples from the alkoxymethylene series (I), the clearing points increase with increasing distance between the oxygen atom and the benzene ring.

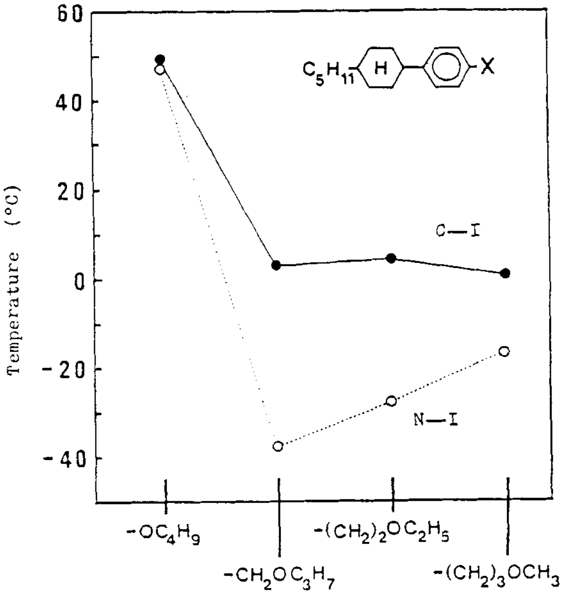


FIGURE 2 Transition temperatures *vs* terminal groups.

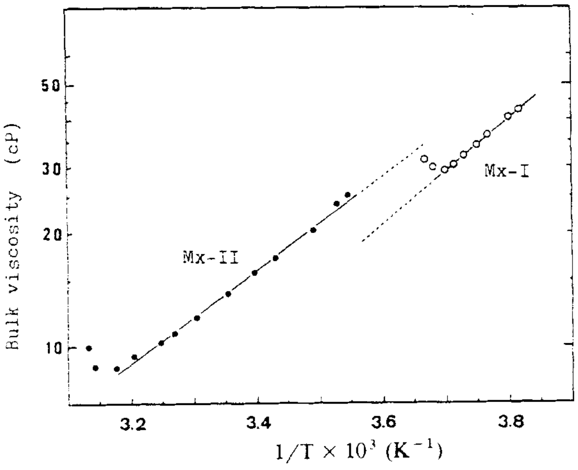


FIGURE 3 Bulk viscosities of the mixtures.

The use of alkoxymethylene groups as terminal groups also brought about a reduction in bulk viscosity in the nematic phase. Figure 3 shows the bulk viscosities of two equimolar mixtures, Mx-I composed of 6a and 6e, Mx-II composed of 4-pentyl-(4′-ethoxyphenyl)cyclohexane and 4-heptyl-(4′-ethoxyphenyl)cyclohexane. Although these mixtures did not each show a nematic phase at the same temperature, apparently the viscosity of Mx-I was lower than that of Mx-II.

We assume that alkoxymethylene groups have a larger flexibility and a lower polarizability than alkoxy groups. Therefore, the replacement of the alkoxy groups by the alkoxymethylene groups affects the packing of the molecules, and consequently, the alkoxymethylene series (I) shows lower clearing points and bulk viscosities than the alkoxy series (II).

These results further emphasize that terminal groups, as well as the hard rod core, have a remarkable influence on the properties of mesogens. Studies of syntheses aimed at examining other hard rod core systems having alkoxymethylene terminal groups are now being carried out and will be reported in future publications.

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