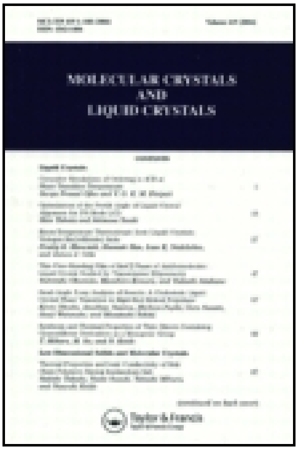

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Synthesis and Physical Properties of Alkoxymethylene Substituted Phenyl Cyclohexanecarboxylates

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Version of record first published: 20 Apr 2011.

To cite this article: Teruo Kitamura, Akio Mukoh, Susumu Era & Tsunenori Fujii (1985): Synthesis and Physical Properties of Alkoxymethylene Substituted Phenyl Cyclohexanecarboxylates, Molecular Crystals and Liquid Crystals, 130:3-4, 231-247

To link to this article: http://dx.doi.org/10.1080/00268948508079514

Mol. Cryst. Liq. Cryst., 1985, Vol. 130, pp. 231–247
0026-8941/85/1304-0231/$20.00/0

Synthesis and Physical Properties of Alkoxymethylene Substituted Phenyl Cyclohexanecarboxylates

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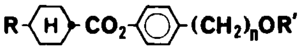
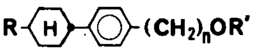
(*Received February 13, 1985; in final form April 9, 1985*)

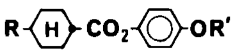
The homologous series of 4-alkoxymethylene-substituted-phenyl 4′-alkylcyclohexanecarboxylates are prepared. And their transition temperatures, bulk viscosities and birefringences have been measured comparing with the series of 4-alkoxy-substituted-phenyl 4′-alkylcyclohexanecarboxylates. The differences between the alkoxymethylene-substituted series and alkoxy-substituted series are discussed. Alkoxymethylene groups contribute to lowering the transition temperatures, and also reducing the bulk viscosities and optical anisotropy compared to the alkoxy groups as terminal groups of mesogens. This is apparently due to the higher flexibility of the alkoxymethylene groups, which affected the packing of molecules.

INTRODUCTION

In previous papers,[1,2] we reported our initial works on the transition temperatures of new mesogens with the alkoxymethylene groups as terminal groups. These compounds were 4-alkoxymethylene-substituted-phenyl 4′-alkylcyclohexanecarboxylates (I)[2] and 4-alkoxymethylene-substituted-phenyl 4′-alkylcyclohexanes (II).[1] These materials exhibit monotropic or/and smectic phases, and their clearing points are lower than those of alkoxy-substituted materials.[3,4] In phenylcyclohexane series (II),[1] another effect of reduction the bulk viscosity of alkoxymethylene groups was noticed. However, in the cyclohexanecarboxylate series (I),[2] the other effects were not yet examined. In this paper, homologous series of 4-alkoxymethylene-substituted-phenyl 4′-alkylcyclohexanecarboxylates (I) are synthesized and their physical properties are examined compared with the corresponding 4-alkoxy-substituted-phenyl 4′-alkylcyclohexanecarboxylates (III).[3] In addition, we discuss about the effect of substitution of alkoxy groups by the alkoxymethylene groups as terminal groups.


(I)


(II)


(III)

Preparation of materials

An outline of the preparation is given in the Scheme 1. The esters (I) were prepared from the 4-alkoxymethylene-substituted-phenols and 4-alkylcyclohexanecarboxylic acid chlorides. 4-Alkoxymethyl-phenols (n = 1) were prepared from 4-formylphenols by two reaction steps, reduction and etherification. 4-Alkoxyethyl-phenols (n = 2) were prepared from β-phenylethanol via acylation,[5] etherification, oxidation[6] and so on.

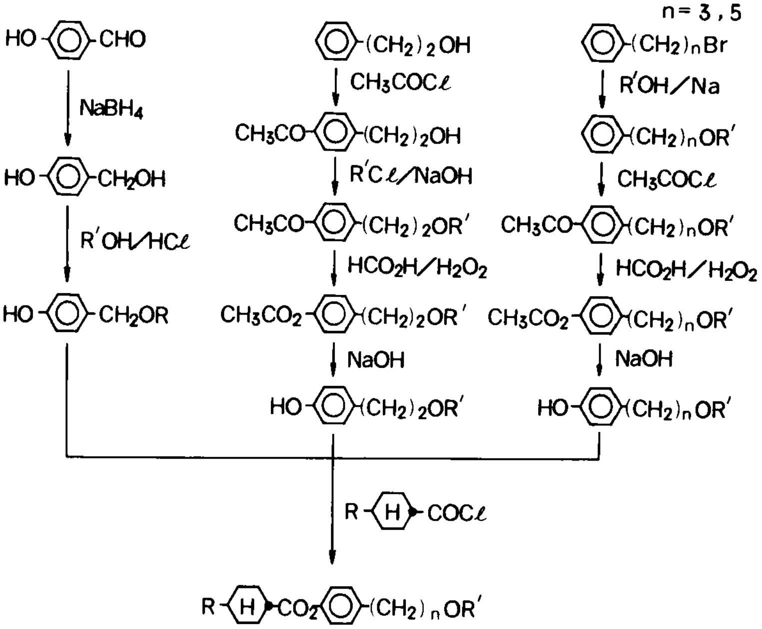
4-Alkoxypropylphenols (n = 3) and 4-alkoxypentylphenols (n = 5) were prepared from appropriate phenyl-alkylbromides via the similar route as that of alkoxyethyl-phenols. Experimental procedures are given in another section for a representative member of each class.

Purifications were achieved by repeated recrystallizations and distillations under reduced pressure. The structures of new synthesized esters were established by analysis of I.R., N.M.R. and mass spectra, and purity of each esters were checked by G.L.C.

RESULTS AND DISCUSSION

Transition temperatures

Thirty-nine materials were prepared; these are esters (I) having alkoxymethyl-, alkoxyethyl-, alkoxypropyl-, or alkoxypentyl groups.

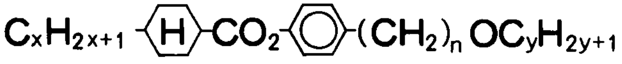


Scheme 1 Route of synthesis for 4-alkoxymethylene-substituted-phenyl 4'-alkylcyclohexanecarboxylates. Left route; 4-alkoxymethylphenols, center route; 4-alkoxyethylphenols, right route; 4-alkoxypropyl- and 4-alkoxypentylphenols (n = 3,5). The structural elements R- and R'- are normal alkyl chain.

Transition temperatures for these esters (I) are shown in Table I. It can be seen that almost of all materials (I) exhibit nematic mesophase, and the compounds with from n = 1 to n = 3 show monotropic transitions, the compounds with n = 5 show enantiotropic transitions. The members of esters (I) show generally lower transition temperatures. Particularly their clearing points (cl.p. : nematic-isotropic phase transition temperatures) are lower than 50°C. The lowest value of them is −24°C. Figure 1 shows the relationships between clearing points and the length of the alkoxy chain of the alkoxymethyl series (I) and alkoxy series (III).[3] The clearing points of alkoxymethyl series (I) are lower than those of alkoxy series (III).[3] And the relationships between clearing points and chain length of series (I) are remarkably different from that of series (III). In two examples of alkoxymethyl series, the clearing points decreased steeply from y = 1 to y = 2 and then showed an alternating and diverging pattern. On the other hand, alkoxy series shows a general alternating and converging pattern. These relationships illustrate the differences in behavior between alkoxymethyl groups and alkoxy groups in mesogenic molecules.

TABLE I

Single compounds with their phase transition temperatures in degree centigrade, crystal-nematic phase transition and nematic-isotropic phase transition. The abbreviations mean respectively, C; Solid phase, N; Nematic phase, I; isotropic phase. Points beneath the symbols given indicate the existence of the phase concerned, and the absence of the phase is indicated by strokes -. Transitions which only appear in an unstable area—usually called "monotropic"—have been placed in brackets.



No.	n	x	y	Transition Temperature (°C)*		
				C	N	I
1a	1	2	1	•19	—	•
1b	1	2	2	•15	—	•
2a	1	3	1	•27	•(18)	•
2b	1	3	2	•19	•(−11)	•
2c	1	3	3	• 4	•(−15)	•
2d	1	3	4	• 1	•(−22)	•
2e	1	3	5	• 4	•(−15)	•
2f	1	3	6	•12	•(−24)	•
2g	1	3	7	•13	•(−12)	•
3a	1	4	1	•39	•(13)	•
3b	1	4	2	•27	•(− 7)	•
3c	1	4	3	•11	•(−19)	•
4a	1	5	1	•53	•(34)	•
4b	1	5	2	•23	•(10)	•
4c	1	5	3	• 6	•(4.5)	•
4d	1	5	4	•10	•(− 3)	•
4e	1	5	5	• 8	•(3)	•
4f	1	5	6	•22	•(− 3)	•
4g	1	5	7	•16	•(5)	•
5a	1	6	1	•43	•(29)	•
5b	1	6	2	•25	•(8)	•
5c	1	6	3	•12	•(3)	•

TABLE I (continued)

No.	n	x	y	Transition Temperature*(°C)		
				C	N	I
6a	1	7	1	•49	•(34)	•
6b	1	7	2	•18	• 19	•
6c	1	7	3	•19	•(14)	•
6d	1	7	4	• 9	•(0)	•
7a	2	5	1	•20	•(11)	•
7b	2	5	2	•30	•(15)	•
8a	2	7	1	•29	•(24)	•
9a	3	3	1	•35	•(17)	•
9b	3	3	2	•14	•(−14)	•
9c	3	3	3	• 5	•(−15)	•
10a	3	5	1	•42	•(32)	•
10b	3	5	2	•29	•(11)	•
10c	3	5	3	•27	•(8)	•
11a	3	7	1	•42	•(40)	•
12a	5	3	1	•27	• 29	•
13a	5	5	1	•32	• 38	•
14a	5	7	1	•36	• 45	•

* , C : Crystal , N : Nematic , I : Isotropic
( ) : monotropic transition

The transition temperatures vs the number of n in the alkoxymethylene chain plot of the series (I) are given in Figure 2. When n-number is zero, the compound is an alkoxy-substituted series (III). The changing pattern of melting points and clearing points are somewhat different each others. The melting points exhibit a marked odd-even pattern, but clearing points show a changing pattern similar to Figure 1. In these compounds, melting points are higher than clearing points with n = 1, 2 and 3, but with n = 5 clearing point is higher than melting point. From this, it is noticed that the turning point from monotropic transition to enantiotropic transition is in from 3 to 5 for n-number.

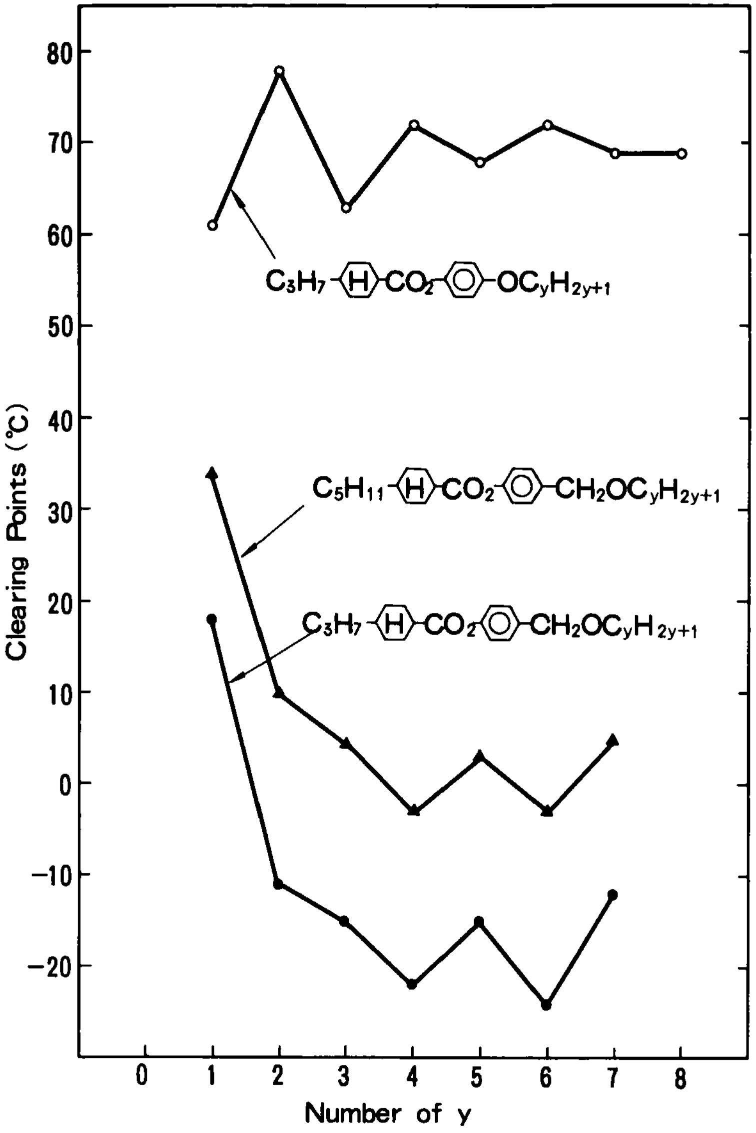


FIGURE 1 Clearing points (nematic-isotropic phase transition temperatures) versus y-number of alkoxymethyl chain in the alkoxymethy-substitited mesogens.

The examples shown in Figures 3 and 4 illustrate the magnitude of the effect of the terminal groups on the clearing points. If the terminal

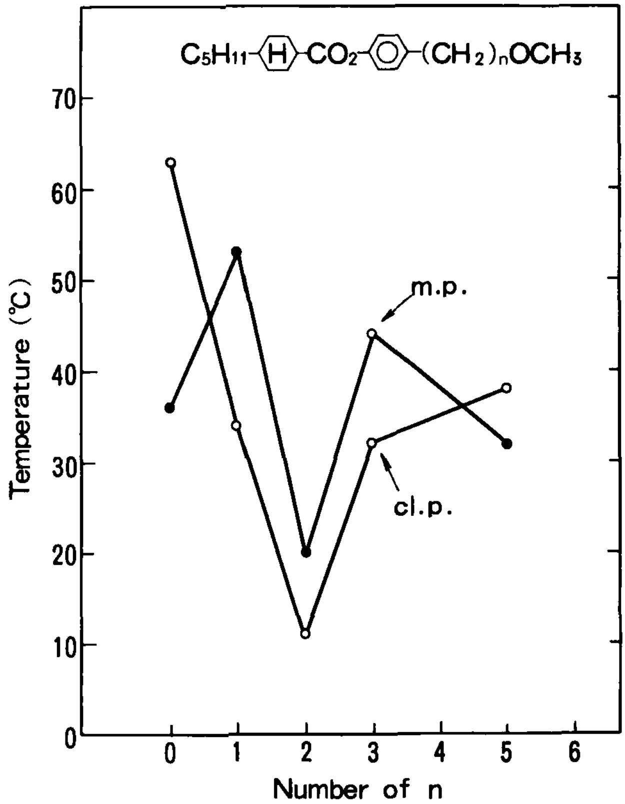


FIGURE 2 Transition temperatures (cl.p. and m.p.) versus n-number of methoxymethylence chain in appropriate mesogens.

groups are arranged in order of decreasing clearing points, the following relationships are obtained.

(1) $-OC_4H_9 > -(CH_2)_3OCH_3 > -(CH_2)_2OC_2H_5 > -CH_2OC_3H_7$

(2) $-OC_6H_{13} > -(CH_2)_5OCH_3 > -(CH_2)_3OC_3H_7 > -CH_2OC_5H_{11}$

These terminal groups are similar length, but the alkoxymethylene groups show lower clearing points than the alkoxy groups. In the members of alkoxymethylene groups, the clearing points increase with increasing the distance between the oxygen atom and the benzene ring. These order of decreasing clearing points on terminal groups

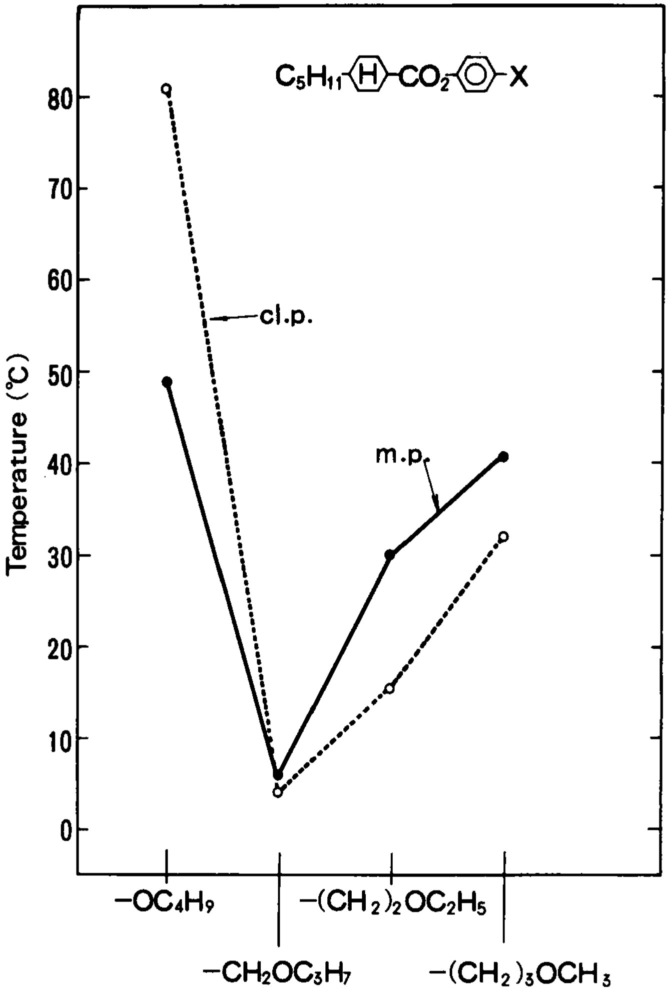
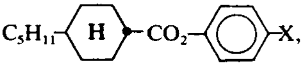


FIGURE 3 Transition temperatures versus substituted groups, which are butoxy-, propyloxymethyl-, ethoxyethyl-, and methoxypropyl- groups. Plot represents transition temperatures of the compounds:  X indicates respectively four terminal groups above.

is in agreement with the order in the phenylcyclohexane series (II) which previously reported.[1]

Figure 5 shows a diagram of state for the mixtures of alkoxymethyl series. The species used in Figure 5 are 2a and 6b, which show a

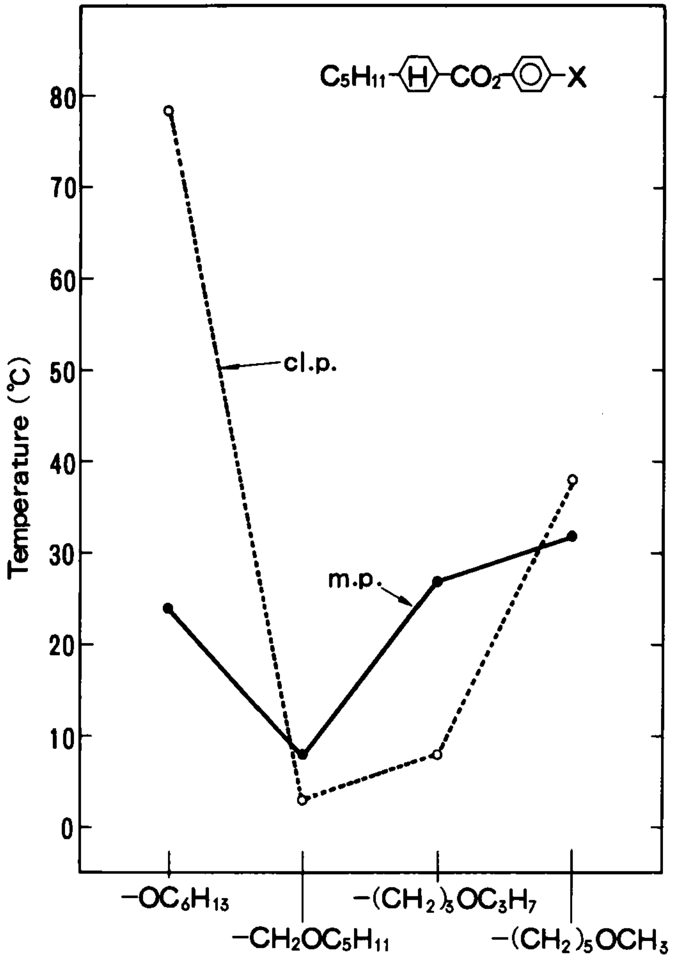
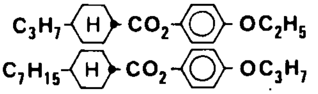


FIGURE 4 Transition temperatures versus substituted groups, which are hexyloxy-, pentyloxymethyl-, propyloxypropyl-, and methoxypently- groups. Plots represent same as Figure 3, these mesogens are different from those of Figure 3 in molecular length that is length of terminal chain.

monotropic phase as mentioned above. However, it can be seen that the eutectic mixture shows a enantiotropic phase. The nematic range of the eutectic mixture is from 5 to 19°C. On the contrary, the mixture of alkoxy series (III);[3]

and



(equimolar mixture)

shows a nematic range from 24 to 73°C. It is noticed that the nematic

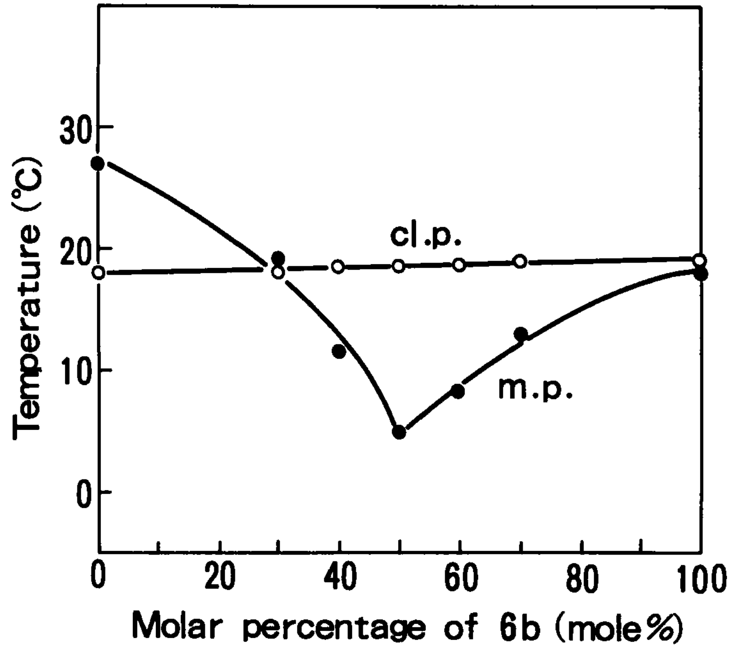
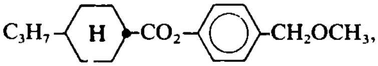
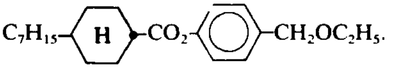


FIGURE 5 Phase diagram of state for mixtures of 2a and 6b. The 2a and 6b are described in Table 1, 2a;


, 6b;

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The eutectic mixture is composed of equimolar 2a and 6b. Closed circuits indicate the melting points of mixtures, and open circuits do the clearing points.

range of mixture of alkoxymethyl series shows somewhat narrow but very low.

BULK VISCOSITY

It was reported[1] that the alkoxymethyl-substituted phenyl-cyclohexanes (II) showed lower viscosity in nematic phase than the alkoxy-substituted phenylcyclohexanes did. But that comparison was not done at the same temperatures. In this ester series, eutectic mixture of alkoxymethyl series 2a and 6b shows a nematic phase at a room temperature. And the mixture of alkoxy series does so in a supercooled state. Therefore, the bulk viscosities are measured by a rotatory cone plate viscometer. Figure 6 shows the temperature de-

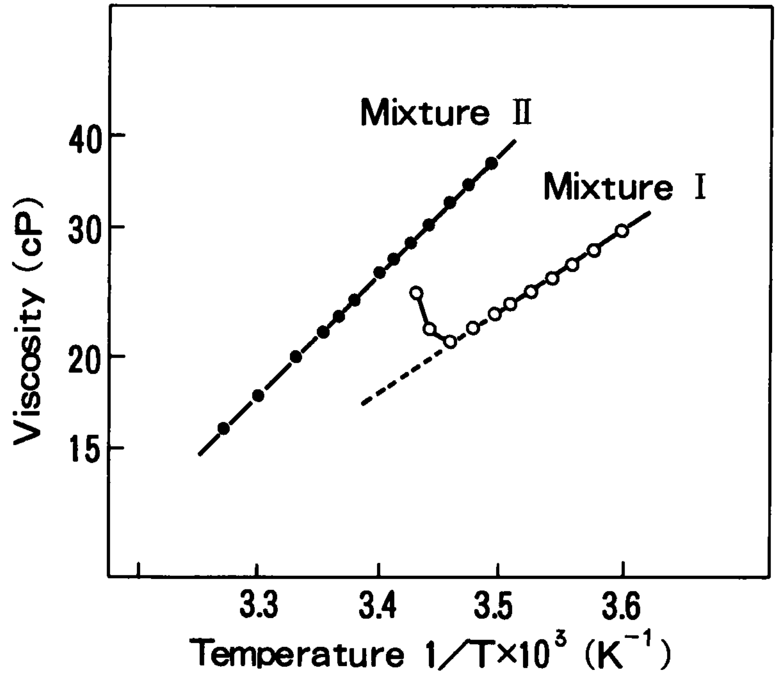
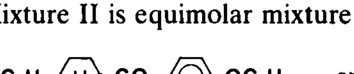


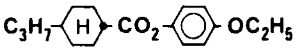
FIGURE 6 Temperature dependences of the bulk viscosities of Mixture I and II. Mixture I is an equimolar mixture of 2a and 6b, Mixture II is an equimolar mixture of



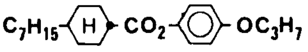
and

and these two mixtures are of equal molecular weight and similar length of molecules.

pendence of the bulk viscosities for the two mixtures. Mixture I is a eutectic mixture composed of 2a and 6b (equimolar mixture), and Mixture II is equimolar mixture composed of



and



The order of bulk viscosities for the two mixtures having the same average molecular weight is the following:

Mixture II ⩾ Mixture I
(alkoxy series) (alkoxymethyl series)

At 15°C, the Mixture I shows the value η = 21 cP and the Mixture II does the value η = 34 cP. In addition, it is noticed that the dependences of the viscosity value on the temperatures are different from each other, the degree of dependence of Mixture I is lower than that of Mixture II. From these results, it is concluded that the alkoxymethyl groups have an effect to reduce the bulk viscosity comparing with the alkoxy groups.

OPTICAL ANISOTROPY

The ordinary and extraordinary indices of refraction n_e and n_o of Mixture I and II were measured using the refractometer. Figure 7 shows temperature dependences of these indices and optical anisotropy Δn ($= n_e - n_o$). Mixture I shows the value $n_e = 1.547$, $n_o = 1.491$ and the Mixture II does the value $n_e = 1.533$, $n_o = 1.468$ at the temperature lower by 10°C than cl.p. These indices of Mixture I are higher than those of Mixture II. In contrast, the optical anisotropy Δn is 0.056 and 0.065 for the Mixture I and II. From above results, alkoxymethyl series shows a higher indices but lower optical anisotropy than alkoxy series do. Thus, the alkoxymethylene groups influence to its optical properties in the mesogenic compounds.

EFFECTS OF THE SUBSTITUTION BY ALKOXYMETHYLENE GROUPS

From above results, it is concluded that the substitution of alkoxy groups of mesogenic molecules by alkoxymethylene groups shows remarkable effects on its properties. These effects are the lowering transition temperatures and the reducing bulk viscosity and the optical anisotropy.

One of the reasons for these effects is attributed to the differences of degree in flexibility between the alkoxymethylene groups and alkoxy groups as terminal groups. It was pointed out[7,8,9] that the geometry of the molecules given by the conformational aspects is a determining factor for a packing of the molecules, and this packing of the molecules influences the thermodynamical stability of the nematic phase. Additionally, it can be considered that the decreasing of the orderness of packing results in the reducing of the bulk viscosity and the optical anisotropy. As mentioned in the previous report,[1,2] the degree of the flexibility in the alkoxymethylene chain is higher than that of the alkoxy chain. This higher flexibility of the alkoxymethylene groups reduces the orderness of packing of the molecules, and brings about the above mentioned results.

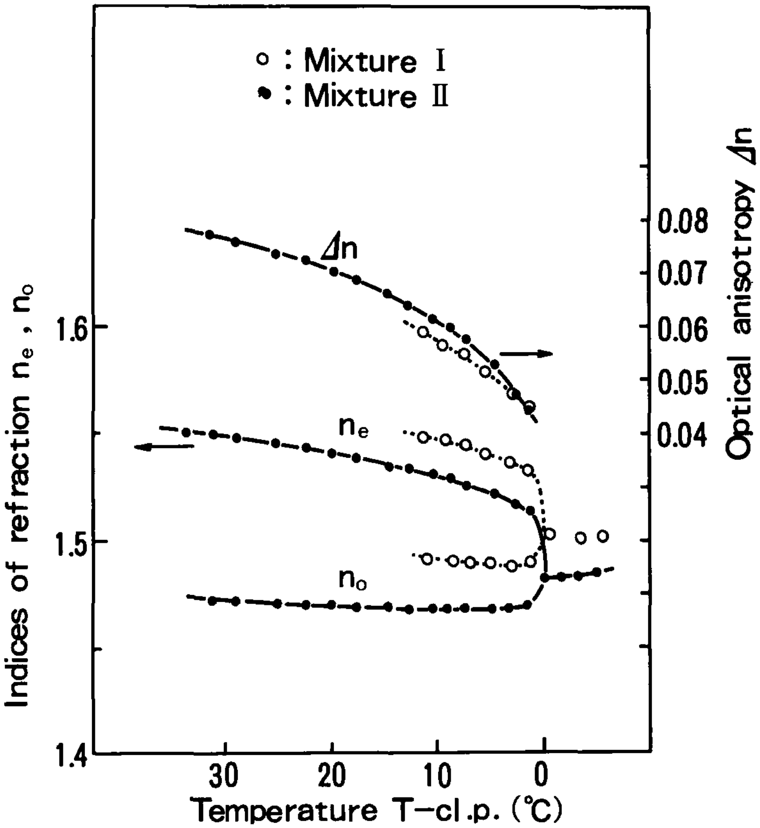


FIGURE 7 Temperature dependences of ordinary and extraordinary indices of refraction n_e and n_o, and optical anisotropy $\Delta n (= n_e - n_o)$ of above mentioned Mixture I and II.

EXPERIMENTS

All transition temperatures were observed by differential scanning calorimeter (DSC-580, Seiko Instruments & Electronics Ltd.). Viscosity was measured on a rotatory cone plate viscometer, and indices were determined by Abbe's refractometer.

SYNTHESES OF 4-ALKOXYMETHYLPHENOLS

(4-Hydroxymethylphenol)

4-Hydroxymethylphenols were prepared by a modification of the literature[10] procedure.

To 91.6 g of 4-formylphenol and 600 mL of ethanol, 17.7 g of sodium borohydride was added portionwise with stirring at 20–30°C. After the addition was completed, the stirring was continued for 2 h at room temperature. When the evolution ceased, 20 mL of acetic acid was added dropwise. After the addition of 250 mL of water to this solution, ethanol was distilled off under reduced pressure. The residual solution was cooled in an ice bath, and then the yellow precipitates were crystallized. The precipitates were collected and recrystallized from water-charcoal, 48 g of 4-hydroxymethylphenol with a melting point of 43°C was obtained as a colorless powder.

(4-Methoxymethylphenol)

To a solution of 213 g of concentrated hydrochloric acid, 430 mL of methanol and 1300 mL of water, 64 g of 4-hydroxymethyl-phenol was added in one portion at room temperature. After stirring for 1 h, sodium chloride was added to the mixture until the solution was saturated. Then, extraction with 500 mL of isopropylalcohol gave a solution containing 68.7 g of 4-methoxymethylphenol. (This concentration was determined by G.L.C.) This solution can be supplied to the next esterification after drying by anhydrous sodium sulfate.

SYNTHESIS OF 4-METHOXYETHYLPHENOLS

(β-Phenethyl acetate)

To a mixture of 167 g of phenylethanol, 300 mL of benzene, and 130 mL of pyridine, 129 g of acetyl chloride was added dropwise at 25–30°C with stirring. After stirring for 5 h, the mixture was filtered off to remove the pyridine hydrochloride. The residual solution was washed with water, and then the most of benzene was distilled off in vacuo. The distillation of the residue under reduced pressure gave the 207 g of β-phenylethyl acetate as a colorless oil. (B.p. 120–124°C/21 mmHg)

(β-(4-Acetyl phenyl)ethyl-acetate)

The acylation step was carried out in the normal way.[5]

To a suspension of 1500 mL of dichloromethane and 179 g of anhydrous aluminium chloride, 106 g of acetylchloride was added gradually and then 100 g of β-phenylethyl acetate was added dropwise at room temperature with vigorous stirring. After stirring for 3 h, 90 g of anhydrous aluminium chloride and 50 g of acetylchloride were added and the mixture was stirred for more 3 h. Then the mixture was poured into dilute hydrochloric acid and ice by degrees. The organic layers was separated and washed with water and with aqueous sodium hydrogen carbonate. After drying over anhydrous sodium sulfate, the dichloromethane was removed under reduced pressure and the residue was distilled in vacuo. Then 218 g of the β-(4-acetylphenyl)ethyl acetate was obtained as a colorless oil. (b.p. 120–124°C/0.15 mmHg)

(4-Acetylphenylethylalcohol)

A mixture of 218 g of β-(4-acetylphenyl)ethyl acetate, 400 mL of ethanol, and 89 g of sodium hydroxide was refluxed with stirring for 5 h. After removal of the ethanol, the mixture was poured into 500 mL of water. Then, the mixture was acidified with concentrated hydrochloric acid and extracted three times with 100 mL of benzene.

The combined organic layers were washed with water, dried over anhydrous sodium sulfate, and concentrated in vacuo. The distillation of the residue under reduced pressure gave the 71 g of 4-acetylphenylethylalchol. (b.p. 120.5–124°C/0.25 mmHg)

(4-Ethoxyethylacetophenone)

The etherification was carried out in a modified way of the literature method.[11]

To the mixture of 70 g of 4-acetylphenylethanol, 400 mL of dimethylsulfoxide, and 45 g of sodium hydroxide, 140 g of ethylbromide was added dropwise with stirring at room temperature. After the addition, the mixture was heated to 60°C, and stirred for 4 h at 50–60°C. Then, the mixture was poured into water and acidified with concentrated hydrochloric acid, and extracted twice with 100 mL of benzene. The combined organic layers were washed with water and dried over anhydrous sodium sulfate, and concentrated in vacuo. The distillation of the residue under reduced pressure gave the 46 g of 4-ethoxyethylacetophenone as a colorless oil. (b.p. 90–103°C/0.25 mmHg)

(4-Ethoxyethylphenol)

The oxidation was carried out in the normal way.[6]

A mixture of 46 g of ethoxyethylacetophenone, 430 mL of formic acid (88%), 210 mL of acetic anhydride, 3 mL of concentrated sulfuric acid, and 80 mL of hydrogen peroxide (35%) was stirred at 40–50°C on a water bath for 3 h. Then, the mixture was poured into water, and this solution was stirred for half an hour, and extracted three times with 100 mL of ether. The combined organic layers were washed with water and dried over anhydrous sodium sulfate, and concentrated in vacuo.

To this residue, 20 g of sodium hydroxide and 150 mL of ethanol were added, and the mixture was stirred under reflux for 4 h. After cooling, the mixture was poured into water and washed with ether. The aqueous layer was acidified with concentrated hydrochloric acid and extracted three times with 100 mL of ether. The combined organic layers were washed with water and dried over anhydrous sodium sulfate and concentrated in vacuo. The distillation of the residue under reduced pressure gave 8 g of 4-ethoxyethylphenol as a colorless oil. (b.p. 106.5–107°C/0.4 mmHg)

SYNTHESIS OF 4-METHOXYPROPYLPHENOL

(γ-Methoxypropylbenzene)

120 g of γ-bromopropylbenzene was added dropwise to the refluxing solution of 600 mL of anhydrous methanol and 20 g of metallic sodium. After the addition, the mixture was refluxed for 2 h, and then cooled to room temperature. And the mixture was poured into 1500 mL of water, and extracted three times with 100 mL of benzene. And the combined organic layers were washed with water, dried over anhydrous sodium sulfate, and concentrated in vacuo. The distillation of the residue under reduced pressure gave the 51 g of γ-methoxypropylbenzene. (b.p. 96°C / 15 mmHg)

(4-(γ-methoxypropyl)-acetophenone)

The acylation was essentially the same as that above mentioned in the section on 4-ethoxyethylacetophenone. The yield was 52%, (b.p. 93.5–95.5°C/0.25 mmHg)

(4-Methoxypropylphenol)

The oxidation and hydrolysis were essentially the same as that mentioned in the section on 4-ethoxyethylphenol. The yield was 20%. (b.p. 106–108°C/10.3 mmHg)

Esterification

The esters were prepared from appropriate 4-alkoxymethylene-substituted-phenols and 4-alkylcyclohexanecarboxylic acid chlorides. The reaction procedure of esterification was the same as the literature method.[12] 4-Alkylcyclohexanecarboxylic acid chloride were prepared from thionyl chloride and commercially available 4-alkylcyclohexanecarboxylic acides according to standard method.

Acknowledgments

The authors would like to thank K. Suzuki, M. Yoshida, H. Ohkawa, and Y. Okabe, who carried out the experimental chemical work and the performance of the physical measurements.

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