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H. Takatsu , K. Takeuchi & H. Sato

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Synthesis and some Physical Properties of *trans*-4-{ β -(*trans*-4'*n*-Alkylcyclohexyl)-1'} -Ethylcyclohexane-1-Carboxylates

H. TAKATSU, K. TAKEUCHI and H. SATO

Dainippon Ink & Chemicals, Inc., 3-35-58, Sakashita, Itabashi, Tokyo, Japan

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A series of *trans*-4-{ β -(*trans*-4'-*n*-alkylcyclohexyl)-1'}-ethylcyclohexane-1-carboxylates, which show nematic phases, was prepared. Their transition temperatures and enthalpies were measured. Their bulk viscosities and birefringences were determined by extrapolation. The influence of terminal halogeno and alkyl groups on the N-I transition temperatures and the C-N transition enthalpies for the *trans*-4-{ β -(*trans*-4'-*n*-alkylcyclohexyl)-1'}-ethylcyclohexane-1-carboxylates is discussed and compared with the influence for the 1-(*trans*-4'-*n*-alkylcyclohexyl)-2-(4"-halobiphenyl-4'-yl)ethanes. The bulk viscosity as a function of the third power of the van der Waals radius of the halogeno group for the 4-halophenyl *trans*-4'-{ β -(*trans*-4''-*n*-propylcyclohexyl)-1"}-ethylcycloh

INTRODUCTION

Since interesting new mesomorphic compounds containing fluoro substituents were reported in 1978,¹ other nematic fluoro compounds have been synthesized.²⁻⁶ The small volume of the fluoro substituent does not increase the viscosity of the nematic compound compared with other substituents like alkoxy or cyano. We have reported⁶ the influence of the halogeno group on the properties for the 1-cyclohexyl-2-(4"halobiphenyl-4'-yl)ethanes. The 4-substituted cyclohexane-1carboxylates are of low viscosity with high clearing points⁷ and suitable for high level multiplexed LCDs,⁸ and new nematic compounds of low viscosity, containing the ethylene linkage (CH_2CH_2) , have been reported.^{9,10} This ethylene linkage maintains the straightness of the nematogenic molecules and has flexibility.

We have now synthesized a new series of *trans*-4-{ β -(*trans*-4'-*n*-alkylcyclohexyl)-1'}-ethylcyclohexane-1-carboxylates of formula (I) in order to establish the influence of each terminal halogeno substituent and of an alkyl group on transition temperature, transition enthalpy, bulk viscosity and birefringence, and to achieve a nematic compound of low viscosity, high clearing point and low birefringence.

$$R-(H)-CH_{2}CH_{2}-(H)-COO-Y$$
(I)

$$R= n-alkyl$$

$$Y= -(O)-X, -(O)-R', -(H)-R',$$

$$-(O)-(O)-F$$
(X= H, F, Cl, Br)
(R'= n-alkyl)

PREPARATION OF MATERIALS

The trans-4-{ β -(trans-4'-n-alkylcyclohexyl)-1'}-ethylcyclohexane-1carboxylates were prepared according to the following scheme:

$$R-H-CH_{2}COC1 \xrightarrow{(M)}_{A1C1_{3}} R-H-CH_{2}CO-\bigcirc \xrightarrow{(MH_{2}NH_{2} \cdot H_{2}O)}_{KOH}$$

$$R-H-CH_{2}CH_{2}-\bigcirc \xrightarrow{(CH_{3}COC1)}_{A1C1_{3}} R-H-CH_{2}CH_{2}-\bigcirc \xrightarrow{(COCH_{3})}_{COCH_{3}} \xrightarrow{(NaC1O)}_{R-H-CH_{2}CH_{2}-\bigcirc \xrightarrow{(COCH_{3})}_{COCH_{3}}$$

$$R-H-CH_{2}CH_{2}-\bigcirc \xrightarrow{(COOH)}_{2.HC1} R-H-CH_{2}CH_{2}-H-COOH \xrightarrow{(CH_{3}-CH_{2}-CH_{2}-H)}_{2.HC1} COOH \xrightarrow{(CH_{3}-CH_{2}-CH_{2}-H)}_{COOH}$$

$$\xrightarrow{(SOC1_{2})} R-H-CH_{2}CH_{2}-H-COC1$$

$$(II)$$

$$R-H-CH_{2}CH_{2}-H-COO-\bigcirc -R' (III)$$

$$R-H-CH_{2}CH_{2}-H-COO-\bigcirc -R' (IV)$$

$$R-H-CH_{2}CH_{2}-H-COO-\bigcirc -F (V)$$

The *p*-halophenols were obtained commercially and *trans*-4-*n*-propylcyclohexan-1-ol was prepared from *p*-*n*-propylphenol. The 4-fluoro-4'-hydroxybiphenyl was synthesized from 4-methoxyphenylmagnesium bromide and *p*-iodofluorobenzene using the catalyst $PdCl_2$ in boiling THF, followed by cleavage of the methoxy group by acetic acid and hydrobromic acid.

Each compound was purified by chromatography on silica gel, eluting with a mixture of hexane and benzene, followed by recrystallization from ethanol. The structures were confirmed by NMR spectrometry and mass spectrometry. The purity was tested by high pressure liquid chromatography and gas-liquid chromatography.

RESULTS AND DISCUSSION

Mesomorphic and thermodynamic properties

The transition temperatures for the *trans*-4-{ β -(*trans*-4'-*n*-alkylcyclohexyl)-1'}-ethylcyclohexane-1-carboxylates were measured by using a polarizing microscope equipped with a heating stage. The transition enthalpies (Δ H) were measured by differential scanning calorimetry. These thermal data are listed in Table I.

TABLE I

Transition temperatures and enthalpies (ΔH) for the trans-4-{ β -(trans-4'-n-alkylcyclohexyl)-1'}-ethylcyclohexane-1-carboxylates

Compound	R	Y	Transition temp. (° C)						ΔH (kcal/mole)		
			c		s		N		I	$\frac{C-N \text{ or }}{C-S + S-N}$	N-I
(<i>a</i>)	C ₃ H ₇ -	$\overline{\langle O \rangle}$	•	79		80	•	123		6.08	0.285
<i>(b)</i>	C_3H_{7}			81	•	_	·	156	•	5.12	0.293
(<i>c</i>)	C_3H_{7}	-Ó-C1	•	76	•	80	•	181	•	6.07	0.316
(<i>d</i>)	C_3H_7 -	- O-Br		90				184	•	5.33	0.315
(<i>e</i>)	C ₂ H ₅ -	-{F		70	•	-		136	•	7.63	0.294
(f)	C ₃ H ₇ -	-{O}-С ₃ н ₇		128	•	131	·	165	•	1.47	0.314
(g)	C_3H_7	-(H)-C ₃ H ₇		142		145		159	•	1.31	0.189
(<i>h</i>)	C ₃ H ₇ -		•	88	•	159	•	260	•	7.19	0.442

R-{H}-СH2CH2-{	н)-соо-ч
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The effect of the terminal halogeno substituent X in formula (II) on the nematic-to-isotropic (N-I) transition temperature can be established by comparing the transition temperatures for the 4halophenyl trans-4'-{ β -(trans-4''-n-propylcyclohexyl)-1''}-ethylcyclohexane-1'-carboxylates. With increase in the volume of the terminal halogeno substituent X from $H \rightarrow F \rightarrow Cl \rightarrow Br$, the N-I transition temperatures increase; 33°C from H to F, 25°C from F to Cl, 3°C from Cl to Br. The increases in the N-I transition temperatures can be explained in terms of changes in the terminal attractions. The differences in the terminal attraction for H and F and Cl are large compared with the difference for Cl and Br. The behaviour is very similar to that for the 1-(trans-4'-n-propylcyclohexyl)-2-(4"-halobiphenyl-4'-yl)ethanes.⁶ The increase for the 4-halophenyl trans-4'-{ β -(trans-4"-n-propylcyclohexyl)-1"}-ethylcyclohexane-1'-carboxylates is smaller than the increase for the 1-(trans-4'-n-propylcyclohexyl)-2-(4"-halobiphenyl-4'-yl)ethanes. Their behaviours are compared in Figure 1.

The enthalpy values for the crystal-to-nematic (C–N) or crystal-tosmectic (C–S) + smectic-to-nematic (S–N) transitions for each 4-halophenyl *trans*-4'-{ β -(*trans*-4''-*n*-propylcyclohexyl)-1''}-ethylcyclohexane-1'-carboxylate remains nearly constant, being in the range 5.12–6.08 kcal/mole. A similar result is obtained for the 1-(*trans*-4'*n*-propylcyclohexyl)-2-(4''-halobiphenyl-4'-yl)ethanes.

The effect of a terminal alkyl group on the transition temperature and enthalpy can be established by comparing the transition temperatures and enthalpies of compounds (a), (f) and (g). The terminal *n*-propyl group increases the N-I transition temperature and reduces the C-N or C-S + S-N transition enthalpy, remarkably. The terminal alkyl group plays an important role in determining nematic thermal stability.

Physical properties

As the 4-halophenyl trans-4'-{ β -(trans-4''-n-propylcyclohexyl)-1''}ethylcyclohexane-1'-carboxylates do not exhibit nematic phases at room temperature, their bulk viscosities at 20 °C and birefringences at 25 °C were determined by extrapolation from data obtained using a series of solutions of the compounds in a mixture of 4-alkoxyphenyl trans-4'-alkylcyclohexane-1'-carboxylates and trans-4-alkyl-1-(4'cyanophenyl)cyclohexanes; results are listed in Table II. The composition and physical properties of the mixture used as host are shown in a previous paper.⁶

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FIGURE 1 The influence of the terminal halogeno substituent X on the N-I transition temperature for the 4-halophenyl *trans-4'*-{ β -(*trans-4''-n*-propylcyclohexyl)-1"}-ethylcyclohexane-1'-carboxylates and the 1-(*trans-4'-n*-propylcyclohexyl)-2-(4"-halobiphenyl-4'-yl)ethanes.

TABLE II

Bulk viscosities at 20 °C and birefringences at 25 °C of the 4-halophenyl trans-4'-{ β -(trans-4''-npropylcyclohexyl)-1''}-ethylcyclohexane-1' -carboxylates



x	Bulk viscosity at 20 ° C (c.p.)	Birefringence at 25 °C (—)
н	27.0	0.092
F	29.1	0.102
Cl	38.5	0.122
Br	45.2	0.126

The viscosity measurements were made using a rotating cone-plate viscometer at 20°C. The bulk viscosities for the 4-halo-phenyl *trans*-4'-{ β -(*trans*-4''-*n*-alkylcyclohexyl)-1''}-ethylcyclohexane-1'-carboxylates increase with increase in the volume of the terminal group from $H \rightarrow F \rightarrow Cl \rightarrow Br$. The bulk viscosity as a function of van der Waals radius of the halogeno substituent³ is shown in Figure 2. A linear relationship between the logarithm of the bulk viscosity and the van der Waals radius of the halogeno substituent³ is obtained as for the 1-(*trans*-4'-*n*-propylcyclohexyl)-2-(4''-halobiphenyl-4'-yl)ethanes. The logarithm of the bulk viscosity increases linearly with increase in the volume of the terminal group. This result is referred to in the following equations¹¹:

 $\eta \propto \exp(\Delta G/RT)$ $\Delta G = P\Delta V + \Delta U$

where,

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η: viscosity
G: free energy
R: gas constant
T: absolute temperature

P: pressure*V*: volume*U*: internal energy



FIGURE 2 Bulk viscosity vs. van der Waals radius of the terminal substituent³ for the 4-halophenyl trans-4'-{ β -(trans-4''-n-propylcyclohexyl)-1''}-ethylcyclohexane-1'-carboxylates and the 1-(trans-4'-n-propylcyclohexyl)-2-(4''-halobiphenyl-4'-yl)ethanes.

The gradient in Figure 2 shows that the influence of the volume of the terminal group for the 4-halophenyl *trans*-4'-{ β -(*trans*-4''-*n*-propylcyclohexyl)-1''}-ethylcyclohexane-1'-carboxylates is smaller than the influence for the 1-(*trans*-4'-*n*-propylcyclohexyl)-2-(4''-halobiphenyl-4'-yl)ethanes.

Birefringences were measured by polarizing microscopy using a compensator. The birefringences increase as the halogeno substituents become larger, and a terminal halogeno substituent conjugated with an aromatic system apparently enhances the birefringence. The birefringences for the 4-halophenyl *trans*-4'-{ β -(*trans*-4''-*n*-propylcy-clohexyl)-1'}-ethylcyclohexane-1'-carboxylates are plotted as a function of van der Waals radius of the terminal group in Figure 3. This shows a linear relationship between the birefringence and the van der Waals radius of the terminal substituent as for the 1-(*trans*-4'-*n*-propylcyclohexyl)-2-(4''-halobiphenyl-4'-yl)ethanes, such that the birefringence



FIGURE 3 Birefringence vs. van der Waals radius of the terminal substituent for the 4-halophenyl trans-4'-{ β -(trans-4''-n-propylcyclohexyl)-1'}-ethylcyclohexane-1'-carboxylates and the 1-(trans-4'-n-propylcyclohexyl)-2-(4''-halobiphenyl-4'-yl)ethanes.

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gence increases linearly with increase in the ratio of the conjugated part of the molecule to the total molecular length. The gradient for the 4-halophenyl trans-4'-{ β -(trans-4''-n-propylcyclohexyl)-1'}-ethylcyclohexane-1'-carboxylates is smaller than that for the 1-(trans-4'-npropylcyclohexyl)-2-(4''-halobiphenyl-4'-yl)ethanes.

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