January, 1984] © *1984 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 57, 283—284 (1984)* 283

The Thermal Properties of (4-Substituted Cyclohexyl) 4-Substituted Cinnamates

Shigetsugu Hayashi, Shunsuke Takenaka,* and Shigekazu Kusabayashi
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565

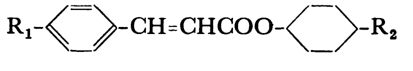
(Received July 13, 1983)

Synopsis. The thermal properties for a homologous series of 4-alkylcyclohexyl 4-alkoxy- and 4-cyanocinnamates are examined. They exhibit nematic phases with low melting points. The effect of the cyclohexyl group on the mesophase stability is discussed.

(4-Substituted phenyl) 4-substituted benzoates have been known to be good nematogens for devices employing a twisted nematic mode, as one of the substituents is a polar group, such as cyano, and the guest-host and dynamic scattering modes, as both substituents are the nonpolar groups, such as an alkyl and/or alkoxyl.[1] For practical purposes, (4-substituted cyclohexyl) 4-substituted benzoates are also good nematogens, because the cyclohexyl group tends to lower the melting point and increases the clearing point. In this paper, we will demonstrate the preparation and thermal properties of (4-substituted cyclohexyl) 4-substituted cinnamates; the effect of the cyclohexyl group on the thermal properties is also discussed.

Preparation

The 4-alkylcyclohexanols were obtained by the hydrogenation of the corresponding 4-alkylphenols in the presence of Ranney nickel under 150X10^5 Pa at 150 °C. The cis and trans mixtures of the cyclohexanols were reacted with benzoyl chloride, giving 4-alkylcyclohexyl benzoates. The esters were purified by column chromatography over silica gel, using a mixed solvent of hexane-ether (98:2—95:5). After repeating the chromatographic purification, the esters were hydrolyzed with methanol- 2 mol dm^{-3} potassium hydroxide (1:1), thus giving *trans*-4-alkylcyclohexanols. The purity was checked by means of the NMR spectrum. The NMR spectrum for *trans*-4-heptylcyclohexyl benzoate shows a multiplet at 4.7—5.1 ppm arising from the methine proton at the 1 position, and the cis form a broad singlet at 5.3 ppm (Δ) in $CDCl_3$. The yields of the materials with a purity of more than 99% were less than 20%. 4-Alkyl-, 4-alkoxy-, and 4-cyanocinnamoyl chlorides were reacted with *trans*-4-alkylcyclohexanols according to the usual method. The esters prepared here were purified by column chromatography over silicagel, using a mixed solvent of hexane-ether (98:2), followed by recrystallization from absolute ethanol. The data of elemental analysis are shown in Table 1.



Results and Discussion

The melting points and mesomorphic transition temperatures for the cinnamate esters are given in Table 2. Compounds **1**—**11** have melting points that lie between 53 and 99 °C, while compounds **12** and **13** have somewhat lower melting points. The nematic-isotropic transition temperatures for the homologous series of 4-heptylcyclohexyl cinnamates show a typical even-odd effect. Compounds **12** and **13** have low melting points and enthalpies, being good nematogens.

Table 1. Elementary analysis data

Compound	R_1	R_2	Calcd (%) C	Calcd (%) H	Calcd (%) N	Found (%) C	Found (%) H	Found (%) N
1	CH_3O	C_7H_{15}	77.05	9.56		76.99	9.56	
2	C_2H_5O		77.37	9.74		77.28	9.71	
3	C_3H_7O		77.67	9.91		77.44	9.95	
4	C_4H_9O		77.95	10.07		78.12	9.87	
5	$C_5H_{11}O$		78.21	10.21		78.10	10.25	
6	$C_6H_{13}O$		78.45	10.35		78.28	10.33	
7	$C_7H_{15}O$		78.68	10.48		78.38	10.55	
8	CH_3O	C_3H_7	75.46	8.67		75.17	8.69	
9		C_4H_9	75.91	8.92		75.81	8.92	
10		C_5H_{11}	76.32	9.15		76.22	9.16	
11	$C_5H_{11}O$	C_5H_{11}	77.67	9.91		77.39	9.95	
12	C_5H_{11}	C_3H_7	80.65	10.01		80.60	10.03	
13		C_5H_{11}	81.03	10.34		81.25	10.40	
14	CN	C_4H_9	77.13	8.09	4.50	77.11	8.12	4.56
15		C_5H_{11}	77.50	8.36	4.30	77.35	8.42	4.19
16		C_7H_{15}	78.14	8.84	3.96	77.83	8.95	4.02

TABLE 2. THERMAL PROPERTIES

Compound	C		N		I	$\frac{\Delta H_{\mathrm{mp}}}{\mathrm{kJ\ mol^{-1}}}$	$\frac{\Delta H_{\mathrm{NI}}}{\mathrm{kJ\ mol^{-1}}}$
1	.	52.7	.	95.3	.	36.0	1.3
2	.	98.8	.	104.3	.	30.6	1.4
3	.	85.0	.	92.8	.	34.0	1.1
4	.	75.8	.	97.5	.	24.6	1.5
5	.	61.0	.	92.5	.	47.2	1.4
6	.	69.7	.	94.5	.	48.1	1.7
7	.	77.2	.	92.5	.	40.8	1.6
8	.	67.0	.	91.0	.	19.5	0.9
9	.	57.4	.	87.2	.	26.7	0.7
10	.	56.5	.	97.2	.	24.0	0.9
11	.	66.1	.	95.3	.	20.1	1.2
12	.	45.3	.	65.4	.	18.2	1.0
13	.	36.5	.	69.0	.	22.5	0.9
14	.	121.0	.	(104.0)a)	.	25.5	—
15	.	122.0	.	(109.0)a)	.	27.5	—
16	.	112.5	.	(110.0)a)	.	28.6	0.9

a) Parentheses indicate monotropic transition temperatures.
The transition temperatures were measured using a Nikon polarized microscope POH equipped with a Mettler FP 52 heating stage and a control unit. The transition enthalpies were measured by means of a Daini Seikosha SSC 560 differential scanning calorimeter, using indium (99.9%) as the calibration standard at a heating rate of 5 °C/min.

As the alkoxyl group is replaced by a cyano group, both melting and clearing points increase, showing monotropic nematic properties. These results may be compared with those of the corresponding phenyl cinnamates. It has been known that a cyclohexyl group is less favorable for the thermal stability of the mesophase than a phenyl, because the former is more flexible than the latter. For example, 4-alkylbenzoic acids have higher melting and clearing points than 4-alkylcyclohexanecarboxylic acids.

For compounds **1**—**13** having nonpolar substituents, the melting points are lower by 10—30 °C than those for the corresponding phenyl cinnamate esters.3,4) On the other hand, the clearing points for the present series are also lower by 5—40 °C than those for the corresponding phenyl cinnamate esters. The difference tends to become larger with increase in the carbon number in the alkyl and alkoxyl chains. These trends are probably connected with the flexibility of the cyclohexyl group.

As the terminal group is replaced by a cyano group, the circumstances differ significantly. Usually, as the phenyl group with the alkyl chain in 4-cyano-4′-alkylbiphenyls and 4-cyanophenyl 4-alkylbenzoates is replaced by a cyclohexyl group, the clearing points increase by *ca.* 20 °C, whereas the melting points are almost unchanged. These trends have been interpreted in terms of the structural difference in the antiparallel dimer of the molecules in the mesophase.5) Indeed, X-ray measurements indicate that the "overlapping core" formed by the 4-cyanobiphenyls and 4-cyanophenyl benzoates differs significantly from the "partially overlapping" one formed by the corresponding cyclohexyl compounds.6) For the present series (**14**—**16**), by contrast, the melting points are higher by 30—40 °C, and the clearing points are lower by 10—20 °C than those for the corresponding 4-alkylphenyl 4-cyanocinnamates.7,8) These facts indicate that the enhancement of the nematic stability upon the replacement of the phenyl group with the cyclohexyl one does not occur in this system. A possible explanation is that the "overlapping core" for the phenyl 4-cyanocinnamates differs from those for the 4-cyanobiphenyls and 4-cyanophenyl benzoates and is rather similar to those for the cyclohexyl compounds, while the flexibility of the cyclohexyl group decrease the stability of the nematic phase, as has been mentioned above.

In conclusion, the replacement of the phenyl ring by the cyclohexyl in the phenyl cinnamate core leads to a decrease in the thermal stability of the nematic phase, presumably because of an increase in the flexibility of the core, even though both terminal substituents are nonpolar alkyl and/or alkoxyl groups or a polar cyano.

References

1) G. J. Sprokel, "The Physics and Chemistry of Liquid Crystal Devices," Plenum Press, New York (1980).

2) D. Demus, H. Demus, and H. Zasche, "Flüssig Kristalle in Tabellen," VEB Deutscher Verlag für Grundstoff Industries, Leipzig (1974).

3) F. B. Jones, Jr., and J. J. Ratto, U. S. Patent 3926834 (1973).

4) F. J. Jun and J. Ratto, *J. Chem. Soc., Chem. Commun.*, **1973**, 841.

5) G. W. Gray, *Mol. Cryst. Liq. Cryst.*, **63**, 3 (1981).

6) A. J. Leadbetter and A. I. Mehta, *Mol. Cryst. Liq. Cryst.*, **72**, 51 (1981).

7) F. B. Jones, Jr., and J. J. Ratto, *J. Phys. C*, **36**, Cl-413 (1975).

8) V. V. Titov, E. I. Kovshev, A. I. Pavluchenko, V. T. Lazareva, and M. F. Grebenkin, *J. Phys. C*, **36**, Cl-387 (1975).