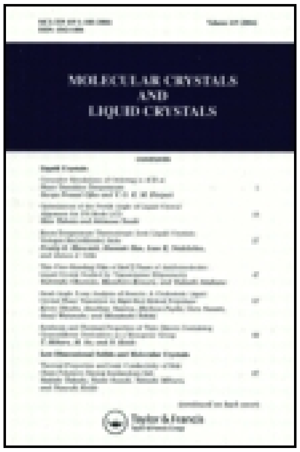

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New Mesogens with Terminal Cyclohexyl Group

R. A. Vora [a] , Renu Mahajan [a] & Himani Nandedkar [a]
[a] Applied Chemistry Department, Faculty of Technology and Engineering, M.S. University of Baroda, Post Box No. 51, VADODARA, 390 001, India

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NEW MESOGENS WITH TERMINAL CYCLOHEXYL GROUP

R.A.Vora, Renu Mahajan and Himani Nandedkar

Applied Chemistry Department, Faculty of Technology and Engineering,
M.S. University of Baroda, Post Box No. 51
VADODARA - 390 001 (India).

Three homologous series were synthesized to evaluate the effect of mono substituted cyclohexyl ring system on mesomorphic properties.

Keywords : Cyclohexyl, Smectogenic, Mono-substituted.

INTRODUCTION

It has been shown that Active Matrix Displays (AMLCDs) require liquid crystals with low viscosity. Since Demus et al[1] reported the nematic cyclohexane carboxylates in 1973, several kinds of nematic compounds containing cyclohexyl ring have been synthesized[2-4]. Their nematic phases, which are low in viscosity and mesomorphic ranges near room temperatures are suitable for TN-display devices. Most of the compounds reported so far are trans - 1,4 - substituted Cyclohexane ring system. The present work gives the idea about the effect of mono substituted terminal Cyclohexyl group on mesomorphic properties. Series (I), Cyclohexyl 4 (4' - n-alkoxy benzoyloxy) benzoates, exhibits monotropic smectic phase from pentyloxy derivative which persists upto the hexadecyloxy derivative. Series (II), Cyclohexyl 4 (4'-n-alkoxy Cinnamoyloxy) benzoates, behaves like a normal nematogenic series.

EXPERIMENTAL

1. 4-n-alkoxy benzoic acids and 4-n-alkoxy benzoyl chlorides were synthesized as described by Dave and Vora[5].

2. 4-n-alkoxy cinnamic acids and 4-n-alkoxy cinnamoyl chlorides were synthesized by the known method of Gray and Jones[6].

3. Cyclohexyl 4-hydroxy benzoate : The mixture of absolute cyclohexanol (40 ml.), 4-hydroxy benzoic acid (10 gms.) and conc. sulfuric acid (2ml.) was refluxed on a sand bath for about 8 hours. After allowing it to cool, the mixutre was poured in cold water and then extracted with solvent ether. The ethereal solution was washed with saturated sodium bicarbonate solution followed by water and the ether was evaporated under reduced pressure. The ester was obtained as a thick viscous liquid. The yield is about 60 percent.

4. Cyclohexyl 4(4'-n-alkoxybenzoyloxy) benzoates (I) : 4-n-alkoxy benzoyl chloride (0.01 mol.) was esterified in cold with cyclohexyl 4-hydroxy benzoate (0.01 mol.) taken in pyridine (5 ml.). The mixture was heated on water bath for an hour and kept over night. It was acidified with cold 1:1 hydrochloric acid, precipitated (I) was filtered, washed with little cold 1:1 hydrochloric acid, followed by saturated solution of sodium bicarbonate and finally with water. Crystallization from ethanol gave very fine white needles. The yield is about 50 percent. Elemental analysis for dodecyl derivative; required C=75.58; H=8.66; Found C=75.18; H=8.19.

5. Cyclohexyl 4(4'-n-alkoxy cinnamoyloxy) benzoates (II), were synthesized in a similar manner using 4-n-alkoxy cinnamoyl chlorides.

6. 4(4'-n-alkoxy benzoyloxy) benzylidene cyclohexyl amines (III) were synthesized by condensing respective 4(4'-n-alkoxybenzoyloxy) benzaldehydes[7] with cyclohexylamine in absolute ethanol, using molecular sieve $3A^0$. Crystallization from absolute ethanol gave fine white needles. The yield is about 80 percent.

7. Determination of transition temperatures was carried out by using Leitz Laborlux 12 POL microscope equipped with a hot stage. The melting points and transition temperatures are given in Table 1 and 2.

8. Characterization of Smectic Phases.

The smectic phases exhibited by series (I) and (II) are focal conic in nature. Few photographs of the smectic phases are given in Fig. 1 and 2. The smectic phases appear like Smectic "A" Type. The smectic phases of homologues of Series (I) and (II) are intermiscible with each other and hence they are of same type.

The IR analysis of the representative two compounds is given in Table 3.

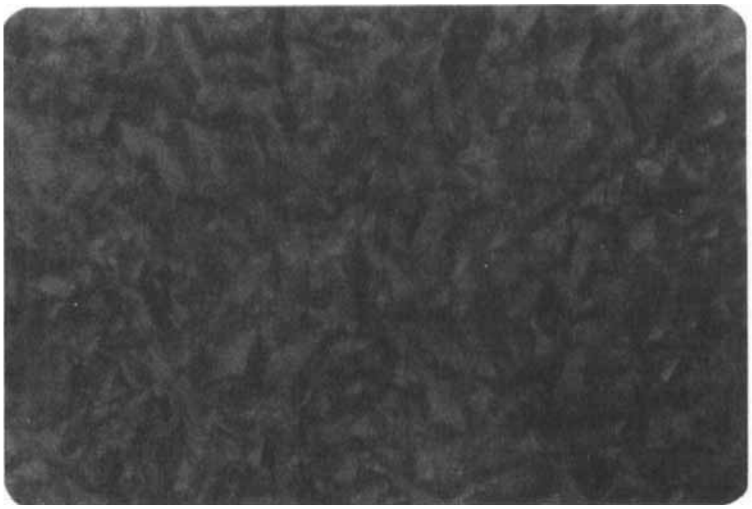


Fig. 1

Smectic-A phase, exhibited by dodecyl derivative of Series I at 59°C on cooling. (See Color Plate XXV).

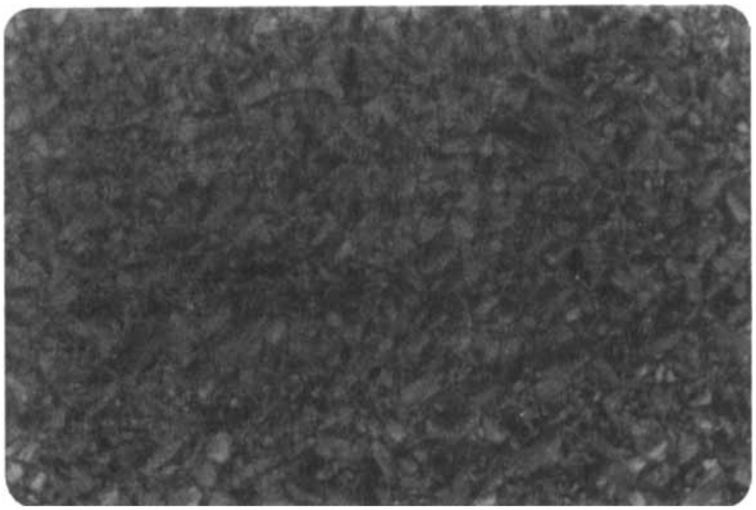


Fig. 2

Smectic-A phase, exhibited by dodecyl derivative of Series II at 64°C on cooling. (See Color Plate XXVI).

Both the photographs are taken under Cross Polarizers.

Magnification 20 x 10

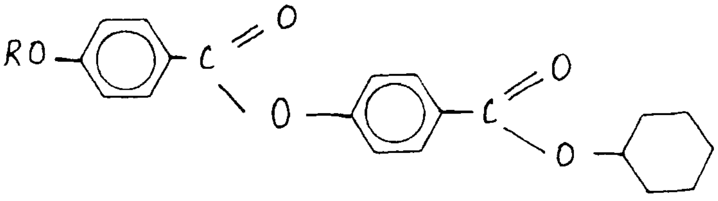
RESULTS AND DISCUSSION

Ten homologues of (I) were synthesized. From pentyl derivatives onwards series exhibits monotropic smectic mesophases. It was observed in some series[8-10] that replacement of a benzene ring with cyclohexane ring enhances the occurance of smectic phases. In some series where 1,4-phenylene system is replaced by trans 1,4-disubstituted cyclohexane system, melting points and transition temperatures are lower[9,11] while in some cases the change increases the melting points and transition temperatures[10]. Gray[10] has suggested that the relative nematic thermal stabilities of cyclohexane systems could not be explained by assuming an increase in molecular flexibility as 1,4-phenylene system is replaced by trans 1,4-disubstituted cyclohexane system. It depends on whether the cyclohexane ring is situated centrally or terminally and if situated terminally, on the extent of the rigid core to which it is attached. The plot of transition temperatures versus number of carbon atoms are given in Fig. 3.

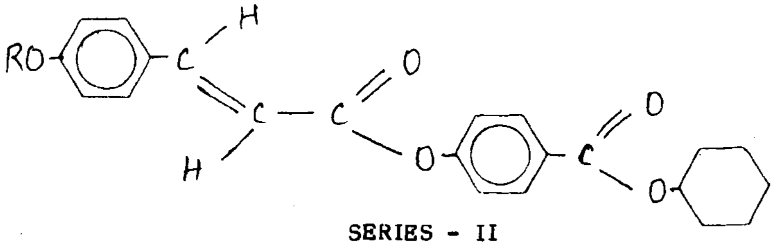
The homologous series (II) with cinnamoyl central linkage is more mesogenic in nature and behaves like a normal nematogenic series. In this series also smectic mesophase is more pronounced than nematic phase. The increased mesophase thermal stabilities of series (II) as compared to series (I) may be attributed to longer central linkage (-CH=CH=COO). The plot of transition temperatures versus number of carbon atoms is given in Fig. 4.

The present series (I) and (II) are compared with other structurally compounds to evaluate the effect of terminally situated cyclohexyl ring system.

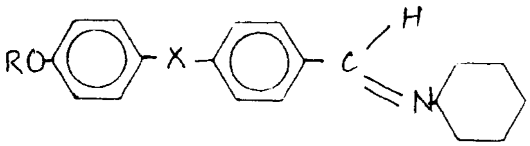
The present homologous series (I) and (II) are compared with structurally related series.



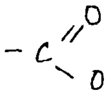
SERIES - I



SERIES - II



SERIES - III   R = C_4 to C_{16} , X =



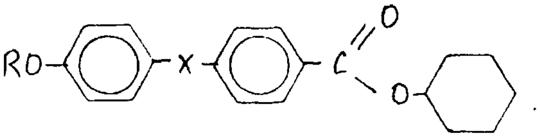
$-C(=O)O-$

SERIES - IV   R = C_7 and C_{10} , X = $-CH=CH-COO-$

comparision of Series (I) and (II) with Series (III) and (IV) respectively gives insight to the role played by the central linkage. The structural difference between the two series is one of the central linkages. The compounds of Series (III) and (IV) are non mesogenic (Table - 2). The binary mixture of the two homologes of Series (III) also did not exhibit any mesomorphism.

In conclusion it may be said that terminally situated cyclohexyl ring system favours smectic mesophase and lowers down the transition temperatures.

TABLE - 1



R = C_1 to C_{16} n-alkyl groups.

	R = N-alkyl Gr.	Transition Temperatures °C Smectic	Nematic	Isotropic
Series I				
X = -COO	Methyl	-	-	117.5
	Butyl	-	-	109.0
	Pentyl	(66.0)+*	-	98.0
	Hexyl	(61.0)	-	85.0
	Heptyl	(62.0)	-	88.0
	Octyl	(65.0)++	-	81.0
	Decyl	(69.0)	-	70.0
	Dodecyl	(73.0)	-	81.0
	Tetradecyl	(73.0)	-	85.0
	Hexadecyl	(72.0)	-	89.0
Series II				
X = -CH=CH-COO	Methyl	-	(78.0)*	101.0
	Propyl	-	-	123.0
	Butyl	(103.0)	(104.6)	130.0
	Pentyl	(98.0)	(100.0)	126.0
	Hexyl	(75.0)	100.0	102.0
	Heptyl	87.0	98.0	99.0
	Octyl	82.0	-	103.0
	Decyl	74.0	-	104.0
	Dodecyl	71.0	-	100.0

* Values in the parentheses indicate monotropy.

\+ Monotropic phase obtained on quenching, immediately followed by crystallization.

++ Monotropic phase obtained by quenching.

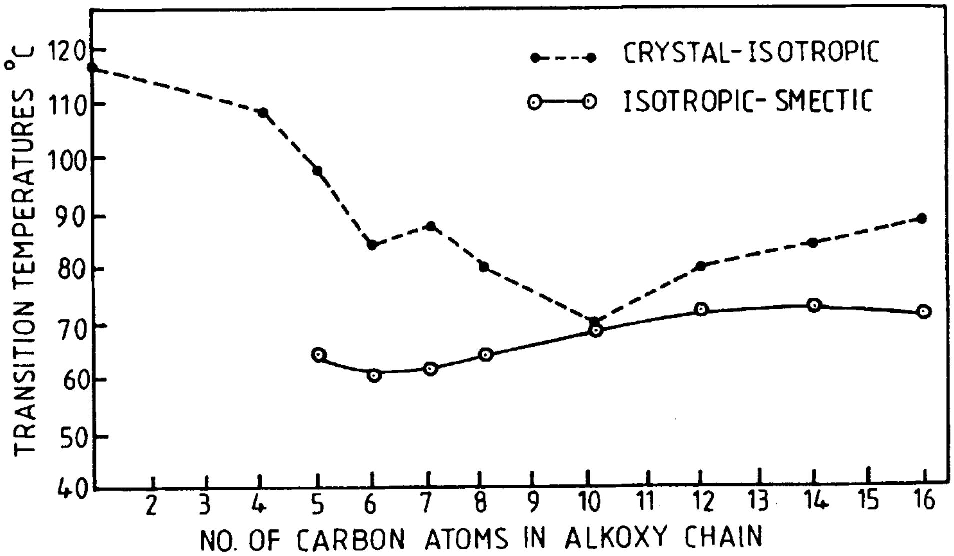

CRYSTAL-ISOTROPIC
ISOTROPIC-SMECTIC
TRANSITION TEMPERATURES °C
120
110
100
90
80
70
60
50
40
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
NO. OF CARBON ATOMS IN ALKOXY CHAIN

Fig. 3

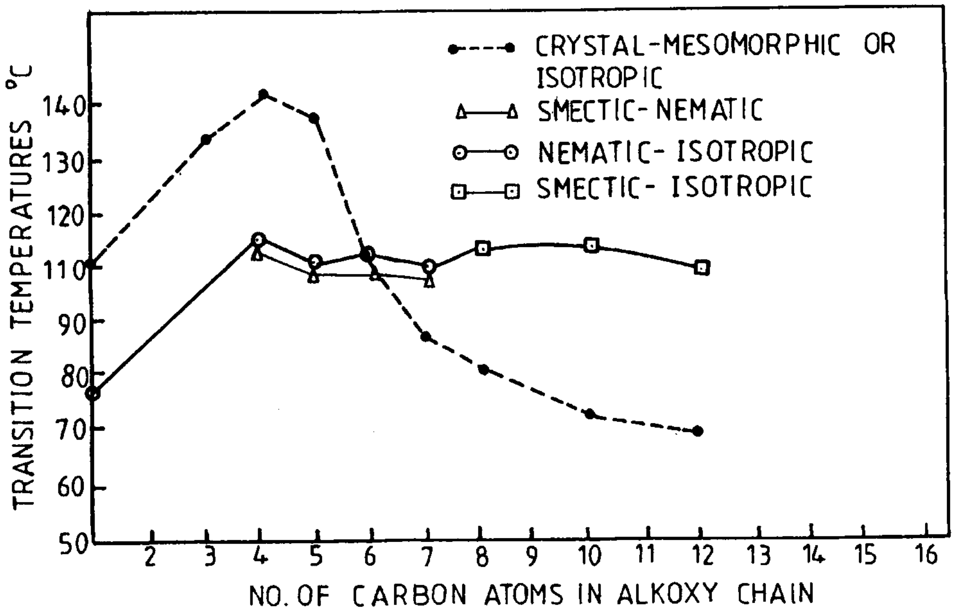
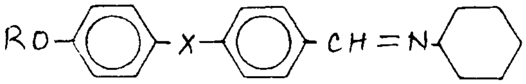

CRYSTAL-MESOMORPHIC OR ISOTROPIC
SMECTIC-NEMATIC
NEMATIC-ISOTROPIC
SMECTIC-ISOTROPIC
TRANSITION TEMPERATURES °C
140
130
120
110
90
80
70
60
50
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
NO. OF CARBON ATOMS IN ALKOXY CHAIN

Fig. 4

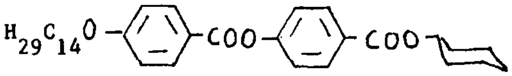
TABLE - 2



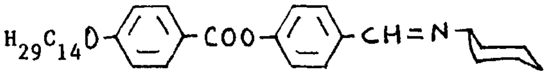
X = -COO	R = n-alkyl Gr.	Melting points °C
	Butyl	140.0
	Hexyl	140.0
	Heptyl	142.0
	Octyl	136.0
	Decyl	133.0
	Tetradecyl	127.0
	Hexadecyl	115.0
X = -CH=CH-COO	Heptyl	139.0
	Decyl	130.0

TABLE - 3

IR ANALYSIS

(I) 

Cm^{-1} 2900, 2850, 1740, 1710, 1600, 1510, 1260, 1200, 1160, 1110, 1060, 1010, 760.

(II) 

Cm^{-1} 3400, 2900, 2850, 1710, 1620, 1610, 1540, 1510, 1470, 1330, 1250, 1180, 1110, 1080, 1040, 890, 770, 720.

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