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New Mesogenic Homologous Series of Schiff Base Cinnamates Comprising Naphthalene Moiety

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NEW MESOGENIC HOMOLOGOUS SERIES OF SCHIFF BASE CINNAMATES COMPRISING NAPHTHALENE MOIETY

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New mesogenic homologous series of Schiff base cinnamates comprising a naphthalene moiety were prepared by condensing different $4(4^{\circ}-n-alkoxy cinnamoyloxy)$ benzaldehydes with 2-amino naphthalene. All the synthesized compounds were characterized by combination of elemental analysis and spectroscopic techniques. All the homologues synthesized exhibit mesomorphism. The mesomorphic properties of the present series are compared with other structurally related series.

Keywords: Schiff's base cinnamates; naphthalene moiety; mesomorphism

INTRODUCTION

The mesomorphic behavior of an organic compound is sensitive to its molecular architecture; a slight change in the molecular geometry brings about considerable change in its mesomorphic properties. The detailed study of many mesogenic homologous series has helped to evolve some general rules for the effect of chemical constitution in the nematogenic and smectogenic compounds [1]. Most of these studies have been on Schiff bases or esters containing benzene or biphenyl nuclei; comparatively few studies have been done on the influence of naphthalene nucleus on mesomorphism. Gray [1] has reported that 6-n-alkoxy-2-naphthanoic acids

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are mesomorphic whereas 1,4- and 1,5-alkoxy naphthoic acids core nonmesomorphic. Dave and coworkers [2, 4] have synthesized a number of 4-n-alkoxy-1-naphthylidene Schiff bases and cholesteryl naphthoates and studied their mesomorphism. Interest in naphthalene liquid crystal (LC) cores has revived in the last decade, as indicated by a significant number of research papers [5–13]. Previously we have reported few mesogenic homologous series of Schiff's base ester [14, 15] and azo-esters [16, 17] containing naphthalene moiety. The ethylene linking group is very useful structural unit connecting one part of a rigid core with another in calamitic mesogene molecules. This fully conjugative group enhances the longitudinal polarizability and extends the molecular length maintaining linearity of the molecule. The present investigation was undertaken with a view to study the effect of an ethylene linking group (cinnamoyl linkage) and naphthalene moiety on the mesomorphic properties of such molecules.

EXPERIMENTAL

Malonic acid, n-alkyl halide, K_2CO_3 , p-hydroxy benzaldehyde, and 2-amino naphthalene were used as received. Solvents were dried prior to use. Microanalyses of compounds were performed on Coleman Carbon-Hydrogen analyzer. Infrared (IR) spectra were determined via KBr pellets using Shimadzu IR-408 spectrophotometer. ¹H NMR spectra were obtained with a Perkin-Elmer-32 spectrometer, using tetra methyl silane (TMS) as an internal reference standard. The chemical shifts are quoted as δ (parts per million) downfield from the reference. CDCl₃ was used as a solvent. Ultraviolet (UV) spectra were recorded on a Hitachi U 2000 spectro photometer. Liquid crystalline properties were investigated on a Leitz Laborlux 12 POL microscope provided with heating stage. The synthetic route of series I is illustrated in Scheme 1.

Synthesis of Series I

First 4-n-Alkoxy benzaldehydes (A) and 4-n-alkoxy cinnamic acids (B) were prepared by the method of Gray and Jones [18], and 4-n-alkoxy cinnamoylchlorides were prepared by following the method described in the literature [19]. Also, 4-(4'-n-alkoxy cinnamoyloxy) benzaldehydes (C) were synthesized by the method of Lohar and Patel [20].

The 12 Schiff's bases of series I were synthesized by condensing equimolar quantities of appropriate 4-(4'-n-alkoxy cinnamoyloxy) benzaldehydes with 2-aminonaphthalene in boiling ethanol. The Schiff's bases of the series I were crystallized from ethanol till the constants' transition temperatures were obtained. The elemental analysis of all the compounds



SCHEME 1 Synthetic route to series I.

was found to be satisfactory, and all are listed in Table I. The UV, IR, and ¹H NMR spectral data of all the compounds were found to be consistent with the proposed structure. As a representative case we provide spectral data for the compound **6**: UV(CHCl₃) λ_{max} : 271 and 292 nm; IR ν_{max} /cm⁻¹: 3055, 2930, 1724(-COO-), 1633, 1602(-CH=N), 1510, 1423, 1142, 1174, 814; ¹H NMR(CDCl₃): δ 0.95(t, 3H, -CH₃), 1.35–1.8(m, 8H, 4 x -CH₂-), 3.95(t, 2H, Ar-O-CH₂-), 6.5(d, J = 18.6 Hz, 2H, -CH=CH-), 6.9(d, J = 9 Hz, 2H, ArH), 7.2–7.4 (m, 2H, ArH), 7.4–7.6(m, 7H of naphthalene ring system), 7.7–7.9(m, 2H, ArH), 8.0(d, J = 9 Hz, 2H, ArH), 8.6(s, 1H, -CH=N).

RESULTS AND DISCUSSION

The transition temperatures of the compounds of series I are recorded in Table II.

All the twelve members exhibit enantiotropic nematic phase. The SmC phase commences from the n-octyloxy derivative as enantiotropic meso-phase.

	$R = -C_n H_{2n+1} n -$	Molecular formula	% Required (Found)			
Sr. No			С	Н	Ν	
1	1	C ₂₇ H ₂₁ O ₂ N	82.86 (82.66)	5.37 (5.45)	3.58 (3.50)	
2	2	C ₂₈ H ₂₃ O ₂ N	82.96 (82.94)	5.67 (5.62)	3.46 (3.62)	
3	3	C ₂₉ H ₂₅ O ₂ N	83.05 (82.89)	5.97 (5.80)	3.34 (3.32)	
4	4	C ₃₀ H ₂₇ O ₂ N	83.52 (83.54)	6.26 (6.15)	3.25 (3.28)	
5	5	C ₃₁ H ₂₇ O ₂ N	83.97 (83.88)	6.55 (6.64)	3.16 (3.28)	
6	6	C ₃₂ H ₂₉ O ₂ N	84.03 (83.94)	6.76 (6.83)	3.06(3.15)	
7	7	C ₃₃ H ₃₁ O ₂ N	84.43 (84.54)	7.04 (7.15)	2.99 (3.06)	
8	8	C ₃₄ H ₃₃ O ₂ N	84.95 (84.85)	7.25 (7.38)	2.90 (2.83)	
9	10	C ₃₆ H ₃₇ O ₂ N	85.32 (85.38)	7.63 (7.78)	2.74 (2.73)	
10	12	C ₃₈ H ₄₁ O ₂ N	86.08 (86.08)	7.98 (7.86)	2.60(2.62)	
11	14	C ₄₀ H ₄₅ O ₂ N	86.77 (86.87)	8.29 (8.52)	2.47 (2.58)	
12	16	$C_{42}H_{49}O_2N$	87.39 (87.48)	8.57 (8.55)	2.35 (2.31)	

TABLE I Elemental Analysis for Series I Compounds

Figure 1 shows the plot of transition temperatures against the number of carbon atoms in the alkoxy chain, from which it can be noticed that crystal mesophase transition temperatures decrease with the increase in the length of terminal alkoxy tail. The nematic-isotropic transition temperatures also decrease with increase in the number of carbon atoms in the alkoxy chain, whereas it exhibits a tendency for rising smectic C-nematic transition temperature in ascending series, which levels off slightly in the higher homologues.

Compound	n	Cr		SmC		Ν		Ι
1	1	•	131	_	_	•	265	•
2	2	•	126		_	•	261	•
3	3	•	122		_	•	254	•
4	4	•	117		_	•	249	•
5	5	•	114		_	•	247	•
6	6	•	112		_	•	245	•
7	7	•	110		_	•	236	•
8	8	•	98	•	146	•	230	•
9	10	•	93	•	161	•	224	•
10	12	•	89	•	155	•	215	•
11	14	•	86	•	141	•	197	•
12	16	•	85	•	138	•	193	•

TABLE II Transition Temperatures (°C) for Series I Compounds

Cr, crystal; SmC, smectic C phase; N, nematic phase; I, isotropic liquid state; n, number of carbon atoms in the alkoxy chain.



FIGURE 1 The phase behavior of series I.

Table III shows the average mesophase range of the present series I and structurally related series A [14], B [14], and C [21] reported in the literature. The average smectic mesophase range of series I is higher by 66.0° C compared to the respective mesophase ranges of series A. This is understandable, as the molecules of series I are longer and more polarizable compared to the molecules of series A due to the presence of additional cinnamoyloxy (-CH=CH-COO-) central linkage and benzene moiety.

Reference to Table III indicates that the average width of smectic and nematic mesophase of series I is higher by 25.6°C and 14.5°C, respectively compared to series B. The molecules of series I and series B differ only at the central linkages. The molecules of series I have cinnamoyloxy (-CH=CH-COO-) central linkage, while series B have ester (-COO-) central linkage. Gray [1] has explained that the addition of double bond in

Series	Smectic	Nematic	Commencement of smectic phase
I(C ₈ -C ₁₂)	67.1	69.0	C ₈
$A(C_{12})$	01.0	03.0	Only for C_{12}
$B(C_{10}, C_{12})$	41.5	54.5	C_7
C(C ₈ -C ₁₂)	69.8	17.5	C_6

TABLE III Average Mesophase Range in °C



Comparative Molecular Structure of Series I, A, B, and C.

the system increases the length and polarizability of the rodlike molecules. Therefore the greater mesophase thermal stability of the present series I must be explained in terms of the greater molecular length and polarizability of the molecule resulting from additional -CH=CH- units in the central linkage.

The naphthalene moiety at the terminus of the present series I has a pronounced effect on the mesophase transition temperatures when compared with the parent compound of series C having benzene moiety at the terminus. A comparison of mesophase thermal stabilities of series I and series C reveals that there is an average decrease of about 1.7° C in smectic mesophase range and average increase of about 51.5° C in nematic mesophase range of series I. Compared with molecules of series B, the molecules of series I are a little longer and more polarizable, but have increase breadth due to the naphthalene moiety. The reduction of average smectic mesophase range has been attributed to a thickening effect [1]

caused by the presence of naphthalene moiety. However, this thickening effect is not so prominent due to 2-substitution in the naphthalene nucleus of the molecules, making them linear. Therefore, nematic thermal stability of series I is probably higher. Thus it seems that the smectic mesophase is more affected by thicking effect than the nematic mesophase. This is in accordance with Gray's [1] work on various mesomorphic homologous series of compounds, which show a similar behavior.

CONCLUSION

In this article we have presented the synthesis and characterization of new mesogenic homologous series of Schiff's base cinnamates comprising naphthalene moiety. All the compounds of the series exhibit enantiotropic mesomorphism. The mesophase range of present series I is higher than those of structurally related compounds that has been attributed to the high polarizability of the molecule. However, the smectic mesophase phase is more adversely affected than the nematic mesophase by the thickening effect due to presence of naphthalene moiety.

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