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Ashish K. Prajapati [a]

[a] Applied Chemistry Department, Faculty of Technology and Engineering, P.B. No. 51, Kalabhavan, M.S. University of Baroda, Vadodara, 390 001, INDIA

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Synthesis of a New Mesogenic Homologous Series Containing Naphthalene Moiety

ASHISH K. PRAJAPATI*

Applied Chemistry Department, Faculty of Technology and Engineering, P.B. No. 51, Kalabhavan, M.S. University of Baroda, Vadodara – 390 001, INDIA

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A new series of mesogenic Schiff's base esters, 4-(4′-n-Alkoxybenzoyloxy) 3-methoxy benzylidene 2″-aminonaphthalenes has been synthesized. The synthesized compounds were characterised by elemental analysis and standard spectroscopic methods.

All the homologues synthesized exhibit mesomorphism. The mesomorphic properties of the present series are compared with other structurally related series.

Chiral nematic mesophase (N^*) is induced in the system by doping a derivative of naturally occurring chiral compound.

Keywords: Mesogenic naphthyl derivatives; Non-mesogenic chiral dopant; Induced chiral nematic mesophase (N^*)

INTRODUCTION

Dave et al.[1,2] and Wiegand[3] have reported number of Schiff's base compounds containing a naphthalene nucleus. The effect of chemical constitution on 1,4-, 1,5- and 2,6- substituted naphthalene derivatives has also been studied[4].

It seems, the interest in naphthalene nucleus is again revived in the last few years and a number of research papers published have mesogens with naphthalene nuclei[5–10]. Polymeric liquid crystals[11] and ferroelectric liquid crystals[12] have also been studied extensively which has shown very attractive properties for various applications.

In continuation of our work on 2-aminonaphthalene[13,14] a new series of Schiff's base esters containing naphthalene moiety has been synthesized.

* Corresponding Author.

Recently a number of researchers have tried to induce chirality in the achiral mesogens by doping it with naturally occuring chiral compounds or their derivatives[15–17]. The use of optically active dopant may induce ferroelectricity/ chiral nematic phase. With this view, it was planned to dope a derivative of optically active natural menthol.

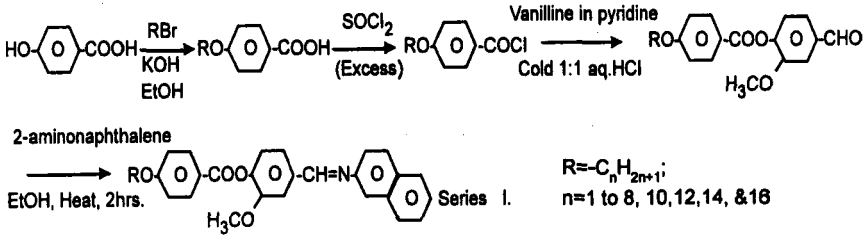
EXPERIMENTAL

Characterization

Microanalyses of the compounds were performed on a Coleman carbon- hydrogen analyser, and IR spectra were recorded on Shimadzu IR-408. NMR spectra were recorded on a Perkin-Elmer R-32 spectrometer. The calorimetric studies were carried out on a Mettler TA-4000 DSC apparatus. Liquid crystalline properties were investigated on a Leitz Labourlux 12POL microscope provided with a heating stage.

Synthesis

The synethetic route to the present series is illustrated in Scheme 1.



SCHEME 1 Synthetic route to series I

4-n-Alkoxybenzoic acids and 4-n-alkoxybenzoyl chlorides were synthesized by the modified method of Dave and Vora[18]. 4-(4′-n-Alkoxybenzoyloxy)-3-methoxy benzaldehydes were prepared by the reported method[19]. All the twelve Schiff's bases s of the present series I were synthesized by condensing equimolar quantities of 4-(4′-n-alkoxybenzoyloxy)-3-methoxy benzaldehydes with 2-aminonaphthalene. All the Schiff's bases of present series were crystallized from ethanol untill constant transition temperatures were obtained. The transition temperatures are recorded in table I.

TABLE I Transition temperatures (°C) of the present series I

R=-C_nH_{2n+1}	*Transition temperatures °C*	
n =	*N*	*I*
1	(145.0)[a]	186.0
2	(156.0)	172.0
3	(136.0)	160.0
4	114.0	143.0
5	103.0	125.0
6	82.0	124.0
7	98.0	118.0
8	87.0	113.0
10	96.0	110.0
12	92.0	108.0
14	86.0	107.0
16	89.0	103.0

a. Values in parentheses indicate monotropic transition.

The elemental analyses of all the compounds are recorded in Table-II.

TABLE II Elemental data of series I

n = (TABLE I)	*Formula*	*Required*			*Found*		
		C	*H*	*N*	*C*	*H*	*N*
1	$C_{26}H_{21}NO_4$	75.91	5.11	3.41	75.78	5.40	3.23
2	$C_{27}H_{23}NO_4$	76.23	5.41	3.29	76.12	5.34	3.36
3	$C_{28}H_{25}NO_4$	76.54	5.69	3.19	76.37	5.58	3.14
4	$C_{29}H_{27}NO_4$	76.82	5.96	3.09	76.68	5.80	2.94
5	$C_{30}H_{29}NO_4$	77.09	6.21	3.00	76.89	6.12	3.27
6	$C_{31}H_{31}NO_4$	77.34	6.45	2.91	77.56	6.53	2.98
7	$C_{32}H_{33}NO_4$	77.57	6.67	2.83	77.44	6.62	2.65
8	$C_{33}H_{35}NO_4$	77.80	6.88	2.75	77.78	6.84	2.92
10	$C_{35}H_{39}NO_4$	78.21	7.26	2.61	78.44	7.12	2.84
12	$C_{37}H_{43}NO_4$	78.58	7.61	2.48	78.41	7.55	2.60
14	$C_{39}H_{47}NO_4$	78.92	7.93	2.36	78.84	8.08	2.28
16	$C_{41}H_{51}NO_4$	79.23	8.21	2.25	79.34	8.44	2.14

Spectral data of n-butyloxy derivative are given below.

IR (KBr) spectra

2900, 1720 (S, -COO-), 1610 (S, -CH=N-), 1510, 1475, 1430, 1270, 1200, 1165, 1070, 1010, 840, 755 cm^{-1}.

NMR spectra

(Solvent $CDCl_3$, standard TMS, 90MHz) δ 0.90 (J=6.8 Hz, 3H, $-CH_3$), 1.1- 1.5 (m, 4H of 2 × $-CH_2-$), 3.8–4.2 (m, 5H, 2H of $ArOCH_2$ at C-4′ and 3H of $ArOCH_3$at C-3), 6.8 (d, J=9Hz, 2H at C-3′ and C-5′), 7.1–7.3 (m, 3H at C-5, C-2 and C-6), 7.7–8.3 (m, 9H, 7H of naphthalene ring system and 2H at C-2′ and C6′), 8.6 (S, 1H for -CH=N-).

DSC

Data are given in Table-III.

TABLE III DSC data of series I

Sr. No.	*n= (TABLE I)*	*Heating Rate /°C min^{-1}*	*Transition State*	*$\Delta H/Jg^{-1}$*	*$\Delta S/Jg^{-1}k^{-1}$*
1	4	5	Cr-N	21.363	0.0547
			N-I	1.013	0.0020
2	8	5	Cr-N	56.965	0.1269
			N-I	1.334	0.0028

Synthesis of Chiral Dopant

The chiral dopant (1R, 2S, 5R)-(-) menthyl 4-nitrobenzoate was synthesized by condensing 4-nitrobenzoyl chloride with (1R, 2S, 5R)-(-)-menthol using pyridine as solvent[17]

Binary systems

Binary systems of chiral dopant with n-butyloxy, n-hexyloxy and n-octyloxy derivatives were prepared by a standard method[20]. The transition temperatures are recorded in table-IV.

TABLE IV transition temperatures (°C) for binary systems I-III

System	*Mole% of Chiral Dopant A*	*Transition Temperatures (°C)*	
		$N^*(Ch)$	*I*
1a	6.90	112.0	27.0
	14.14	110.0	18.0
	20.74	(87.0)[a]	111.0
	27 05	--	103.0
1b	7.62	82.0	119.0
	14.88	81.0	110.0
	21.74	(78.0)	103.0

System	Mole% of Chiral Dopant A	Transition Temperatures (°C)	
		$N^*(Ch)$	I
1c	28.26	--	93.0
	8.03	87.0	108.0
	15.61	83.0	101.0
	22.73	(73.0)	98.0
	29.42	--	89.0

a. Values in parentheses indicate a monotropic transition.

RESULTS AND DISCUSSION

Series 1

4-(4′-n-Alkoxybenzoyloxy)-3-methoxy benzylidene-2″-aminonaphthalenes. Twelve members of the series were synthesized. All the members are purely nematogenic in nature. The lower members, i.e. methoxy to n-propyloxy derivatives exhibit monotropic nematic, while n-butyloxy to n-hexadecyloxy derivatives exhibit enantiotropic nematic mesophase. Smectic mesophase is not observed up to the highest homologue of the series.

The plot of transition temperatures against the number of carbon atoms in the alkoxy chain (Figure 1), shows a steady fall in the nematic-isotropic transition temperatures and exhibits a marked odd-even effect up to n-pentyloxy derivative.

Table V summarizes the average thermal stabilities and comparative geometry of the A and B, the moleoules of present series I and the structurally related series A[14], B[13], C[21] and D[22]. The average nematic thermal stabilities of the present series I are lower compared to series A and B. Compared to molecules of series A and B, the molecules of present series I have increased breadth due to lateral methoxy group on the central benzene ring. Gray[4] has explained that the increase in the breadth of the molecules reduces both nematic and smectic thermal stabilities hence the average nemetic thermal stabilities are lower in the present series I. It seems that the lateral methoxy group not only increases the breadth of the molecules of series I but also increases the non-coplanar arrangement of the system due to steric interaction. Both these factors would be responsible to eliminate the smectogenic tendencies from the present series. This is also reflected in series D which is purely nematogenic due to lateral methyl group on the central benzene nucleus.

In present series I, due to 2-substitution in the naphthalene nucleus the molecules become little longer and more polarizable which should increase the average nematic thermal stabilities of series I but series I also possesses the lateral methoxy group which increases the breadth of the molecules and hence should

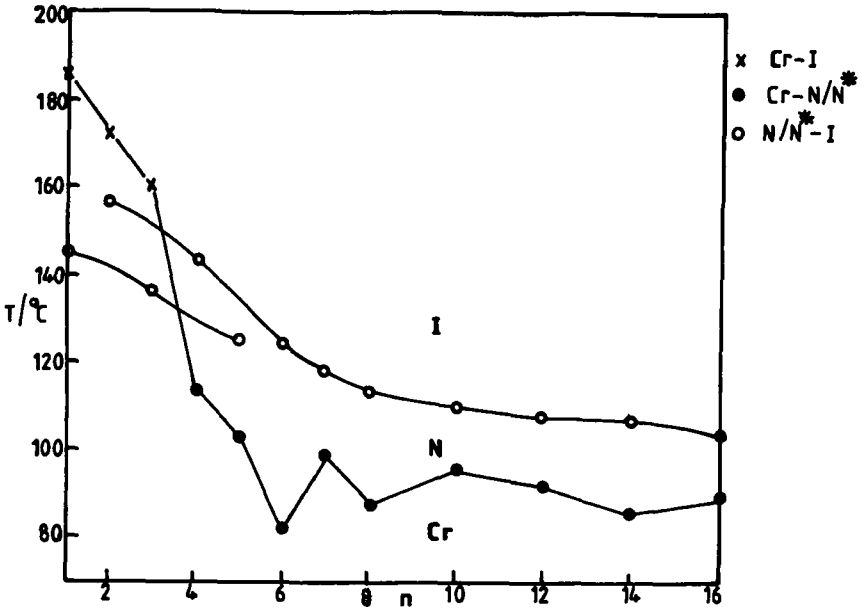


FIGURE 1 The phase behaviour of the present series-I

decrease the average nematic thermal stabilities. Reference to table V indicates that the effect of increase in breadth is dominated in series I as its average nematic thermal stabilities are lower compared to series C.

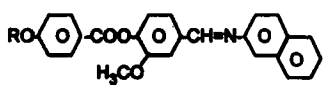
Table V shows that the average nematic thermal stabilities of series I are lower than those of series D. This is understandable as the molecules of series I possess little bulkier lateral group compared to series D.

Binary Systems

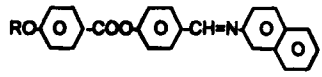
The following three binary systems are studied.
(i) Binary system 1a: (Figure 2a)
Component A: (1R, 2S, 5R)-(-)-Menthyl 4-nitrobenzoate (MNB)
Component B: n-Butyloxy derivative of present series I
(ii) Binary system 1b: (Figure 2b)
Component A: MNB
Component B: n-Hexyloxy derivative of present series I
(iii) Binary system 1C: (Figure 2c)
Component A: MNB
Component B: n-Octyloxy derivative of present series I

TABLE V Average thermal stabilities

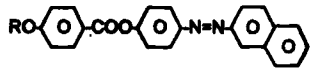
Series	*I*	*A*	*B*	*C*	*D*
N-I (C_1-C_{14})	125.91	231.73	229.18	154.80	177.27
Commencement of Smectic Phase	--	C_7	C_{10}	C_7	--



Series I.



Series A.



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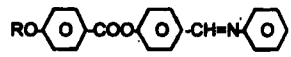
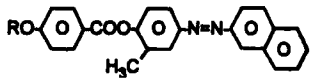


Series C.



Series D.

Comparative geometry of series I,A,B,C and D.

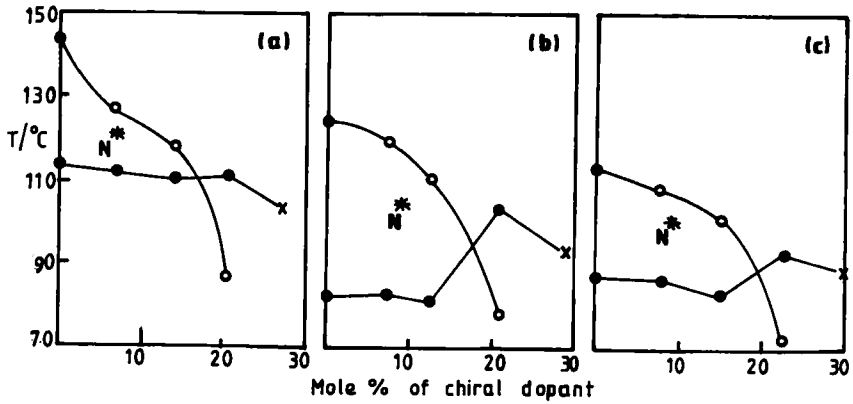


FIGURE 2 The phase behaviour of the system I – III

The phase diagram (Figure 2a, 2b, 2c) is obtained by plotting mole percent composition of chiral dopant (Component A) versus transition temperatures. In

all the three systems enantiotropic cholesteric mesophase (N^*) is induced with lowering in transition temperatures which becomes monotropic and is eliminated from the system when mole percent composition of component A reaches to 30 mole%. All induced cholesteric phases are shown by the observance of oily streaks and brilliant colours. These colours were also seen in the visible region.

The study provides a means to induce cholesteric (N^*) phase in the present series I by doping it with the non-mesogenic derivative of naturally occurring chiral menthol.

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References

[1] J.S. Dave, G. Kurian, A.P. Prajapati and R. A. Vora, *Mol. Cryst. Liq. Cryst.*, **14**, 307 (1971); *Curr. Sci.*, **41**, 415 (1972); *Indian J. Chem.*, **10**, 754 (1972).

[2] J.S. Dave and A.P. Prajapati, *Pramana*, Suppl. No. 1, 435 (1975); *Curr. Sci.* **45**, 95 (1976).

[3] C. Wiegand, *Z. Naturforsch. (b)*, **9**, 516 (1954).

[4] G.W. Gray, *Molecular Structure and Properties of Liquid Crystals*, (Academic press, London, 1962).

[5] M. Marcos, A. Omenat, J.L. Serrano and A. Ezcurra, *Adv. mater.*, **4**, 285 (1992).

[6] M. Hird, K.J. Toyne and G.W. Gray, *Liq. Cryst.*, **14**, 741 (1993).

[7] M. Hird, K.J. Toyne, G.W. Gray, S.E. Day and D.G. McDonnell, *Liq. Cryst.*, **15**, 123 (1993).

[8] Y. Gonzalez, M.B. Ros, J.L. Serrano and A. Perezjubind, *Liq, Cryst.*, **18**, 751 (1998).

[9] A. Suste, D. Moslavac and V. Sunjic, *Liq. Cryst*, **21**, 383 (1996.).

[10] B.K. Sadashiva and C.R. Gopalakrishnan, *Macromol. Rapid Commun.*, **19**, 97 (1998).

[11] G. Calundann, M. Jaffe, R.S. Jones and H. Yoon, *in Fibre Reinforcements for Composite Materials*, edited by A.R. Bunsell (Amsterdam, 1988) p. 211.

[12] J.W. Goodby, *Ferroelectric Liquid Crystals: Principles, Properties and Applications*, edited by J.W. Goodby, R. Blinc, N.A. Clark, S.T. Lagerwall, M.A. Osipov, S.A. Pinkin, T. Sakurai, K. Yoshino, B. Zeks (Gordon and Breach Science Publishers, Philadelphia, Reading, Paris, Montreux, Tokyo, Melbourne, 1991).

[13] R.A. Vora and A.K. Prajapati, *Proceeding of the V National Seminar on Liquid Crystals* (Patiala, India, 1996) p. 97.

[14] R.A. Vora and A.K. Prajapati, *Liq. Cryst.*, **25**, 567 (1998).

[15] J.C. Bhatt, S.S. Keast, M.E. Neubert and P.G. Petschek, *Liq. Cryst.*, **18**, 367 (1995).

[16] C.J. Booth, D.A. Dunmur, J.W. Goodby, J. Haley and K.J. Toyne., *Liq. Cryst.*, **20**, 387 (1996).

[17] A.K. Prajapati and N. Patel, *Presented at the 17th International Liquid Crystal Conference*(Strasbourg, France, 1998) Abst. No. P4–200.

[18] J.S. Dave and R.A. Vora, *Liquid Crystals and Ordered Fluids*, edited by J.F. Johnson and R.S. Porter (Plenum Press) p. 477 (1970).

[19] Renu Gupta, *Ph. D. Thesis*, M.S. University of Baroda, Vadodara India (1980).

[20] J.S. Dave and M.J.S. Dewar, *J. Chem, Soc.*, 4617 (1954).

[21] J.S. Dave, G. Kurian and N.R. Patel, *Indian J. Chem.*, **19A**, 1161 (1980).

[22] A.K. Prajapati, Communicated for Publication in Liquid Crystals.