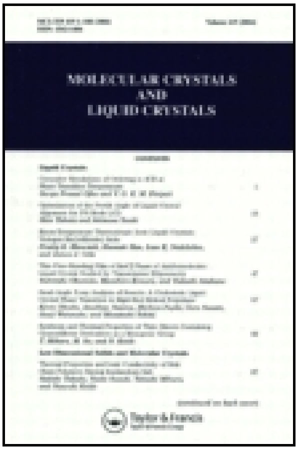

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Liquid Crystalline Homologous Series with Biphenyl Nucleus

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Liquid Crystalline Homologous Series with Biphenyl Nucleus

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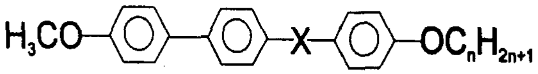
In order to investigate the influence of the less studied central linkage like amide and α – methylazine on mesomorphism, two homologous series having following structure have been synthesized.



Series	X	n
I	-CONH-	1to 8, 10, 12, 14 & 16.
II	$-\underset{CH_3}{C}=N-$	1 to 8 & 10.

The study has shown that amido central linkage endows the system with high smectogenic tendencies. The α – methyl linkage of schiff bases retards the commencement of smectic phase up to n-decyloxy derivative.

Keywords: Biphenyl derivatives

INTRODUCTION :

Advent of applications of mesogenic polyamides generated interest in the mesogenic model compounds with central amide linkage.

However, due to the belief that amide linkage may not be conducive to mesomorphism, hardly any mesogenic homologous series with amide linkage were known.

Vora and Gupta[1] were first to report mesogenic homologous series with amide linkage, subsequently Kalyvas and McIntyre[2] and Vora and Patel[3] reported a symmetrical homologous series with amide and ester linkages.

It was proposed to synthesize homologous series with amide central linkage and α - methyl azomethine central linkage containing series to evaluate the effect of these two central linkages on mesomorphism having biphenyl nucleus.

EXPERIMENTAL

Characterization :

Microanalysis of the compounds was performed on a Coleman carbon-hydrogen analyser and IR spectra were recorded on a Shimadzu IR - 408. NMR spectra was recorded on a Perkin - Elmer R -32 spectrometer. Liquid crystalline properties were investigated on a Leitz Laborlux 12 POL microscope provided with a heating stage. DSC was investigated on a Mettler TA - 4000 system.

Synthesis

The synthetic route to series I & II is illustrated in figure - 1.

4 - n Alkoxy anilines were prepared by the method reported by Criswell et al[4]. 4 - Methoxy - 4' - acetylbiphenyl and 4 - methoxybipheyl - 4'-carboxylic acid were prepared by the method reported by Gray et al [5]. 4 - methoxy - 4' - biphenyl carboxyl chloride was synthesized by using thionyl chloride as per the general procedure and was used without any further purification. 4(4' - Methoxy phenyl) 4''-n - alkoxy

- benzanilides (series - I) were synthesized by condensing 4 methoxy - 4' - biphenyl carboxyl chloride with appropriate 4 - n- alkoxy anilines using pyridine as solvent[6]. All the benzanilides were purified by recrystallization from DMF till constant transition temperatures were obtained.. The transition temperatures are recorded in Tabel - I.The elemental analysis for all the compounds was found to be satisfactory. IR (KBr):3200 Cm^{-1} (- NH Stretching vibrations for secondary amide linkage) and 1640 Cm^{-1} (- C = O stretching vibrations for secondary amide linkage). NMR for Ethyl derivative : 200 MHz, solvent $CDCl_3$ + DMSO - d_6, standard TMS) : δ 9.9 (S, 1H for - CONH -) 8.0-8.1 (m, 2H at C - 2" and C - 6") 7.5 - 7.7 (m, 6H at C-2, C-6, C-2', C-6', C-3' and C-5') 6.95-7.15 (m, 2H at C-3" and C-5") 6.85 (d, 2H at C-3 and C-5) 3.8-4.0 (m, 5H at - $PhOCH_3$ and 2H at - $PhOCH_2$-) 1.4 (t, 3H of - C - CH_3 at C-4").

4' - Methoxy α - methyl biphenylidene 4" - n- alkoxy anilines (series - II) were synthesized by condensing 4 - methoxy 4' acetylbiphenyl with appropriate 4 - n - alkoxyaniline in boiling DME according to the general procedure[7]. The compounds were recrystallized several times from DMF till constant transition temperatures were obtained. Higher members could not be synthesised by a general procedure hence the respective 4 - n- alkoy anilines and 4 - methoxy 4' - acetylbiphenyl were fused together at 175°c in oil bath for one hour. Subsequently they were recrystallised from DMF till constant transition temperatures were obtained. However it is difficult to get n - dodecyloxy onwards derivative fused with 4 - methoxy 4'- acetylbiphenyl to get pure Schiff's bases. Hence, higher members could not be synthesized. The transition temperatures are recorded in Table - I. The elemental analysis for all the compounds was found to be satisfactoy. IR(KBr) : 1605 Cm^{-1} [-$C(CH_3)$ = N - strecthing vibrations]. Calorimetric study of n- heptyl derivative of series - II was carried out by using Metller TA - 4000 DSC apparatus (Table - II).

TABLE - I Transition temperatures for series - I and II

n	Transition temperatures °C		
Series - I	SmA	N	I
1	---	254.0	288.0
2	242.0	247.0	277.0
3	237.0	248.0	270.0
4	227.0	255.0	268.0
5	219.0	---	264.0
6.	215.0	---	270.0
7.	210.0	---	271.0
8	208.0	---	272.0
10	204.0	---	270.0
12	200.0	---	263.0
14	200.0	---	258.0
16	189.0	---	248.0
Series - II	SmA	N	I
1	---	216.0	257.0
2	---	189.0	252.0
3	---	208.0	245.0
4	---	204.0	248.0
5	---	193.0	235.0
6	---	183.0	220.0
7	---	181.0	210.0
8	---	178.0	207.0
10	---	175.0	205.0

TABLE - II DSC data for n - heptyl derivative of series - II.

Substituent at R	Wt mg	Transition state	Peak Temperatures (Microscopic Reading)	Δ H J/G	ΔS J/g⁰k
n-Heptyl	12	K-N	175.9(181.0)	56.965	0.1269
		N-I	203.6(210.0)	1.334	0.0028

Results and Discussion

Series - I : 4(4'-Methoxybiphenyl) 4"-n-alkoxy benzanilides.

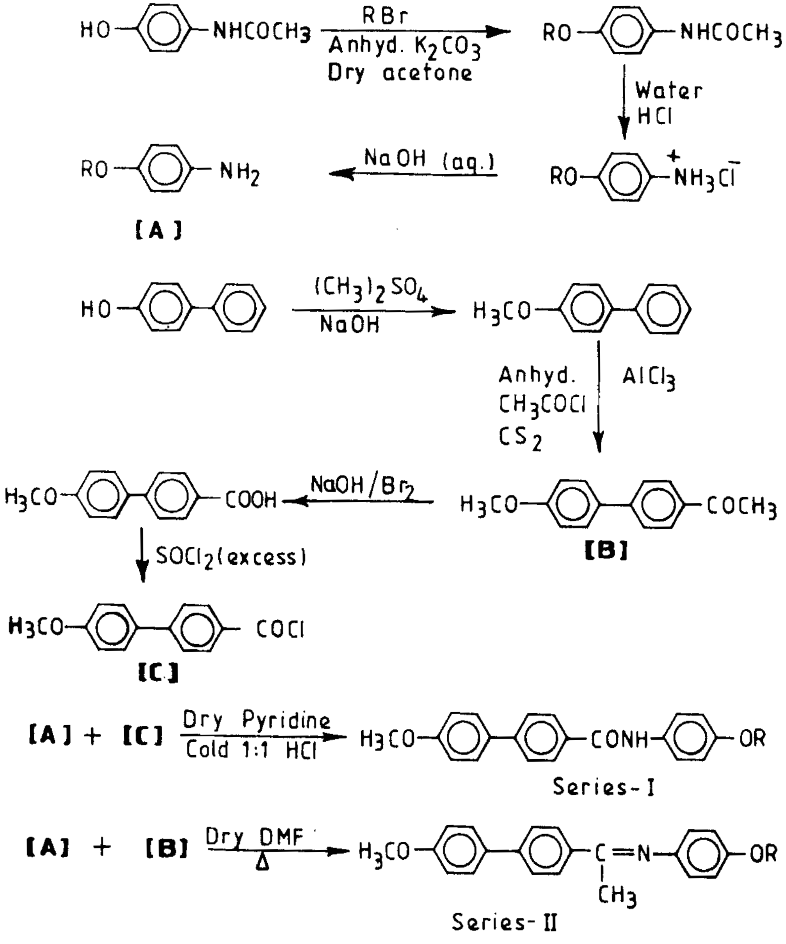
All the members exhibit enantiotropic mesomorphism. Methoxy derivative is purely nematogenic. Ethoxy to n - butyloxy derivatives exhibit enantiotropic smectic A as well as nematic mesophases. n - Pentyloxy to n - hexadecyloxy derivatives exhibit only enantiotropic smectic A mesophases.

Series - II : 4'-Methoxy - α - methylbiphenylidene-4"-n-alkoxy anilines.

All the members synthesized exhibit enantiotropic nematic mesophase.

Common features of series - I and series - II

All the members of series - I and series - II exhibit mesomorphism. The plot of transition temperatures against the number of carbon atoms in the alkoxy chain does not exhibit odd - even effect for nematic - isotropic or smectic - nematic transition temperatures though smectic phase is observed from the second member of the series - I (Fig. - 2) where as series - II (Fig. - 3) exhibits usual odd - even effect for the nematic - istropic transition temperatures.



R = $-C_nH_{2n+1}$, n = 1 to 8, 10, 12, 14 & 16 (Series-I)
n = 1 to 8 & 10 (Series-II)

FIGURE 1. Synthetic route to series I & II.

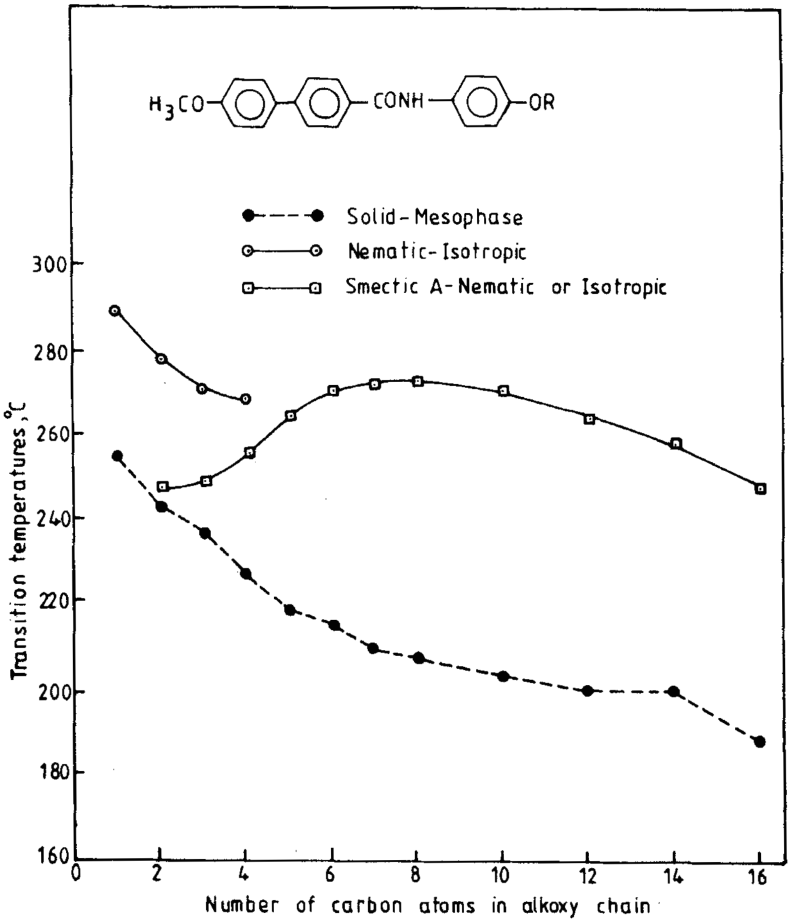


FIGURE 2. The phase behaviour for the series-I

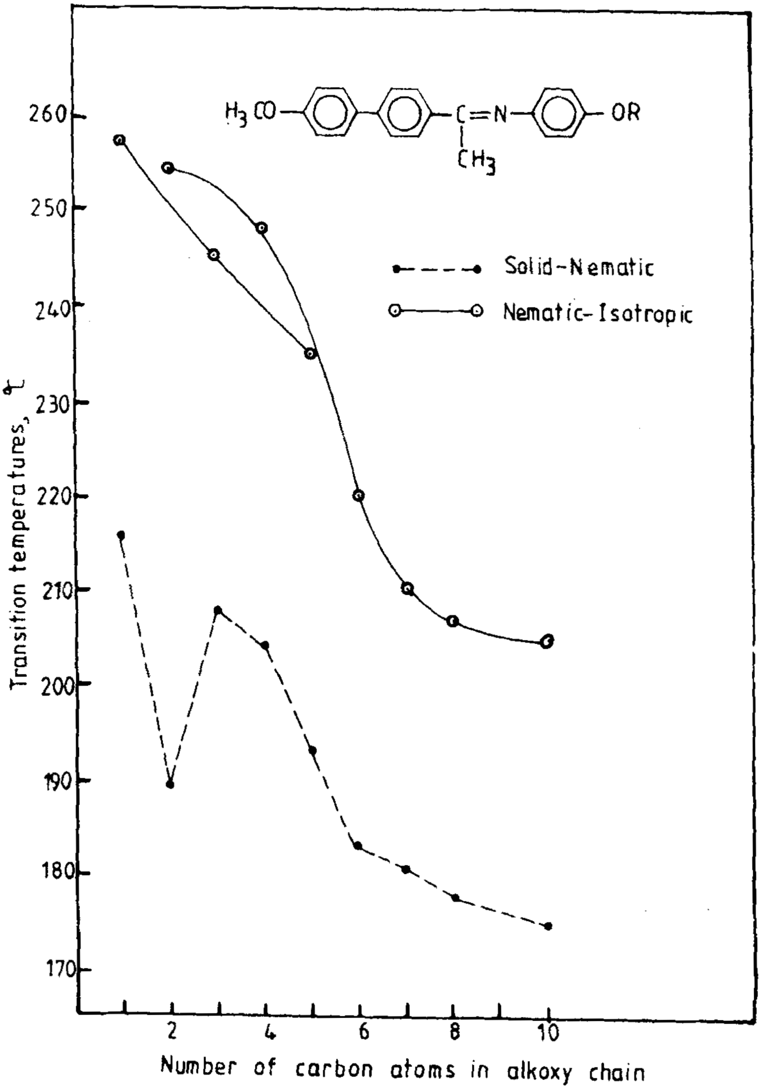


FIGURE 3. The phase behaviour for the series-II

Reference to Tabel - III shows that average nematic thermal stability of series - I is higher than that of series - II. In series - I there is an amide central linkage whereas in series - II there is an α - methyl azomethine central linkage. Comparison of mesogenic properties of these two series indicates that amide linkage endows stong smectogenic tendency to the series - I. Whereas α - methyl azomethine linkage destroys the smectic phase and imparts nematogenic tendency to the compounds of series - II.

TABLE - III Average thermal stabilites °C

Series	I	II
Nematic - Isotropic (C_1-C_4)	275.75	250.50
Smectic - Nematic or Isotropic (C_2-C_{16})	260.54	----
Commencement of smectic mesophase	C_2	----

The observation of Vora and Gupta [1] made it clear that compared to an ester and azomethine linkage, amide central linkage enhances smectic and nematic phases and enhancement is always more in the case of smectic mesophase. It seems that the α - methyl group not only increases the breadth of the molecules of series - II, but also increases the acoplanarity in the system due to steric interaction. Both these factors would be responsible to eliminate the smectogenic tendencies from the series - II.

Acknowledgments

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