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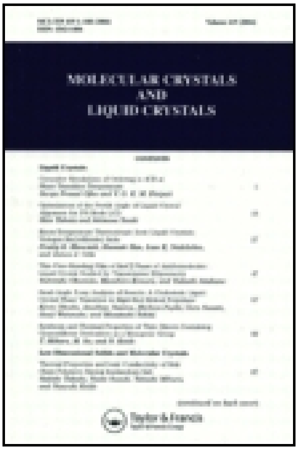

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Synthesis of New Mesogenic Homologous Series with Broken Alkoxy Chain

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Synthesis of New Mesogenic Homologous Series with Broken Alkoxy Chain

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A new mesogenic homologous series with broken alkoxy chain at the terminus of long polarizable molecules having following general formula have been synthesized.

$$RO\text{-}C_6H_4\text{-}COO\text{-}C_6H_4\text{-}CH{=}N\text{-}C_6H_4\text{-}COOCH_2CH_2OCH_2CH_3$$

Where, $R{=}\text{-}C_nH_{2n+1}$; n=1 to 8, 10, 12, 14 and 16.

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

The thermal stabilities and the commencement of smectic phase of the present series are compared with those of other structurally related series.

Keywords: New mesogenic homologous series; broken alkoxy chain; polymesomorphism

INTRODUCTION

Many liquid crystals are reported in the literature.[1-3] However there is great upheaval in the synthesis of liquid crystals from two aspects. One type of synthesis is directed towards synthesis of liquid crystals which can find an application, whereas another direction is to widen the horizon of liquid crystal chemistry by synthesizing new liquid crystals of some novelty in the structural aspects. Compounds having an unconventional molecular structure have been a topic of research for the last 15 years.[4,5]

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Literature survey indicated that esters with broken alkoxy chain are rare. Such esters are expected to exhibit smectic phases at lower temperatures if properly designed. With this expectation, Vora and Prajapati[6,7] have synthesized few mesogenic homologous series of esters with broken alkoxy chain as a novel terminus at the end of long polarizable molecules. In continuation of our work on broken alkoxy chain a new series of Schiff's base esters containing ethoxyethyl terminus has been synthesized and the mesomorphic properties of the present series are compared with those of other structurally related series.

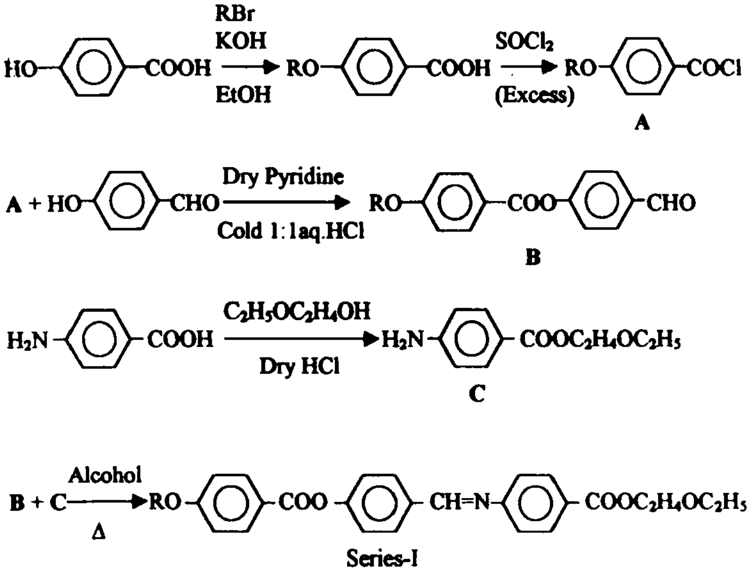
EXPERIMENTAL

4-Hydroxybenzoic acid, the appropriate n-alkylhalides, 4-hydroxybenzaldehyde, 4-aminobenzoic acid and ethoxyethanol were used as received. Solvents were dried and distilled prior to use. Microanalysis 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 by adopting a scanning rate of 5^0c/min. Liquid crystalline properties were investigated on a Leitz Labourlux 12POL microscope provided with a heating stage. Fluorescent spectra were recorded on a Shimadzu Rf 540 spectrophotoflurometer.

The synthetic route to series-I is illustrated in scheme-1.

4-n-Alkoxybenzoic acids[8] and 4-n-alkoxybenzoyloxy 4'-benzaldehydes[9] were synthesized as per the methods reported in the literature. Ethoxy ethyl 4-aminobenzoate was synthesized as per the method described below [10].

Dry hydrochloric acid gas was passed in 132 ml (1.37 mole) ethoxyethanol till it was saturated (approximately for about 3 hours). To this saturated solution 12g (0.088 mole) 4-aminobenzoic acid was added and the mixture was refluxed for about 8 to 10 hours. The hot solution was then poured into excess of ice-cold water and sodium carbonate was added to the solution until it was neutral to litmus. The precipitated ester was filtered and dried. The product crystallised from aqueous methanol had mp 82°C (75-80%). Elemental analysis: found, C 63.24, H 7.32 and N 6.45 %. $C_{11}H_{15}NO_3$ requires C 63.16%, H 7.18 % and N 6.70 %. The IR (KBr) spectra of the compound showed two bands for N-H stretching vibrations in the range of 3300-3500 cm^{-1}. The -COO- stretching vibrations were obtained at 1735 cm^{-1}. Other signals observed were at 2900, 1600, 1550, 1500, 1465, 1360, 1270, 1200, 1035, 830 cm^{-1}



Scheme 1: Synthetic route to series-I

The twelve Schiff's base esters of series-I were synthesized by condensing equimolar quantities of 4-n-alkoxybenzoyloxy 4'-benzaldehydes and ethoxyethyl 4-aminobenzoate in boiling ethanol. All the Schiff's base esters were crystallized from ethanol until constant transition temperatures were obtained. The transition temperatures are recorded in Table-I. The elemental analysis of all the compounds are recorded in Table-II.

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

Compound No.	$R = -C_nH_{2n+1}$ n=	Transition Temperatures (°C) SmA	N	I
1	1	-	156.0	203.0
2	2	147.0	162.0	215.0
3	3	151.5	172.0	192.0
4	4	157.0	177.0	207.0
5	5	156.0	180.5	186.0
6	6	105.5	183.5	190.0
7	7	92.5	-	184.0
8	8	112.0	-	182.0
9	10	104.5	-	172.5
10	12	92.5	-	158.0
11	14	83.0	-	143.0
12	16	83.5	-	133.0

TABLE-II Elemental Data of series-I

Compound No. (TABLE-I)	Formula	Required C	Required H	Required N	Found C	Found H	Found N
1	$C_{26}H_{25}NO_6$	69.80	5.59	3.13	69.74	5.63	3.32
2	$C_{27}H_{27}NO_6$	70.28	5.86	3.04	70.12	5.88	3.24
3	$C_{28}H_{29}NO_6$	70.74	6.10	2.95	70.86	6.33	2.78
4	$C_{29}H_{31}NO_6$	71.17	6.34	2.86	70.95	6.18	2.96
5	$C_{30}H_{33}NO_6$	71.57	6.56	2.78	71.68	6.38	2.57
6	$C_{31}H_{35}NO_6$	71.95	6.77	2.71	71.82	6.69	2.58
7	$C_{32}H_{37}NO_6$	72.32	6.97	2.64	72.54	6.84	2.55
8	$C_{33}H_{39}NO_6$	72.66	7.16	2.57	72.45	7.12	2.78
9	$C_{35}H_{43}NO_6$	73.30	7.50	2.44	73.54	7.18	2.66
10	$C_{37}H_{47}NO_6$	73.88	7.82	2.33	73.82	7.65	2.46
11	$C_{39}H_{51}NO_6$	74.40	8.11	2.23	74.74	8.38	2.15
12	$C_{41}H_{55}NO_6$	74.89	8.37	2.13	74.68	8.42	2.38

Spectral data of n-butyloxy derivative of series-I are given below.

IR (KBr) spectra: 2900, 1710(-COO-), 1610(-CH=N-), 1510, 1475, 1435, 1265, 1200, 1160, 1075, 1010, 845, 755 cm^{-1}.

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NMR spectra: (Solvent $CDCl_3$, standard TMS, 200 MHz) δ 0.9(t, 3H, $-CH_3$), 1.3(t, 3H, $-O-C-CH_3$). 1.5-1.9(m, 4H, 2 x $-CH_2-$), 3.2-3.5(m, 4H, $-CH_2OCH_2-$), 4.2(t, 2H, $ArOCH_2-$), 4.45(t, 2H, $-COOCH_2-$), 6.9(d, J=8.7Hz, 2H, ArH), 7.15-7.3(m, 4H, ArH), 7.8(d, J=8.5Hz, 2H, ArH), 8.0-8.15(m, 4H, ArH).

DSC: Data are given in Table-III.

TABLE-III DSC data of series-I

Compound No (TABLE-I)	Transition state	$\Delta H/Jg^{-1}$	$\Delta S/Jg^{-1}k^{-1}$
4	Cr-SmA	12.34	0.0290
	SmA-N	0.08	0.0002
	N-I	1.12	0.0023
8	Cr-SmA	18.85	0.0490
	SmA-I	1.86	0.0041
10	Cr-SmA	16.48	0.0451
	SmA-I	1.64	0.0038

Fluorescence spectra: Data for n-butyloxy and n-dodecyloxy derivatives are given in Table-IV. Table-IV indicates that all the homologues of the present series-I would exhibit fluorescence property.

TABLE-IV Data of fluorescence spectra for series-I

Compound No (TABLE-I)	Wavelength n.m. (Powder form)		Wavelength n.m. (Solution form)	
	Excitation	Emission	Excitation	Emission
4	240	386	220	398
12	240	286	340	470

RESULTS AND DISCUSSION

Series-I: Ethoxyethyl 4(4'-n-alkoxybenzoyloxy benzylidene) 4"-amino-benzoates.

Twelve members of the series-I were synthesized. All the members exhibit enantiotropic mesomorphism. Methoxy derivative is purely nematogenic. Ethoxy to n-hexyloxy derivatives exhibit enantiotropic smectic A as well as nematic mesophases. n-Heptyloxy to n-hexadecyloxy derivatives exhibits only enantiotropic smectic A mesophases.

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It is clear from the plot of transition temperatures against the number of carbon atoms in the alkoxy chain (Figure-1) that the nematic-isotropic transition temperatures exhibit the usual alternations associated with homologous series of mesomorphic ethers containing alkyl chain made up of odd and even number of carbon atoms. Hence, these transition points lie on two falling curves, the upper one determined by those ethers containing an even number, and the lower by those with an odd number of carbons in the alkoxy chain. As a result of this alternation, the highest nematic-isotropic transition temperature is 215 °C found for the ethyl ether. The smectic-nematic transition temperature curve smoothly rises in the ascending series. Both the falling nematic-isotropic transition temperature curve and rising smectic-nematic transition temperature curve merges with the falling smectic-isotropic transition temperature curve at the n-heptyloxy derivative.

Table-V summarizes the average thermal stabilities and comparative geometry of the present series-I and the structurally related series A[6], B[11] and C[12]. Series-I exhibits nematic and/or smectic mesophases whereas series A and B exhibit only smectic mesophases. Also the comparison of the n-octyl to hexadecyl ethers in series-I, A and B shows that the average relative thermal stability of the smectic phase in the series-I is greater by 89.5 °C and 40 °C compared to series A and B, respectively. The reference to geometry indicates that the molecules of the series-I are longer than the molecules of series A and B because of the third aromatic ring and a central azomethine linkage. Gray[13] has explained that the increase in the length of the molecules, as a result of its polarisability, increases the intermolecular cohesive forces which would be responsible for induction of nematic mesophase and the higher smectic thermal stabilities of the present series-I.

Table-V shows that compare to series C the average thermal stabilities of smectic-nematic and nematic-isotropic transition temperatures for n-propyl to n-hexyl derivatives of series-I are lower by about 12 °C and smectic-isotropic transition temperatures for n-octyl to n-hexadecyl are lower by 23.5 °C.

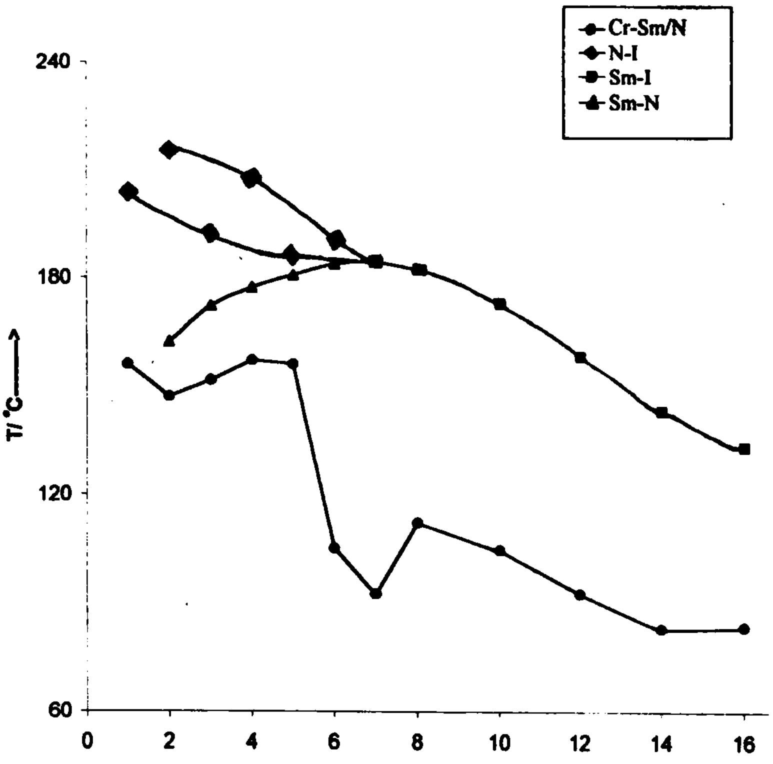

Figure 1

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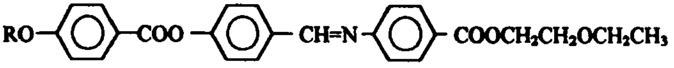
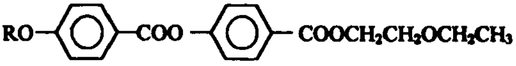
TABLE-V Average Thermal Stabilities °C

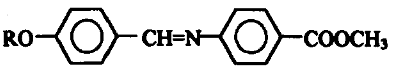
Series	I	A	B	C
Sm-N (C_3-C_6)	178.25	-	-	190.50
N-I (C_3-C_6)	193.75	-	-	206.25
Sm-I (C_8-C_{16})	157.70	68.20	117.70	181.20
Commencement of Smectic Phase	C_2	C_5	C_4	C_3



Series-I



Series A



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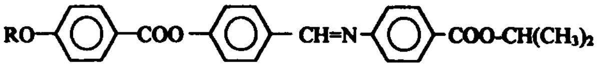

Series C

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

The molecules of series-I and series C differ only at the terminus. series-I has broken alkoxy chain ($-C_2H_4OC_2H_5$) at the terminus whereas series C has branched chain [$-CH(CH_3)_2$] at the terminus. It has been observed that lateral substituent or branching lowers the mesophase thermal stabilities in many cases and the extension of methylene spacer beyond certain number also lowers the transition temperatures. It seems number of spacer group and the presence of ether linkage at the terminus of the present series-I must be playing some role resulting in lower mesophase thermal stabilities compared to series C. Data for more such series would help in understanding such trends.

CONCLUSION

Broken alkoxy terminal chain with three phenyl rings having ester and azomethine central linkages exhibit nematic and/or smectic mesophases. The study indicated that broken alkoxy terminal chain affect more adversely on mesophase thermal stabilities as compared to branched chain terminus.

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