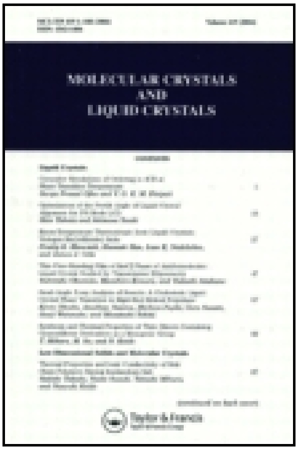

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Synthesis and Mesomorphic Characteristics of Mesogens with Branched Isoamyloxy and Isobutyloxy Terminal Groups

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Two new homologous series, each consisting of 12 mesogens with isoamyloxy and isobutoxy branching terminal groups, have been synthesized, and their mesomorphic properties are studied. All the derivatives are mesomorphic in nature, with the lower members exhibiting nematic mesophase and the higher derivatives showing smectic-c and nematic phase. The effect of branching on mesomorphism has been investigated by comparing them with structurally similar unbranched homologous series.

Keywords: effect of terminal branching, mesomorphism, smectic c, nematic

INTRODUCTION

Terminal substituents play a vital role in imparting liquid crystallinity to a potentially mesogenic compound. Generally in a liquid crystal compound, the end groups known are compact units like -CN, -NO_2, and halogen, or unbranched groups like n-alkyl and n-alkoxy chains, as the flexible chain is then at its narrowest in the extended form [1,2]. A survey of the literature indicates that generally branched chain compounds were less conducive to mesomorphism; in this connection, systematic studies have been carried out by various researchers [3,4]. However, it was then

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found that, although branched alkyl chains usually suppress orthogonal smectic phases, they can be used to introduce tilted smectic phases into a system [5].

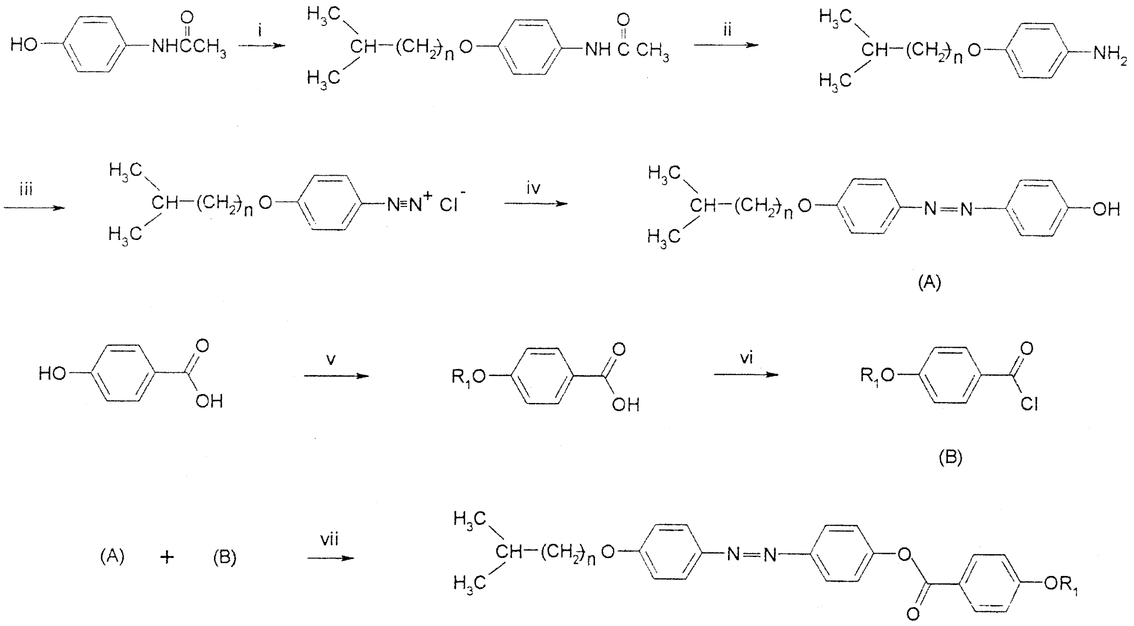
A number of homologous series that have different molecular structures were synthesized by us earlier [6,7] in order to establish the corelation between chemical constitution and mesomorphism. In continuation of our work, we have synthesized two new homologous series consisting of azo and ester central linkages and isoamyloxy and isobutoxy terminal groups, respectively, in order to study the mesogenic behavior of the compounds with branched terminal groups. A comparative assessment with those and similar other homologous series has also been attempted.

Experimental

4-Hydroxy benzoic acid, the appropriate n-alkyl halides, and paracetamol were used as received. Solvents were dried and distilled prior to use. Microanalysis of the compounds was performed on Coleman USA-CHN analyzer. IR spectra were recorded on a Shimadzu IR-408, NMR spectra were measured on a Pruker DRX-300 spectrometer. Liquid crystalline properties were investigated on Leitz Laborlux 12 POL polarizing microscope provided with a kofler heating stage. DSC was performed on a Mettler TA-4000 system.

The synthetic routes of both series are shown in Scheme 1.

1. 4-isoamyloxy aniline and 4-isobutoxy aniline were synthesized by reported methods [8,9].
2. 4-hydroxy phenyl azo-4′-isoamyloxy benzene and 4-hydroxy phenyl azo-4′-isobutoxy benzene were prepared by known procedure [10].
3. 4-n-alkoxy benzoic acids and 4-n-alkoxy benzoyl chlorides were synthesized by the modified method of Dave et al. [11].
4. The two series, namely 4(4′-n-alkoxybenzoyloxy)phenyl [azo-4″-isoamyloxy benzene and 4(4′-n-alkoxybenzoyloxy)phenyl] azo-4″-isobutoxy benzene were synthesized by adding dropwise a solution of 4-hydroxy phenyl azo-4″-isoamyloxy benzene (for Series I) of 4-hydroxy phenyl azo-4″-isobutoxy benzene (for Series II) in pyridine to a cold solution of respective 4-n-alkoxy benzoyl chloride in pyridine. The mixture was allowed to stand overnight at RT. It was acidified with 1:1 cold HCl and the separated solid was filtered and recrystallized from ethanol until constant transition temperatures were obtained. They are recorded in

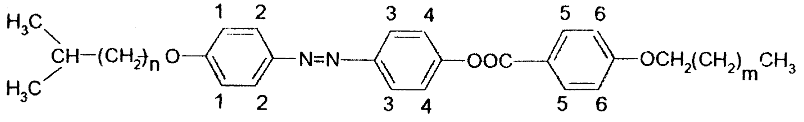


Where n = 1 or 2, R = C_mH_{2m-1} Where m = 1-8, 10, 12, 14 and 16

SCHEME 1 (i) K_2CO_3, isoamylbromide or isobutylbromide; Acetone (ii) H_2O, HCl; (iii) HCl, $NaNO_2$, 0–5°C; (iv) Phenol, aq. NaOH, 0–10°C; (v) RBr, alcohol, KOH; (vi) $SOCl_2$; (vii) pyridine, HCl.

Table 1. The elemental analysis of all the compounds were found to be satisfactory.

FTIR (KBr cm^{-1}): 2923, 1729 (-COO-), 1601 (-N=N-), 1461, 1377, 1256, 1165, 1066, 952, 838, 763, 724, 622, 556;



SCHEME 2

Proton NMR: (CDCl$_3$, 300 MHz, δ, ppm, standard TMS) Series I (Scheme 2): δ 0.9(3H, t, -CH$_3$), 1.00(6H, d, 2x-CH$_3$), 1,2-1.6(m, alkyl chain), 1.75 (2H, m, -C$\underline{H}_2$-CH$_2$O), 1.85(1H, m, -C$\underline{H}$(CH$_3$)$_2$), 4.1(4H, t, 2x -OCH$_2$);

TABLE 1 Transition temperature °C of the present series I and II

R = n-alkyl group	*Transition temperatures °C*		
	Smectic C	*Nematic*	*Isotropic*
Series I: 4(4′-n-alkoxybenzoyloxy)phenyl azo-4″-isoamyloxy benzene			
Methyl	—	149	268
Ethyl	—	130	274
Propyl	—	128	250
Butyl	—	118	250
Pentyl	—	116	240
Hexyl	—	114	232
Heptyl	—	105	226
Octyl	—	99	218
Decyl	95	109	206
Dodecyl	93	119	194
Tetradecyl	75	130	192
Hexadecyl	81	135	191
Series II: 4(4′-n-alkoxybenzoyloxy)phenyl azo-4″-isobutoxy benzene			
Methyl	—	143	229
Ethyl	—	145	238
Propyl	—	113	198
Butyl	—	119	230
Pentyl	—	84	178
Hexyl	—	106	212
Heptyl	—	109	168
Octyl	—	110	197
Decyl	—	94	184
Dodecyl	101	112	182
Tetradecyl	93	123	178
Hexadecyl	102	132	175

6.95(2H, d, H^2), 7.0(2H, d, H^3), 7.35(2H, d, H^5), 7.9(2H, d, H^6), 7.95(2H, d, H^1), 8.15(2H, d, H^4).

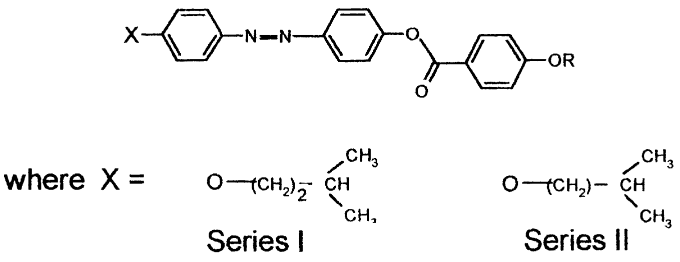
Series II (Scheme 2): 0.9(3H, t, -CH_3), 1.00(6H, d, 2x-CH_3), 1.2–1.6(m, alkyl chain), 1.8(2H, m, -$C\underline{H}_2$-CH_2O), 2.1(1H, m, -$C\underline{H}(CH_3)_2$), 3.9(2H, d, -$OC\underline{H}_2$-$CH(CH_3)_2$), 4.00(2H, t, -$OC\underline{H}_2$-CH_2), 6.95(2H, d, H^2), 7.0(2H, d, H^3), 7.35(2H, d, H^5), 7.9(2H, d, H^6), 7.95(2H, d, H^1), 8.15(2H, d, H^4).

RESULTS AND DISCUSSION

In the present study, 12 homologues from each of the two series, 4(4′-n-alkoxybenzoyloxy)phenyl azo-4″-isoamyloxy benzene (Series I) and 4(4′-n-alkoxybenzoyloxy)phenyl azo-4″-isobutoxy benzene (Series II), are synthesized and their mesomorphic properties are studied.

The general molecular structure of the series is shown in Scheme 3.

The methyl to octyl members of both of the series are purely nematogenic in nature. The smectic-c phase commences in the enantiotropic form in the decyl derivative in Series I and from the dodecyl homologue in Series II and is exhibited along with the nematic phase till the last C_{16} member studied. The early commencement of smectic phase in Series I can be attributed to the additional methylene unit in the isoamyloxy terminal group compared to the isobutyloxy group in Series II. Figures 1 and 2, i.e., the plot of transition temperatures against the number of carbon atoms in the n-alkyl chain, shows that in both the series the N-I-transitions lie on two falling curves showing the odd-even effect with falling tendency as the series is ascended. The S-N curve shows a steady rise in the ascending series. Comparison of phase topology of the series shows a pronounced odd-even effect in the N-I curve for the Series II with an isobutoxy terminal group. This effect is observed to a much lesser degree in Series I with isoamyloxy end group, and the odd-even N-I curves merge at C_5 homologue.



SCHEME 3

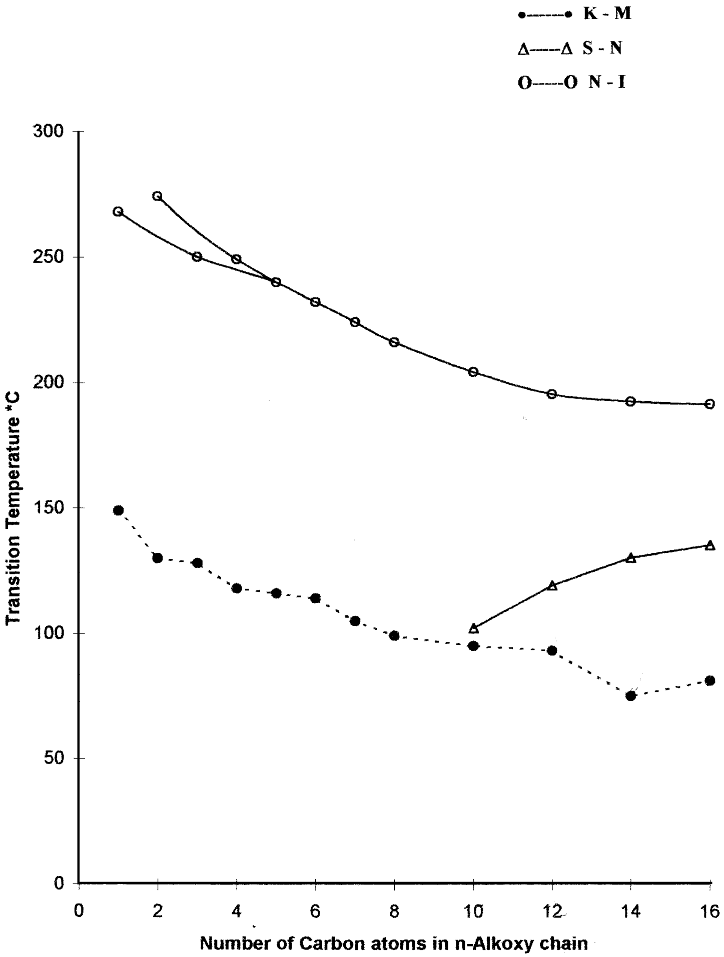


FIGURE 1 4(4′-n-alkoxybenzoyloxy)phenyl azo-4″-isoamyloxy benzene.

The enthalpies of n-dodecyloxy derivatives of each of the series were measured by differential scanning calorimetry. The data is recorded in Table 2 and Figure 3 shows the DSC patterns.

The mesophase range of the present series is compared with structurally similar series. Table 3 and Figure 4 show the average mesophase range for the homologous series shown in Scheme 4 selected for the comparative study.

All the series in comparison are structurally similar, consisting of three aromatic cores, azo and ester central linkages, and n-alkoxy as one of the terminal groups. Molecules of Series I, II, and A (Scheme 4) differ only in

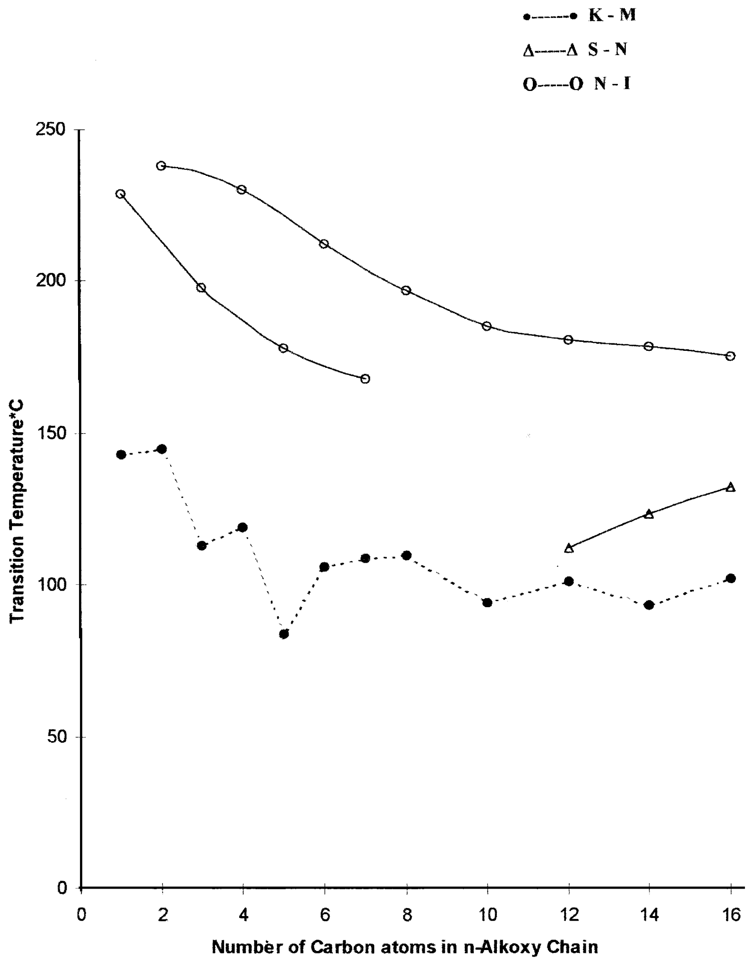


FIGURE 2 4(4′-n-alkoxybenzoyloxy)phenyl azo-4″-isobutoxy benzene.

one of their terminal moieties; Series I has an isoamyloxy group, Series II has an isobutoxy group, and Series A has an isopropoxy group [12]. An increase in the nematic and smectic mesophase range is observed with increasing number of methylene units in terminal group. As pointed out by Gray [15], when branching occurs at the first carbon of the chain, liquid crystal phase stability is affected the most, as there is an increase in the steric hindrance in the system due to acoplanarity. But the movement of point of branching away from the first carbon of the chain towards the end of the chain causes the transition temperatures to rise again. We also

TABLE 2 DSC data

C_{12} member of series	Heating rate/°C min^{-1}	Transition temperature	$\Delta H/Jg^{-1}$	$\Delta S/Jg^{-1}K^{-1}$
I	5	Cr-S 93.9	24.171	0.0658
		S-N 116.9	0.313	0.0008
		N-I 192.2	1.0199	0.0041
II	5	Cr-S 101.7	50.041	0.1335
		S-N 112.0	0.532	0.0013
		N-I 182.9	1.975	0.0043

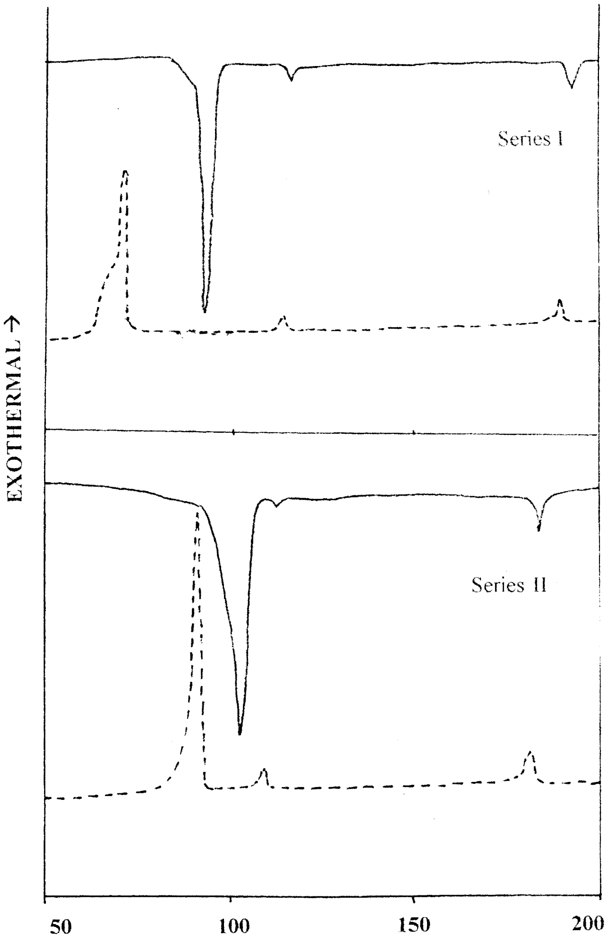


FIGURE 3 DSC curves for C_{12} member of Series I and Series II.

TABLE 3 Average mesophase range °C

Series	*Nematic*	*Smectic*	*Commencement of smectic phase*
I	108 (C_1-C_{16})	35.5 (C_{10}-C_{16})	C_{10}
II	81.58 (C_1-C_{16})	23.66 (C_{12}-C_{16})	C_{12}
A	66.66 (C_1-C_{16})	7.33 (C_{12}-C_{16})	C_{12}
B	125.4 (C_1-C_9)	—	—
C	123.8 (C_1-C_{16})	—	—

observed a similar trend in transitions and phase range of the series studied.

Series B [13] and C [14] consist of unbranched n-amyloxy and n-butoxy terminal groups, respectively, with the rest of the geometry of the molecules being similar to those of Series I and II. It is observed that, although the

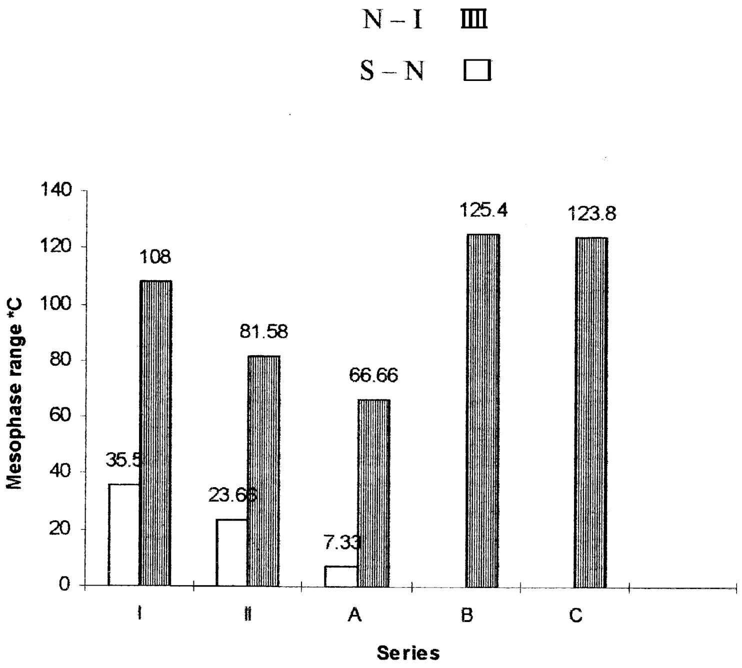
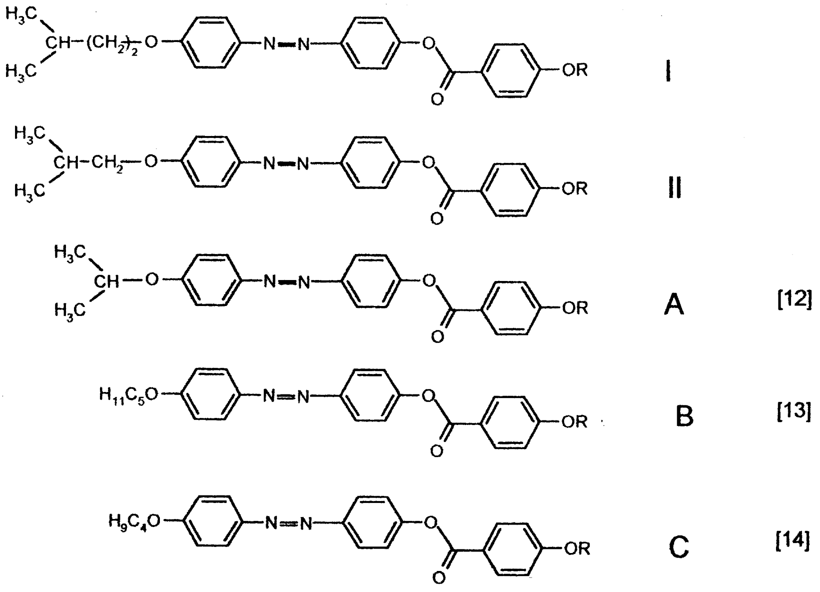


FIGURE 4 Average mesophase range °C.



SCHEME 4

present Series I and II exhibit lower nematic mesophase range, there is exhibition of Smectic phase in both of them, which is absent in the unbranched Series B and C. The effect of the branch in a terminal chain causes disruption in the molecular packing, which reduces the transition temperatures and melting points as well as the mesophase range compared to the unbranched analogues, but as predicted by Coates [5], branching introduces tilted Smectic phase in the series. The present Series I and II exhibit schlieren smectic c textures.

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