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Synthesis and Mesomorphic Characterization of Azoketones*

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Two mesogenic homologous series are synthesised, by fixing a rigid 4′-propiophenone group to 4-Hydroxy phenyl azo moiety. The hydroxy group is etherified and esterified by *n*-alkyl chains and 4-*n*-alkoxy benzoyl groups respectively. The etherified series (I) *viz*: 4-*n*-alkoxy phenyl azo 4′-propiophenones exhibit nematic phase from C_2 to C_4 homologue; smectic A phase emerges from the C_4 derivative in the monotopic form, which becomes enantiotropic in the C_5 homologue and persists till the last C_{16} derivative studied. The esterified series (II) namely: 4-(4′-*n*-alkoxy benzoyloxy) phenyl azo 4″-propiophenones shows only nematic phase in C_1 and C_2 homologues. The smectic phase emerges from C_3 derivative, together with nematic phase and the series exhibits polymesomorphism from C_3 to C_{12} homologue. The last two homologous exhibit only smectic A phase. Both the homologous series are thermally very stable and exhibit a wide mesomorphic range. Their thermal stabilities and other characteristics are discussed.

Keywords: Synthesis; mesogens; azoketones; characterization; smectic-A; nematic

INTRODUCTION

We have synthesised some homologous series, which have been found to exhibit mesomorphism and their existence has been attributed to their molecular geometry and molecular forces arising therefrom [1–7]. We have also studied binary mixtures of structurally similar and dissimilar mesogens [8–11]. It is known that dyes with liquid crystalline properties are used in the liquid crystal display devices using guest–host interactions [12]. In a

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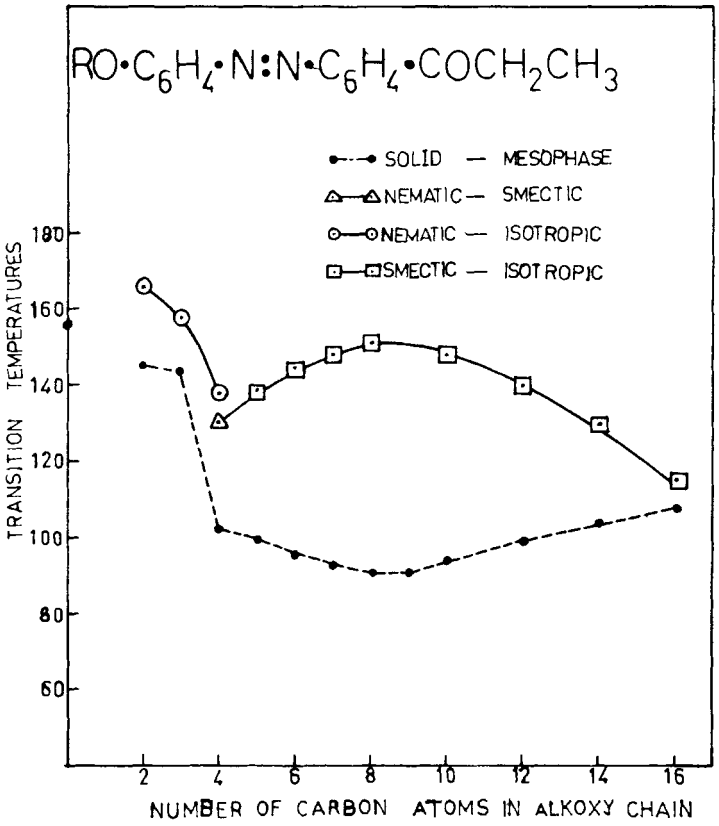


FIGURE 1 4-*n*-alkoxy phenyl azo 4′-propiophenones: transition temperatures against *n*, the number of carbon atoms in the alkoxy chain.

homologous series, phase generations by varied terminal units like $-OCH_3$, $-NO_2$, $-Cl$, $-Br$, $-F$, $-CH_3$, $-CN$, $-NHCOCH_3$, are known in literature. But the effect of a keto terminal group on mesomorphic properties has not been much explored. With this in view, that it may throw some light on this aspect, we have synthesised two new homologous series consisting of an azo central linkage and a keto terminal group. A comparative assessment with those of similar other homologous series has also been attempted.

EXPERIMENTAL

4-Hydroxy phenyl azo 4′-propiophenone (A) was synthesised from acetanilide by reported methods [13]. 4-*n*-alkoxy phenyl azo 4′-propiophe-

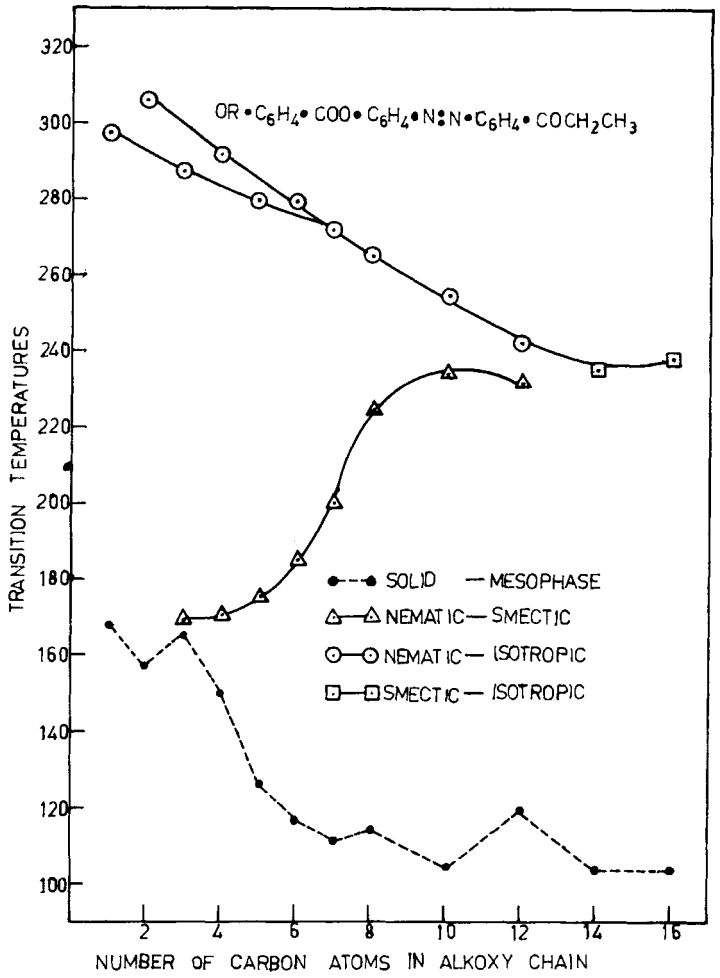


FIGURE 2 4-(4′-*n*-alkoxy benzoyloxy) phenyl azo 4″-propiophenones: transition temperatures against *n*, the number of carbon atoms in the alkoxy chain.

nones (I) was synthesised by alkylating (A) with *n*-alkyl bromides [14]. 4-(4′-*n*-alkoxy benzoyloxy) phenyl azo 4″-propiophenones (II) were synthesised by condensing 4-*n*-alkoxy benzoyl chlorides with (A) [15]. All the compounds were analysed by elemental analysis using Coleman USA-CHN analyser. The elemental data are in conformity with the calculated ones. Transition temperatures and textures of the mesophases were studied by using a Laborlux polarising microscope provided with a kofler heating stage. The analytical spectroscopic data of few of the compounds were obtained on a Perkin-Elmer FTIR (FTIR), JEOL FX 100 Spectro-

photometer (NMR) (recorded in Tabs. IV and V) and HITACHI U-2000 Double beam spectrophotometer (UV-VISIBLE). The melting points, transition temperatures and enthalpies of few compounds were confirmed using a METTLER DSC-20 Differential scanning calorimeter, as shown in Figures 3 and 4.

RESULTS AND DISCUSSION

The transition temperatures of 4-*n*-alkoxy phenyl azo 4′-propiophenones (series I) are summarised in Table I. Figure 1 shows the plot of transition temperature against the number of carbon atoms in the *n*-alkyl chain. All the members *viz*: ethyl upto hexadecyl of the homologous series are

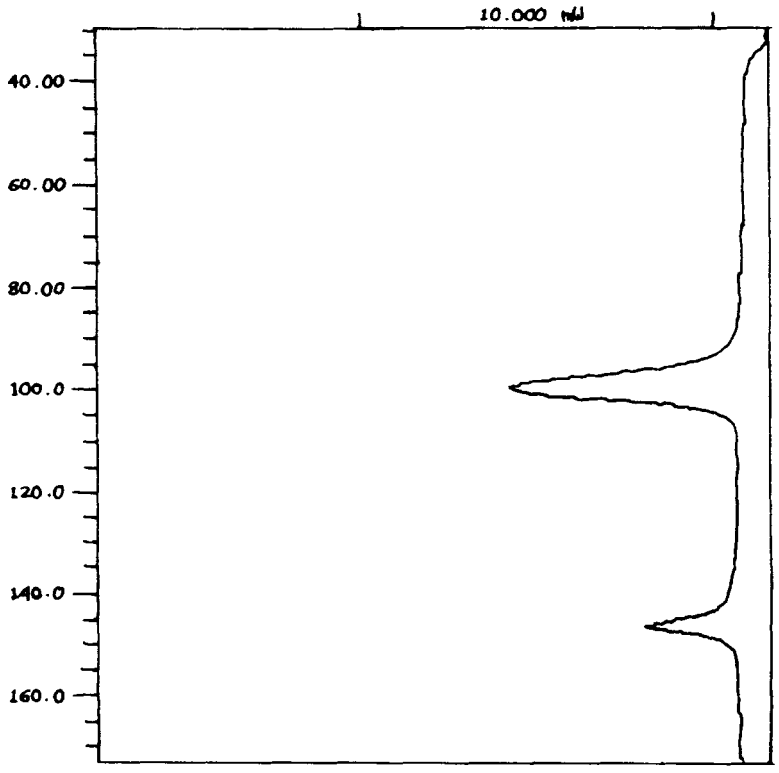


FIGURE 3 DSC heating curve of 4-*n*-hexyloxy phenyl azo 4′-propiophenone. Heating rate was 10°C/min. The scan rate was 10 K/min. The peak maxima was taken as transition temperatures. The ΔH for the transitions were 15.90 J/g and 2.59 J/g.

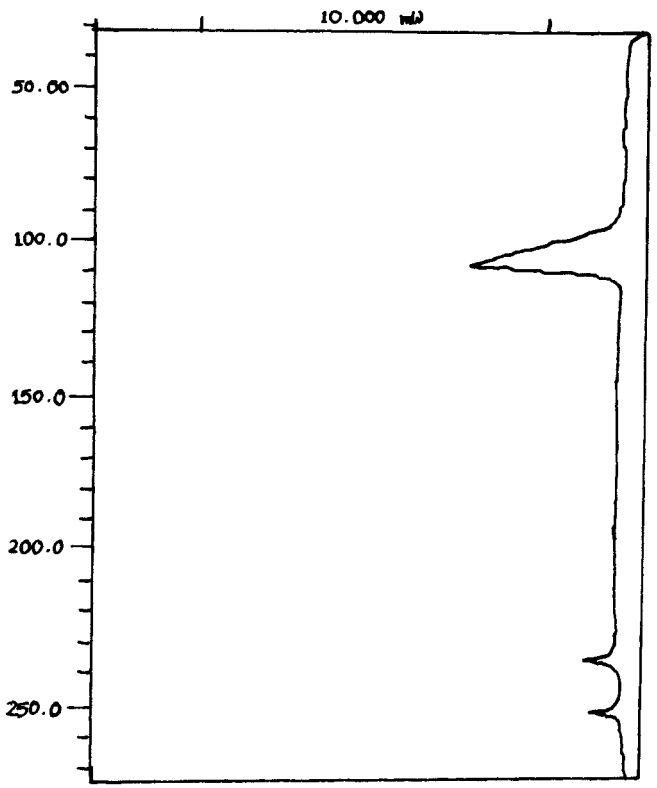


FIGURE 4 DSC curve of 4-(4′-*n*-decyloxy benzoyloxy) phenyl azo 4″-propiophenone. Heating rate was 10°C/min. The scan rate was 5 K/min. The peak maxima was taken as transition temperatures. The ΔH values obtained were 0.426 J/g, 1.844 J/g and 2.183 J/g for the different transitions.

mesogens. The enantiotropic nematic phase commences from the ethyl derivative and is exhibited till the butyl derivative. The monotropic smectic A phase emerges from the fourth homologue, which becomes enantiotropic from the pentyl derivative and persists upto hexadecyl homologue. The K → M curve falls steeply till the C_4 member. As the series is ascended, there is seen a gradual falling tendency upto the octyl derivative; after which it shows a rise till hexadecyl homologue. The N-I transition curve shows a falling tendency in the ascending series. The S-I transition curve rises steadily, forming an arc; and it reaches a maximum at C_8 homologue and falls gradually in the higher homologues and thus shows a maximum S_m mesophase length of 60°C, at C_8 homologue. This series consisting of only

TABLE I Transition temperatures for 4-*n*-alkoxy phenyl azo 4′-propiophenones $RO.C_6H_4.N:N.C_6H_4.COCH_2CH_3$

n-Alkyl group	*Transition temperatures °C*		
	Smectic	*Nematic*	*Isotropic*
Ethyl	–	145	166
Propyl	–	144	158
Butyl	(130)	102	138
Pentyl	100	–	139
Hexyl	96	–	145
Heptyl	93	–	148
Octyl	91	–	151
Decyl	94	–	148
Dodecyl	99	–	140
Tetradecyl	104	–	130
Hexadecyl	108	–	115

Value in paranthesis indicates monotropy.

TABLE II Transition temperatures for 4-(4′-*n*-alkoxy benzoyloxy)phenyl azo 4″-propiophenones $RO.C_6H_4.COO.C_6H_4.N:N.C_6H_4.COCH_2CH_3$

n-Alkyl group	*Transition temperatures °C*		
	Smectic	*Nematic*	*Isotropic*
Methyl	–	168	298
Ethyl	–	157	306
Propyl	165	169	288
Butyl	150	170	292
Pentyl	126	175	282
Hexyl	117	185	280
Heptyl	111	200	273
Octyl	114	225	265
Decyl	105	232	254
Dodecyl	120	228	242
Tetradecyl	114	–	235
Hexadecyl	113	–	238

two aromatic rings, one azo central bridge and two polar terminal groups; namely keto and *n*-alkoxy groups, is a moderate melting series.

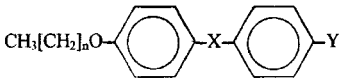
The transition temperatures of 4-(4′-*n*-alkoxy benzoyloxy) phenyl azo 4″-propiophenones (series II) are summarised in Table II. Figure 2 shows the plot of transition temperatures against the number of carbon atoms in the *n*-alkyl chain. In this series all the homologues are enantiotropic in nature. The first two members are purely nematogenic in character; smectic A phase commences from the C_3 homologue and it continues to be exhibited together with nematic phase upto C_{12} homologue; whereas the last two derivatives *viz.* C_{14} and C_{16} are purely smectogenic in nature. The increased length of this series, by introduction of an additional benzene nucleus and —COO— group as central linkage, increases its overall polarizibility. This

may be responsible for the higher transitions, higher degree of mesophase stability and early commencement of S_A phase, compared to that of series I. The S-N curve shows a smooth rise from C_3 to C_{10} homologue and nearly levels off at C_{12} homologue. The N-I transition curves show a falling tendency in the ascending series and it is seen that for these compounds the transition points lie on two smooth falling odd–even curves [16]. Careful supercooling of the isotropic melt do not show the emergence of a monotropic smectic phase at the C_2 homologue. The mesophase textures observed, showed threaded nematic in the lower members and nematic marble texture in the higher members. The smectic mesophase was focal conic fanshaped of smectic A variety [17], which was confirmed by miscibility studies with a known S_A compound *viz*: 4-*n*-dodecyloxy phenyl azo 4′-acetophenone [18].

The thermal stabilities of the new series can be compared with structurally similar series. Table III shows the average thermal stabilities for the following homologous series, selected for comparitive study.

A. 4-*n*-alkoxy 4′-propionoyloxy azo benzene [18]
B. 4-*n*-alkoxy phenyl azo 4′-acetophenone [18]
C. 4-*n*-alkoxy benzoyloxy 4′-propiophenone [19].

The general structure of the series can be given as



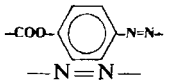
Series	*X*	*Y*
I	—N=N—	—$COCH_2CH_3$
II		—$COCH_2CH_3$
A	—N=N—	—$OCOCH_2CH_3$
B	—N=N—	—$COCH_3$
C	—COO—	—$COCH_2CH_3$

TABLE III Average thermal stabilities (°C)

Series	*I*	*II*	*A*	*B*	*C*
N-I	154 (C_2-C_4)	251.3 (C_8-C_{12})	128.3 (C_2-C_4)	121 (C_2-C_4)	120 (C_5-C_6)
S-N or S-I	148 (C_7-C_{10})	229 (C_8-C_{12})	–	116 (C_4-C_{12})	123.5 (C_7-C_{10})
Commencement of S_m phase	C_4 monotropic	C_3	–	C_4	C_4

TABLE IV Characteristic I.R. absorptions (KBr Pellet)

Characteristic I.R. Absorptions cm^{-1}	*Compound I*	*Compound II*	*Compound III*	*Compound IV*
—COO— stretching	1679	1679	1725	1725
—N=N— stretching	1600	1600	1600	1606
Alkane —CH— stretching	2939	2959	2932	2919
—CO— ketonic stretching	1679	1679	1679	1679
Alkyl aryl ether stretching	1255	1248	1268	1275
Aromatic —C—C— multiple bend stretching	1500	1474	1507	1513
Aromatic substitution type two adjacent hydrogen atoms C—H bending	870	864	835	850

Compound I: 4-*n*-hexyloxy phenyl azo-4′-propiophenone;
Compound II: 4-*n*-octyloxy phenyl azo-4′-propiophenone;
Compound III: 4-(4′-*n*-hexyloxy benzyloxy) phenyl azo-4″-propiophenone;
Compound IV: 4-(4′-*n*-decyloxy benzyloxy) phenyl azo-4″-propiophenone.

The average thermal stabilities of the present series I and II are higher than those of series A, B and C. Series A is purely nematogenic in nature. The replacement of the propionoyloxy group by the propionoyl group in I shows the emergence of smectic phase from the butyl derivative. Compared to B, series I has an additional methylene unit in the propionoyl group and hence it is a little longer and more polarisable; this increases the N-I and S-I thermal stabilities of I compared to that of B. In case of C, commencement of smectic phase is from the butyl homologue like that of B and I. Though series C and I share the same chain length; the S-I thermal stability of I is more than that of C which can be attributed to the fact that the ester linkage in C is replaced by a more coplanar azo linkage in I. In comparison to all the

TABLE V ^{1}H-NMR ($CDCl_3$, 100 MHz, δ, ppm)

Compound I: 8.0 (*m*, 6H at C_2, C_6, C_1', C_2', C_3', C_5'), 7.02 (*d*, 2H at C_3, C_5), 4.04 (*t*, 2H, $-O\underline{CH_2}$ at C_4), 3.05 (*q*, 2H, $-COC\underline{H_2}CH_3$ at C_4'), 1.35 (*m*, 11H, 8H, $-C_4\underline{H_8}-$ and 3H, $-C\underline{H_3}$ at C_4), 0.91 (*t*, 3H, $-COCH_2C\underline{H_3}$ at C_4')

Compound II: 8.0 (*m*, 6H at C_2, C_6, C_1', C_2', C_3', C_5'), 7.05 (*d*, 2H at C_3, C_5), 4.05 (*t*, 2H, $-O\underline{CH_2}$ at C_4), 3.05 (*q*, 2H, $-COC\underline{H_2}CH_3$at C_4'), 1.33 (*m*, 15H, 12H, $-C_6\underline{H_{12}}-$ and 3H, $-C\underline{H_3}$ at C_4), 0.92 (*t*, 3H, $-COCH_2C\underline{H_3}$ at C_4')

Compound III: 8.0 (*m*, 8H at C_2, C_6, C_3', C_5', C_2'', C_6'', C_3'', C_5''), 7.39 (*d*, 2H at C_2', C_6'), 6.98 (*d*, 2H at C_3, C_5), 4.05 (*t*, 2H, $-O\underline{CH_2}$ at C_4), 3.05 (*q*, 2H, $-COC\underline{H_2}CH_3$ at C_4''), 1.35 (*m*, 11H, 8H, $-C_4\underline{H_8}$ — and 3H, $-C\underline{H_3}$ at C_4), 0.9 (*t*, 3H, $-COCH_2C\underline{H_3}$ at C_4'')

Compound IV: 8.0 (*m*, 8H at C_2, C_6, C_3', C_5', C_2'', C_6'' C_3'', C_5''), 7.40 (*d*, 2H at C_2', C_6'), 7.00 (*d*, 2H at C_3, C_5), 4.06 (*t*, 2H, $-O\underline{CH_2}$ at C_4), 3.05 (*q*, 2H, $-COC\underline{H_2}CH_3$ at C_4''), 1.37 (*m*, 19H, 16H, $-C_8\underline{H_{16}}-$ and 3H, $-C\underline{H_3}$ at C_4), 0.92 (*t*, 3H, $-COCH_2C\underline{H_3}$ at C_4'')

above discussed series, series II is far more thermally stable; the smectic phase emerges early, from C_3 homologue and it also exhibits a wide mesophase range. This may be attributed to the longer and more polarizable molecules of series II, consisting of three aromatic nuclei, azo and ester central linkages and a polarizable keto terminal group.

CONCLUSION

A propiophenone keto moiety in a homologous series with azo central linkage, increases the molecular polarisability and hence the degree of the molecular order. It is seen that smectic phase appears for compounds with relatively short *n*-alkyl chains. The terminal keto group contributes to the fact that, the entire series is more smectogenic in nature; it exhibits mesomorphism of a long mesophase order, making the series highly thermally stable.

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