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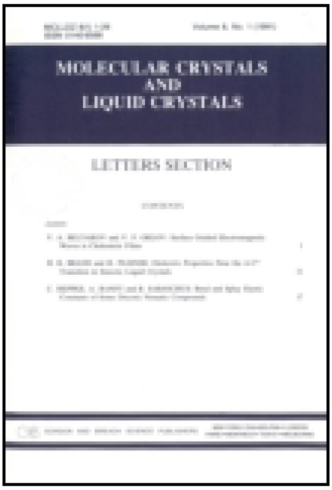

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Novel Azoester Compounds with a Lateral Methyl Substituent

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Novel Azoester Compounds with a Lateral Methyl Substituent

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Twelve novel homologues with an azo linkage of the series 4-carbethoxy-[3′methyl-4′ (4″-n-alkoxy benzoyloxy)] azobenzenes have been synthesized. The methyl to n-hexyl homologues exhibit only nematic mesophases, while the n-heptyl to n-tetradecyl homologues exhibit both smectic and nematic mesophases. The n-hexadecyl homologue exhibits only a smectic mesophase. The plot of transition temperatures versus number of carbon atoms in alkoxy chain exhibits an odd-even effect for the nematic-isotropic transitions. The mesogenic behavior of present series is explained by comparing each homolog of the related mesogenic series. The synthesized compounds were characterized by a combination of elemental analysis and standard spectroscopic methods. For the exhibition of mesomorphic property the role of ester and azo linkages has been discussed. The impact of the lateral methyl group on mesomorphism is also discussed.

Keywords Liquid crystals; mesomorphic; monotropic; nematic; smectic

1. Introduction

Thermotropic liquid crystals possess a number of unique properties that have received considerable research attention. Significant efforts have been focused on the synthesis of new compounds [1, 2], and it has been found that molecules having an extended rod like shape often exhibit a thermotropic liquid crystalline phase [3,4]. The design of novel thermotropic liquid crystals as advanced functional materials involves the suitable selection of a core fragment, linking group, and terminal functionality. The aromatic esters are known for their thermal stability, easy synthesis, and relative resistance to hydrolysis. Azo dye liquid crystals have attracted much attention because such photochromic molecules can undergo a reversible photochemical reaction between the trans and cis forms through photoisomerization. The trans form of the azobenzene, with rod-like shape, stabilizes the phase structure of the LC, while the bent cis form tends to stabilize the phase structure. These properties have enabled LCs containing azobenzene chromophores to be widely used in display technologies and various photonic applications, including optical storage, optical switching, optical computers, and integrated optical device for communication [5–10].

It is well known that the mesomorphic properties of calamitic liquid crystals can largely be influenced by the structural variations in terminal and lateral substituents [11–14]. Lateral substitution broadens the molecules, and hence plays an effective role in the mesogenic

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*Address correspondence to S. Dixit, Applied Chemistry Department, Faculty of Technology and Engineering, The M.S. University of Baroda, Kalabhavan, Vadodara, Gujarat, India. E-mail: snddxt_20@yahoo.com properties of the material. Studies on the effect of lateral substitution have been carried out by several researchers. A survey of the literature indicates that generally the mesophase range of a mesogen with lateral substituent is less than that of a laterally unsubstituted mesogen [15–20]. Thus, in order to study the correlation between chemical constitution and mesomorphism, a new mesogenic homologous series consisting of three phenyl rings joined through ester and azo linkages and a lateral methyl group with *n*-alkoxy and carbethoxy as terminal end groups was synthesized and its mesomorphic properties were studied.

2. Experimental

2.1 Synthesis

4-Hydroxy benzoic acid, *n*-alkyl halides, thionyl chloride, pyridine, methanol, potassium hydroxide, orthocresol, ethyl 4-amino benzoate, and sodium nitrite were chemically pure of lab grade. Solvents were dried and distilled prior to use.

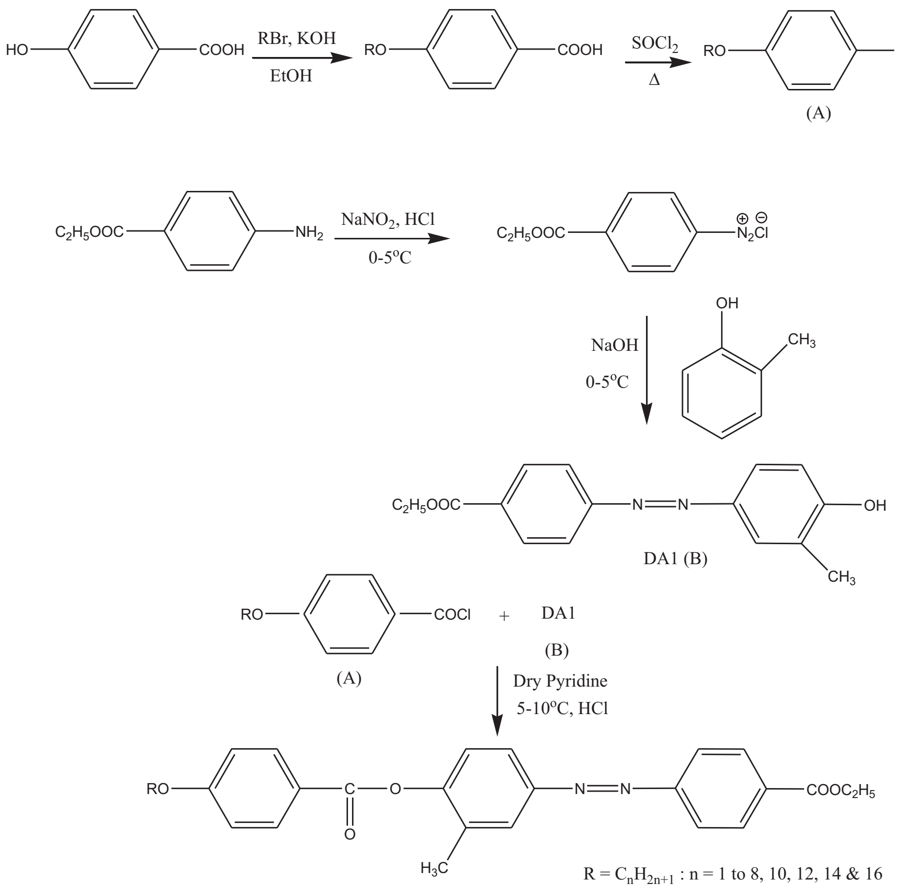
1. 4-*n*-Alkoxy benzoic acids and 4-*n*-alkoxy benzoyl chlorides were synthesized by the modified method of Dave and Vora [21].
2. 4-Carbethoxy-3′-methyl-4-hydroxy azobenzene (DA-1) was synthesized by known method [22].
3. The series namely 4-Carbethoxy-[3′methyl-4′(4″-*n*- alkoxy benzoyloxy)] azobenzene was synthesized by adding dropwise the solution of 4-Carbethoxy-3′-methyl-4-hydroxy azobenzene (DA-1) in dry pyridine to the respective solution of 4-*n*-alkoxy benzoyl chloride at 0–5°C. The mixture was allowed to stand overnight at room temperature. It was acidified with cold 1:1 aqueous hydrochloric acid and the separated solid was washed successively with dilute sodium hydroxide solution and water. The final product obtained was recrystallized several times from glacial acetic acid until constant transition temperatures were obtained which are recorded in Table 1. The elemental analysis of each compound was found to be satisfactory (Table 2). The route of synthesis of series 1 is illustrated in Scheme 1.

2.2 Characterization

Micro analysis of the compounds was performed on a Coleman carbon, hydrogen analyzer. FTIR spectra were determined on Nicolet impact 400 FTIR using Nujol. ^{1}H NMR spectra was performed on Perkin-Elmer (90 MHz) spectrometer using tetra methylsilane (TMS) as internal reference substance and $CDCl_3$ as solvent. Liquid crystalline properties were determined on a Leitz Laborlux 12 POL microscope equipped with a heating stage. Thermodynamic quantities enthalpies (ΔH) and entropies ($\Delta S = \Delta H\backslash T$) of transitions were determined using differential scanning calorimeter (DSC) via a Mettler TA-4000 system and reported in Jg^{-1} at a scanning rate of 5°C min^{-1}. The calorimeter was calibrated using pure indium as standard.

2.3 Analytical Data

FTIR (Nujol) Spectra cm^{-1}. *n*-Butoxy Derivative : 3000 (C-H Str. Aromatic), 2900, 2850 (C-H Str.Aliphatic), 1735 (C=O Str. Ester), 1600 (N=N Str.Azo), 1380, 1280, 1150 (aryl ether), 1050, 870, and 760.



Scheme 1. The route of synthesis to series 1 compounds.

n-Hexadecyloxy derivative : 3000 (C-H Str. Aromatic), 2900, 2850(C-H Str. Aliphatic), 1730 (C=O Str.Ester), 1600 (N=N Str. Azo),1370, 1250, 1160 (aryl ether), 1050, 850, and 770.

Proton NMR spectra (Solvent $CDCl_3$, 90 MHz, δ PPM, standard TMS). *n*-Butoxy Derivative **:** δ 0.9 (t,3H,CH_3), 1.3 (t,3H, CH_3), 1.4–1.9 (m, 4H, Ar-O-$(CH_2)_2$ -), 2.3 (s, 3H, Ar-CH_3), 3.9 (t, 2H, Ar-OCH_2), 4.2 (q, 2H, Ar-$COOCH_2$), 6.8–8.1 (m, 11H, Ar-H).

2.4 Calorimetry

Calorimetry is a valuable method for the detection of phase transitions. Conclusions may be drawn concerning the nature of the phases that participate in the transition with help of calorimetric studies. In the present study, enthalpies of tetradecyl homologue of series 1 are determined by DSC and data is recorded in Table 3.

Table 1. Transition temperature (°C) for Series 1

Compound No.	*n*-Alkyl CnH_{2n+1} group Series I	Transition temperatures (°C)s			
		SmC	SmA	N	I
1	1	—	—	150	230
2	2	—	—	145	235
3	3	—	—	134	210
4	4	—	—	132	224
5	5	—	—	114	192
6	6	—	—	105	200
7	7	(55)*	—	96	173
8	8	(60)	—	78	164
9	10	(70)	—	85	153
10	12	55	—	82	140
11	14	81	-	96	130
12	16	82	105	—	127

()* indicate monotropy, Sm, smectic; N, nematic; I, isotropic.

3. Results and Discussion

The homologous series 4-Carbethoxy [3′methyl-4′-(4″-*n*-alkoxybenzoyloxy)] azobenzenes consisting of 12 mesomorphic homologues have been synthesized. The methyl to *n*-hexyl derivatives exhibit enantiotropic nematic mesophases. The *n*-heptyl, *n*-octyl, and *n*-decyl derivatives exhibit monotropic smectic mesophases in addition to enantiotropic nematic mesophases. The *n*-dodecyl and *n*-tetradecyl derivatives are enantiotropically smectics and nematics. The *n*-hexadecyl derivative exhibits only an enantiotropic smectic mesophase. The transition temperatures (Table 1) are plotted versus the number of carbon atoms in alkyl chain of *n*-alkoxy terminal end group. The phase diagram showing phase behavior is depicted in Figure 1. The smectic-nematic transition curve shows rising tendency. The nematic-isotropic transition curve shows falling tendency as series is ascended with exhibition of odd-even effect. The nematic phase lengths vary from 15° to 95°C and the smectic phase lengths vary from18°C to 42°C.

There is a close relationship between mesomorphism and molecular constitution of organic compounds. Hence thermal stability, a measure of mesomorphism, can be correlated with the molecular constitution of the compounds. Figure 2 shows the transition

Table 2. Elemental analysis for ethyloxy, pentyloxy, octyloxy, and decyloxy derivative

Molecular formula	Element% found (compared with% calculated)		
	C	H	N
$C_{25}H_{24}O_5N_2$	68.88(68.57)	5.93(5.71)	6.42(6.66)
C_{28} $H_{30}O_5N_2$	69.79(70.12)	6.17(6.49)	5.65(6.06)
$C_{31}H_{36}O_5N_2$	71.84(71.42)	7.07(7.14)	5.82(5.55)
$C_{33}H_{40}O_5N_2$	71.78(72.18)	7.05(7.51)	5.45(5.26)

Table 3. DSC data

Series	Member	Transition	Peak temperature (microscopic reading)	Δ (H/Jg$^{-1)}$	Δ (S/Jg^{-1} K$^{-1)}$
1	Teteradecyl	Cr–Sm	80.9(81)	5.791	0.01636
		Sm–N	92.4(96)	44.345	0.12136
		N-Iso	124.5(130)	5.316	0.01337

temperatures and molecular structures of the *n*-decyloxy derivative (compound 10) of the present series 1 and the structurally related compound A [23], B [24], and C [25] reported in literature. Reference to Figure 2 indicates that the smectic and nematic thermal stabilities of compound 10 is lower by 47°C and 46°C, respectively, than that of compound A. The molecules of compound 10 and A differ only at lateral substituent, other structural features are being the same. Compound 10 has a lateral methyl group ortho to ester linkage whereas compound A has a hydroxyl group ortho to azo linkage. Due to intramolecular association of lateral hydroxyl group with an azo central linkage it is less effective in broadening of the molecules of compound A whereas the effect of increase in breadth is prominent in compound 10 because of lateral methyl group. Therefore, the nematic and smectic thermal stabilities of compound 10 are lower than those of compound A.

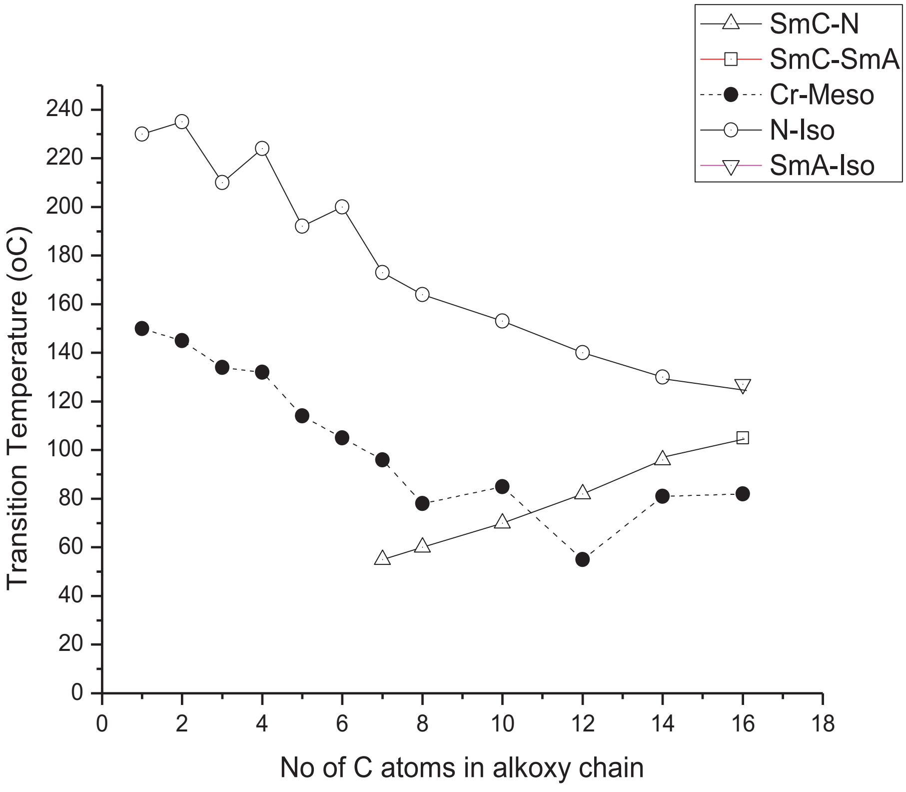
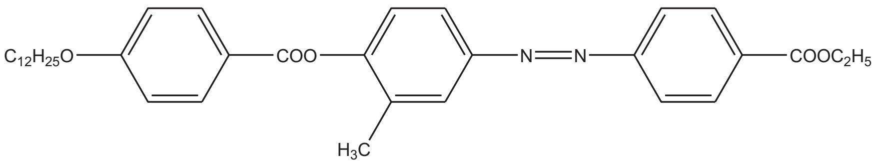
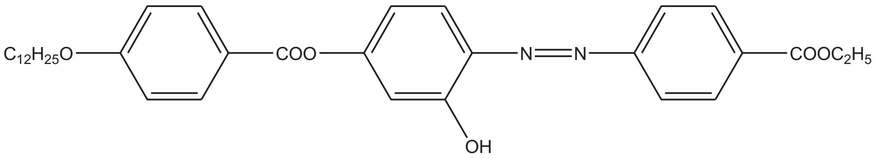


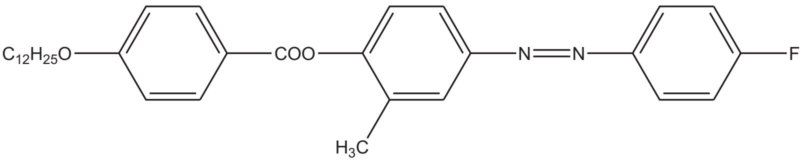
Figure 1. The phase behavior of series 1.



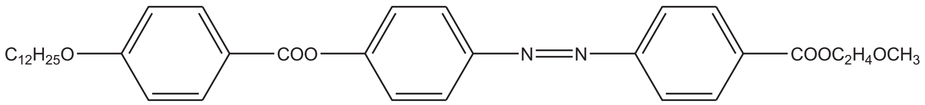
Compound **10** :Cr 55 °C SmC 82 ° C N 140 °C Iso



Compound **A:** Cr 102 °C SmC128 °C N128 °C Iso



Compound **B:** Cr 78 °C N 96 °C Iso



Compound **C:** Cr 97 °C SmA 159 °C N 226° C Iso

Figure 2. The Comparative molecular structures of Compounds 1, A, B, and C.

Figure 2 further shows that the compounds 10 and B consists of three phenyl rings, two central groups –COO– and –N=N–, one *n*-alkoxy terminal end group and laterally substituted methyl –CH_3 group as common identical features. The only one terminal end groups of compounds 10 and B viz. –$COOC_2H_5$ and –F are uncommon features. Figure 2 indicates that the compound 10 exhibits smectic and nematic mesophases whereas compound B exhibits only nematic mesophase. The nematic phase length and thermal stability of compound 10 is higher by 40°C and 44°C, respectively, than those of compound B. Both the compounds under comparison possess laterally substituted methyl groups at the middle phenyl ring which will affect the length to breadth ratio and polarizability to a different extent for compounds 10 and B due to the presence of different end groups –$COOC_2H_5$ and –F. The molecules of compound 10 are longer and highly polarizable due to the presence of longer and polar –$COOC_2H_5$ terminal group at one end, as compared to short polar –F group in compound B at that position. The longer terminal –$COOC_2H_5$ group increases molecular length of compound 10, which interact with one another and stabilizes the molecular packing required for nematic phase. Gray [26] has also explained that increased length and polarizability enhances both mesogenic properties and thermal stabilities. Hence, nematic thermal stability of compound 10 should be higher than that of compound B, which is the case. The exhibition of smectic phase in compound 10 as compared to none in compound B can be explained on the basis of long polar –$COOC_2H_5$ terminal group, which aids the formation of smectic mesophase due to enhanced lateral attraction, as compared to terminal attraction, which facilitates lamellar packing required for the formation of smectic mesophase [26].

The comparison of compound 10 and compound C shows that the smectic and nematic thermal stabilities of compound 10 are lower by 42°C and 86°C, respectively, than those of compound C. This can be explained on the basis of their structural variations. The molecular structure of compound 10 differs from the molecules of compound C in the terminal as well as in the central part of the benzene ring. The molecules of the compound 10 has –$COOC_2H_5$ group at the one terminal and –CH_3 lateral group at the central benzene ring, whereas molecules of compound C has –$COOC_2H_4OCH_3$ group at the same terminal position without any lateral substituent. The presence of lateral methyl group increases the breadth of the molecules of compound 10 and the length is also shorter than the molecules of compound C because of absence of additional –OCH_3 unit. Gray [26] has explained that increase in breadth of molecules reduces both nematic and smectic thermal stabilities. Thus, both reduced length and enhanced breadth factors resulted in lower smectic and nematic thermal stabilities of compound 10 reported in present investigation.

An interesting aspect of the present series is that it exhibits polymorphism of the smectic phase. Five members of the series exhibit the smectic C phase and one member exhibits a smectic A (SmA) phase. In the present series the SmA (focal conic texture) and SmC (Schlieren texture) and nematic (marble texture) are inferred from the textures observed under a polarizing microscope.

4. Conclusion

In this paper, we have presented the synthesis and characterization of a homologous series with central ester and azo linkages and lateral methyl substituent. Compounds of the present series exhibit a nematic mesophase along with the SmC and SmA mesophases. The study revealed that enhanced length of the molecules of the present series due to the presence of the long –$COOC_2H_5$ terminal substituent resulted in higher mesophase thermal stabilities while, increased breadth due to presence of the lateral methyl group lowered its mesophase thermal stabilities. The interesting aspect of the present series is that due to the lateral methyl substituent their solid to mesomorphic transitions (melting points) are lower.

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