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Effect of Lateral Substitution on Mesogenic Properties of Fluoro Aniline Derivatives

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Three new homologous series of liquid crystals with terminal fluoro group and central linkages such as ester and azo groups were synthesized and their mesomorphic properties were studied. All three series are similar in molecular structure with the difference in their lateral substitutions: series I has no lateral substitution, series II has a chloro group as lateral substitution, and series III has a methyl group as lateral substitution. All 12 homologues of each of the series are mesogenic in nature. The nematic phase of the series shows a marble texture and the smectic phase shows a Schlieren texture of the smectic C variety. The mesomorphic characteristics of the series are compared with each other.

Keywords Azo ester; chloro and methyl groups; homologues; lateral substituents; mesophase range; smectic C and nematic mesophase

Introduction

Generally, liquid-crystalline compounds are rod-like molecules with stable central linkages [1–6]. Lateral substitution makes molecules broad; lateral substituents play an effective role in mesogenic properties of a mesogenic compound. 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 mesogens with lateral substituent is less than that for laterally unsubstituted mesogens [7–18]. Thus, in order to study the corelation between chemical constitution and mesomorphism, three new homologous series with ester and azo central linkages, a fluoro terminal group, and chloro and methyl lateral groups were synthesized and their mesomorphic properties were studied.

Experimental

4-Hydroxy benzoic acid, the appropriate n-alkyl halides, p-fluoro aniline, phenol, o-chloro phenol, and ocresol were used as received. Solvents were dried and distilled

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prior to use. Microanalyses of some of the representative compounds were performed on a Perkin Elmer Series II 2400-CHN analyzer; infrared (IR) spectra were recorded on a Perkin Elmer GX-FTIR, and nuclear magnetic resonance (NMR) spectra were measured on a Bruker Avance II-500 spectrometer. Liquid-crystalline properties were investigated on a Leitz Laborlux 12 POL polarizing microscope provided with a Kofler heating stage. Differential scanning colarimetry (DSC) was performed on a Mettler Toledo Star SW 7.01.

1. 4-n-Alkoxy benzoic acids and 4-n-alkoxy benzoyl chlorides were synthesized by the modified method of Dave and Vora [19].
2. 4-Hydroxyphenylazo-4′-fluoro benzene, 3-chloro-4-hydroxyphenylazo-4′-fluoro benzene, and 3-methyl-4-hydroxyphenylazo-4′-fluoro benzene were prepared by a known method [20].
3. The series, namely 4-(4′-n-alkoxybenzoyloxy)-phenylazo-4″-fluorobenzenes, 4-(4′-n-alkoxybenzoyloxy)-3-chlorophenylazo-4″-fluorobenzenes, and 4-(4′-n-alkoxybenzoyloxy)-3-methylphenylazo-4″-fluorobenzenes were synthesized by adding dropwise a cold solution of 4-hydroxy phenylazo-4′-fluorobenzene (for series I), 3-chloro-4-hydroxyphenylazo-4′-fluorobenzene (for series II), and 3-methyl-4-hydroxyphenylazo-4′-fluoro benzene (for series III), respectively, in dry pyridine to a cold solution of 4-n-alkoxy benzoyl chloride. The mixture was allowed to stand overnight at room temperature. It was acidified with 1:1 cold HCl and the separated solid was filtered and recrystallized from ethanol until constant transition temperatures were obtained. These are recorded in Table 1. The elemental analysis of all the compounds was found to be satisfactory (Table 2). The synthetic route of the series is shown in Scheme 1.

Fourier Transform Infrared (Nujol, KBr Pellets, Cm^{-1})

Series I: 4-(4′-n-butyloxybenzoyloxy)phenylazo-4″-fluorobenzenes: 2,937, 1,729 (-COO-), 1,073 (-C-F), 1,597 (-N=N-), 1,496, 1,389, 1,258, 1,169, 1,073, 969, 843, 761, 692.

^1H NMR: ($CDCl_3$, 200 MHz, δ, ppm, Standard Trimethyl Sulfoxane)

Series I: 4-(4′-n-butyloxybenzoyloxy)phenylazo-4″-fluorobenzenes: δ 1.0 (3H, t, $-CH_3$), 1.4–1.79 (m, alkyl chain), 4.05 (2H, t, $-OCH_2-CH_2$), 6.98 (2H, d, H^5), 7.02 (2H, d, H^4), 7.36 (2H, d, H^2), 7.9 (2H, d, H^6), 8.0 (2H, d, H^1), 8.1 (2H, d, H^3).

Fourier Transform, Infrared (Nujol, KBr Pellets, Cm^{-1})

Series II: 4-(4′-n-octyloxybenzoyloxy)3-chlorophenylazo-4″-fluorobenzenes: 2,944, 1,731 (-COO-), 1,066 (-C-F), 1,606 (-N=N-), 850 (-C-Cl), 1,504, 1,420, 1,319, 1,264, 1,041, 953, 839, 755, 689.

^1H NMR: ($CDCl_3$, 200 MHz, δ, ppm, Standard Trimethyl Sulfoxane

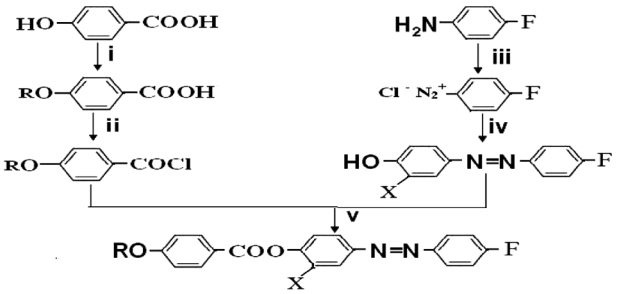
Series II: 4-(4′-n-octyloxybenzoyloxy)3-chlorophenylazo-4″-fluorobenzenes : δ 0.9 (3H, t, $-CH_3$), 1.4–1.79 (m, alkyl chain), 4.05 (2H, t, $-OCH_2-CH_2$), 6.98 (2H, d, H^4), 7.0 (2H, d, H^5), 7.36 (2H, d, H^2), 7.9 (2H, d, H^6), 8.0 (2H, d, H^1), 8.1 (2H, d, H^3).

Table 1. Transition Temperature °C of the Present Series I, II, and III

R=n-alkyl group	Transition temperatures °C		
	Smectic C	Nematic	Isotropic
(Series I) 4-(4′-n-alkoxybenzoyloxy)-phenylazo-4″- fluorobenzenes			
Methyl	—	130	206
Ethyl	—	122	208
Propyl	—	115	205
Butyl	—	110	209
Pentyl	—	100	198
Hexyl	—	91	194
Heptyl		83	182
Octyl	85	93	164
Decyl	89	110	142
Dodecyl	93	—	131
Tetradecyl	04	—	126
Hexadecyl	109	—	124
(Series II) 4-(4′-n-alkoxybenzoyloxy)-3-chlorophenylazo-4″-fluorobenzenes			
Methyl	—	121	159
Ethyl	—	113	167
Propyl	—	105	163
Butyl	—	95	156
Pentyl	—	89	150
Hexyl	—	85	146
Heptyl	—	80	139
Octyl	—	77	126
Decyl	—	75	119
Dodecyl	83	93	113
Tetradecyl	92	—	110
Hexadecyl	96	—	108
(Series III) 4-(4′-n-alkoxybenzoyloxy)-3-methylphenylazo-4″-fluorobenzenes			
Methyl	—	113	148
Ethyl	—	109	139
Propyl	—	100	133
Butyl	—	90	128
Pentyl	—	84	125
Hexyl	—	78	116
Heptyl	—	73	109
Octyl	—	69	103
Decyl	—	72	98
Dodecyl	—	78	96
Tetradecyl	81	85	93
Hexadecyl	86	—	91

Table 2. Elemental Analysis

		Calculated			Found		
Series	Homologue	C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
I	C4	70.40	5.35	7.14	70.24	5.29	7.18
II	C8	67.15	5.80	5.80	67.02	5.66	5.72
III	C6	71.88	6.22	6.45	71.60	5.46	6.31



Scheme 1. Synthetic route for series I, II and III.

Fourier Transform Infrared (Nujol, KBr Pellets, Cm^{-1})

Series III: 4-(4′-n-hexyloxybenzoyloxy)3-methylphenylazo-4″-fluorobenzenes: 2,946, 1,729 (-COO-), 1,065 (-C-F), 1,603 (-N=N-), 1,317 (-C-CH_3), 1,498, 1,317, 1,260, 1,096, 842, 724, 689, 615.

^1H NMR: ($CDCl_3$, 200 MHz, δ, ppm, Standard Trimethyl Sulfoxane)

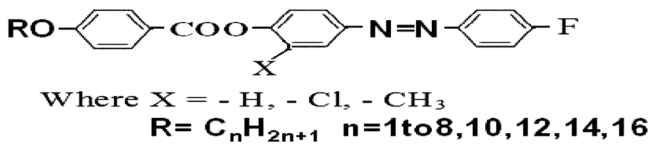
Series III: 4-(4′-n-hexyloxybenzoyloxy)3-methylphenylazo-4″-fluorobenzenes : δ 0.9 (3H, t, -CH_3), 1.3–1.8 (m, alkyl chain), 4.0 (2H, t, -OCH_2-CH_2), 6.98 (2H, d, H^4), 7.0 (2H, d, H^5), 7.30 (2H, d, H^2), 7.9 (2H, d, H^6), 8.1 (2H, d, H^1), 8.2 (2H, d, H^3).

Results and Discussion

In the present study, 12 homologues from each of the three series, 4-(4′-n-alkoxy benzoyloxy)-phenylazo-4″-fluorobenzenes (series I), 4-(4′-n-alkoxy benzoyloxy)-3-chlorophenylazo-4″-fluorobenzenes (series II), and 4-(4′-n-alkoxy benzoyloxy)-3-methylphenylazo-4″-fluorobenzenes (series III), were synthesized and their mesomorphic properties were studied.

The general molecular structure of the series is shown in Scheme 2.

All 12 homologues of series I are mesogens; the nematic phase commences from the first derivative and remains up to the decyl derivative, whereas the smectic C



Scheme 2. General molecular structure of series I, II and III.

phase commences from the octyl derivative and remains to be exhibited up to the last hexadecyl derivative synthesized. Figure 1 shows the plot of transition temperatures against number of carbon atoms in the alkoxy chain; it indicates that N-I curve shows overall falling tendency with a slight increase at the fourth derivative and merges with the falling S-I curve as the series is ascended. No odd–even effect is observed in the N-I curves or S-I curves. The Cr-M transitions show a falling tendency from the methyl to heptyl derivative and then a rising tendency from the octyl derivative to hexadecyl derivative. The nematic phase of the series shows a marble texture and the smectic phase shows a Schlieren texture of the smectic C variety.

All 12 homologues of series II are mesogens; the nematic phase commences from the first derivative and remains up to the dodecyl derivative, whereas the smectic C phase commences from the dodecyl derivative and remains to be exhibited up to the last hexadecyl derivative synthesized. Figure 2, that is, the plot of transition temperatures against number of carbon atoms in the alkoxy chain, indicates that the N-I curve shows an overall falling tendency with a slight increase at the second derivative and merges with the falling S-I curve as the series is ascended.

Here no odd–even effect is observed in the N-I curves or S-I curves. The Cr-M transitions show a falling tendency from the methyl to decyl derivative and a rising tendency from the dodecyl derivative to hexadecyl derivative. Here, too, the nematic phase of the series shows a marble texture and the smectic phase shows a Schlieren texture of the smectic C variety.

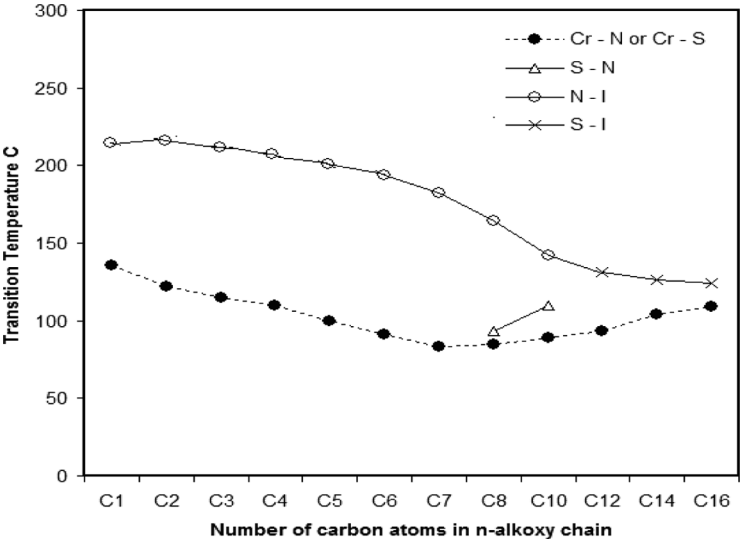


Figure 1. 4-(4′-n-Alkoxybenzoyloxy) phenylazo-4″-fluorobenzenes (series I).

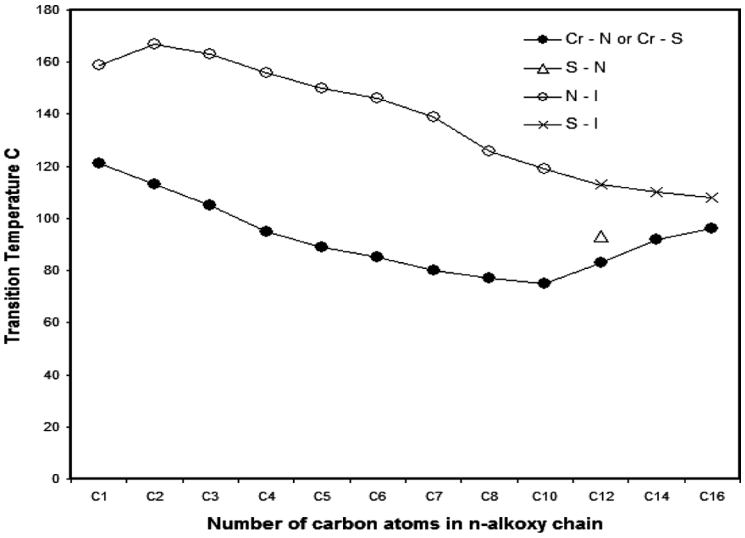


Figure 2. 4-(4′-n-Alkoxybenzoyloxy)-3chloro phenylazo-4″-fluorobenzenes (series II).

All 12 homologues of series III are mesogens; the nematic phase commences from the first derivative and remains up to the tetradecyl derivative, whereas the smectic C phase commences from the tetradecyl derivative and remains to be exhibited up to the last hexadecyl derivative synthesized. Figure 3, that is, the plot of transition temperatures against number of carbon atoms in the alkoxy chain, indicates that the N-I curve shows an overall falling tendency with a slight increase at the fifth derivative and merges with a falling S-I curve as the series is ascended.

No odd–even effect is observed in the N-I curve or S-I curves. The Cr-M transitions show a falling tendency from the methyl to dodecyl derivative and a rising

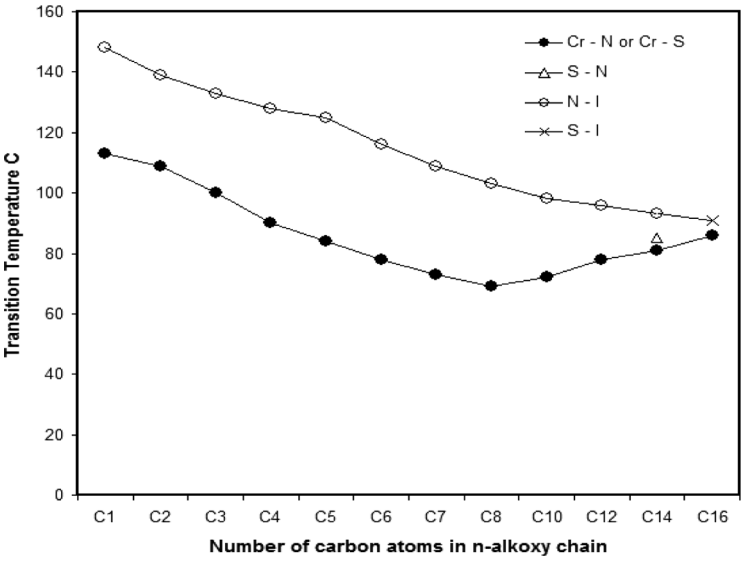


Figure 3. 4-(4-n-Alkoxybenzoyloxy)-3methyl phenylazo-4″-fluorobenzenes (series III).

Table 3. Average Mesophase Range °C

Series	Nematic	Smectic	Commencement of smectic mesophase
I	189.7 (C_1 to C_{10})	116.8 (C_8 to C_{16})	C_8
II	143.8 (C_1 to C_{12})	103.66 (C_{12} to C_{16})	C_{12}
III	117.09 (C_1 to C_{14})	88 (C_{14} to C_{16})	C_{14}

tendency from the dectyl derivative to hexadecyl derivative. Like the other two series, here also the nematic phase of the series shows a marble texture and the smectic phase shows a schlieren texture of smectic C variety.

The average nematic mesophase range of series I is 189.7°C, series II is 143.8°C, and series III is 117.09 °C, similarly the average smectic mesophase range of series I is 116.8°C, that of series II is 103.6°C, and series III is 88°C. Comparison of average mesophase range of all three series (Table 3) shows that both the nematic and smectic mesophase range of series II and series III are lower than those of series I. Here, the nature of lateral substituents has important implications on phase transition temperatures and average mesophase range. The effect of the lateral group in the central benzene ring causes disruption in the molecular packing, which reduces the transition temperatures and melting points as well as the mesophase range compared to the laterally unsubstituted analogues. The introduction of a chloro group (series II) and a methyl group (series III) in the ortho position of the ester linkage of series I effectively reduced both the clearing and melting points compared to those of the parent compound (series I). The commencement of the smectic mesophase is late in series II and series III compared to series I, which is due to the non-coplanarity caused by the molecules. Series II and series III both are laterally substituted in comparison with series I; the breadth of the molecules of series II and III is increased due to the presence of a lateral group on the central benzene ring, which decreases both smectic and nematic thermal stabilities [21]. The difference in commencement of mesophase type is only because of the different nature of the lateral substitution. The smectic tendency of the molecule is less effected by the chloro group than the methyl group [21]. The enthalpies of the butyl derivative of series I, octyl derivative of series II, and hexyl derivative of series III were measured by DSC. The data are shown in Table 4 and Fig. 4 shows the DSC curves of the C4 homologue of series I, the C8 homologue of series II, and the C6 homologue of series III.

Table 4. DSC Data

Series	Member	Heating rate (°C min^{-1})	Transition temperature	Δ (H/Jg^{-1})	Δ ($S/Jg^{-1}K^{-1}$)
I	Butyl	5	Cr-N 110	61.49	0.160
			N-I 211	2.73	0.0066
II	Octyl	5	Cr-N 77	83.00	0.237
			N-I 126	1.65	0.0041
III	Hexyl	5	Cr-N 78	72.77	0.207
			N-I 116	0.92	0.0023

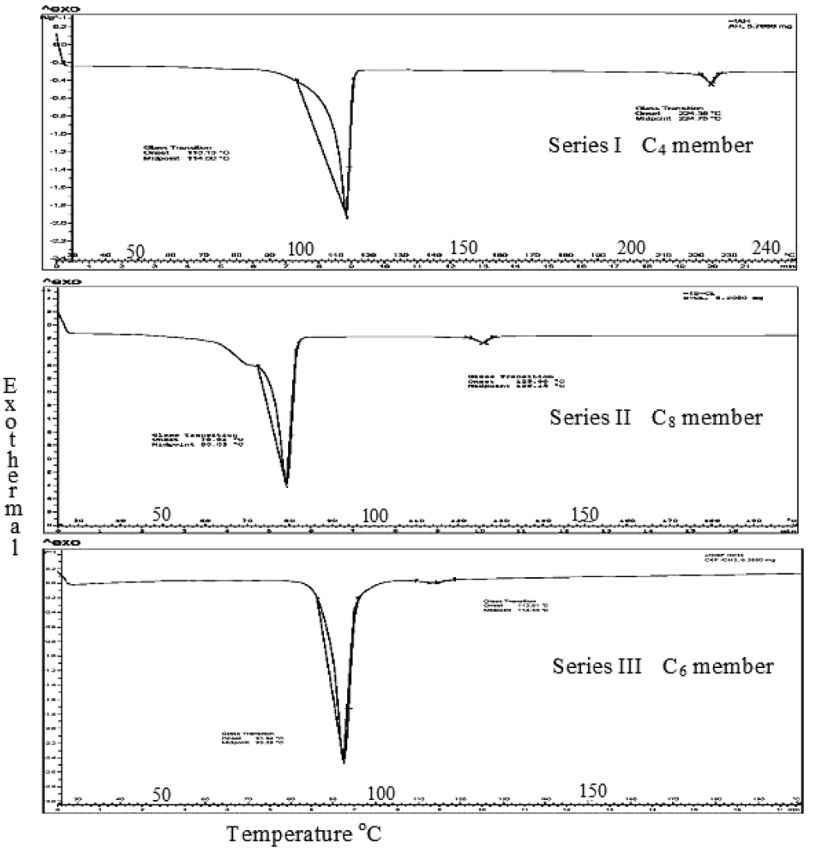


Figure 4. DSC curves.

Conclusion

The effect of –Cl and $-CH_3$ lateral substitutents on phase behavior, and phase transition temperatures was studied. These lateral substituents depress both melting point and clearing points of the liquid crystals. Mesogens with an ortho lateral substitution have a reduced smectic and nematic mesophase range compared to the corresponding unsubstituted homologues.

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