Higher Homologues of Mesomorphic Benzylidene Anilines. Manifestation of Smectic Polymorphism

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The synthesis and characterisation of higher homologues of the well-known benzylidene anilines, viz. N-(*p*-*n*-tridecyloxy, tetradecyloxy, and hexadecyloxy benzylidene)-*p*-*n*-alkylanilines, 13O.*m*, 14O.*m* and 16O.*m* liquid crystalline compounds have exhibited mono, bi and tri phase variant smectic polymorphism. The different liquid crystalline phases are characterized by an optical polarising microscope equipped with a PC based temperature controller. The phase transitions are studied by using differential scanning calorimetry. The results are discussed in the light of the data available on other *n*O.*m* compounds.

Key words: *n*O.*m*; Phase Variants; Polymesomorphism.

Introduction

The research on liquid crystals of N-(*p*-*n*-alkoxybenzylidene)-*p*-*n*-alkylanilines, (*n*O.*m*) series, involves the synthesis and characterisation of phase variants in newly synthesised compounds using techniques like Polarising Microscopy and Differential Scanning Calorimetry.

The data available on *n*O.*m* homologues [1 – 4] show that the homologues with $n \leq 7$ and $m = 1$ to 16 show mainly nematic and orthogonal smectic phases, such as the smectic-A and smectic-B phase, with the rare exhibition of tilted phases, such as smectic-C, -F and -G. However, it has been observed [5 – 8] that the homologues with $n \geq 10$ exhibit both orthogonal and tilted smectic phases with quenching of the nematic phase for all values of *m*, i. e. from 1 to 16. Further, it is interesting to note that with increase of *m*, the orthogonal smectic phases also get quenched with the onset of tilted smectic-F and G phases.

As a part of systematic studies on the synthesis and characterization of *n*O.*m* compounds of different *n* and *m* values, this paper presents the results on three homologous series, viz. N-(*p*-*n*-tridecyloxybenzylidine)-*p*-*n*-alkylanilines (13O.*m*), N-(*p*-*n*-tetradecyloxybenzylidene)-*p*-*n*-alkylanilines (14O.*m*) and N-(*p*-*n*-hexadecyloxybenzylidene)-*p*-*n*-alkylanilines (16O.*m*).

Experimental

The compounds were prepared [3] by condensation of the respective alkoxy benzaldehydes (0.1 mole) and alkyl anilines (0.1 mole) in absolute ethanol by using glacial acetic acid (2 – 3 drops) as a catalyst. After refluxing the reactants during about four hours, the solvent was removed by distillation under reduced pressure. The crude samples were subjected to repeated recrystallisation with absolute ethanol till the transition temperatures were found to be concordant.

The corresponding *p*-alkoxybenzaldehydes (which are not available commercially) viz., *p*-tridecyloxy, *p*-tetradecyloxy and *p*-hexadecyloxybenzaldehydes were prepared [9] by following the standard procedure as given below.

To a cyclohexanone solution of *p*-hydroxy benzaldehyde (1.22 g) and anhydrous potassium carbonate (1.38 g), *n*–tridecyl bromide (1.63 g) or *n*–tetradecyl bromide (2.77 g) or *n*-hexadecyl bromide (3.46 g) was added drop by drop with constant stirring at its boiling temperature. The mixtures were then refluxed for 3 hours. After cooling to room temperature, the mixtures were filtered off to remove K_2CO_3 and KBr, formed during the reaction. On evaporating the cyclohexanone under reduced pressure, colorless oily products, which are the respective alkoxybenzaldehydes

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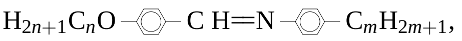
(~ 80% yield) were obtained. These oily products were purified by passing through a silica gel column using a mixture of benzene and acetone (1:4) as eluent.

The general molecular formulae of N-(*p*-*n*-alkoxybenzylidene)-*p*-*n*-alkylanilines, i. e. *n*O.*m* compounds is given by



$$H_{2n+1}C_nO-⌬-CH{=}N-⌬-C_mH_{2m+1},$$

where '*n*' and '*m*' represent the number of atoms in the alkoxy and alkyl end chains, respectively. Most of the compounds in the present work were synthesised for the first time.

The optical textural studies were carried out by using a Hertel-Reuss Super Pan II polarizing microscope, and a PC monitored INSTEC mK1 temperature controller with a temperature accuracy of ±0.01 K. A Perkin Elmer DSC 7 system was used to record the phase transition temperatures along with the change in enthalpies involved at the phase transitions.

Results and Discussion

Characterization of the liquid crystalline phases of N-(p-n-tridecyloxybenzylidene)-p-n-alkylani lines (13O.m)

It is very interesting to note that the 13O.*m* compounds exhibit six different types of phase variants, namely two different types of mono variant, three different types bi variants and a single type tri variant. The compounds 13O.1 and 13O.10 show two different types of mono phase variant. The lower alkyl chain members, viz. 13O.2, 13O.3, 13O.6 and 13O.7, exhibit one kind of bi phase variant, whereas the higher homologues, viz., 13O.9, 13O.12, 13O.14 and 13O.16 exhibit another kind of bi phase variant. The middle member of this series, viz. 13O.8, alone exhibits a different bi phase variant. The other two compounds, viz. 13O.4 and 13O.5 of this series show a tri phase variant behaviour.

The compounds with $m = 1$ to 8 on cooling from the isotropic melt, show a smectic phase S_1 in the form of batonets at 76.3, 75.0, 84.8, 84.5, 89.1, 85.5, 88.6, and 89.0 °C in the above compounds, respectively. These batonets that float in the isotropic melt, coalesce to form a focal fan texture with decrease of temperature. This phase also exhibits a pseudo isotropic texture in the homeotropic region, indicating that it has an orthogonal phase structure. Further, it is observed that the texture exhibited by these compounds is similar to that reported [10] for N-(*p*-*n*-octyloxybenzylidene)-*p*-*n*-pentylaniline. These observations indicate that the phase is smectic-A. In case of the compound 13O.1, on further cooling this liquid crystalline phase becomes solid (crystal) at 61.0 °C, i.e. this compound exhibits a mono variant liquid crystalline phase, smectic-A.

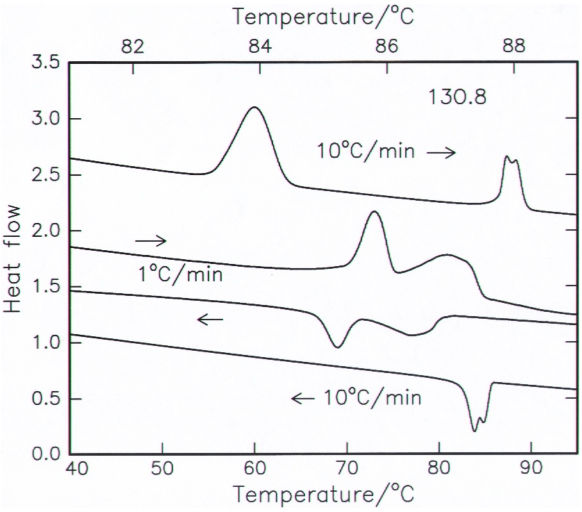


Fig. 1. D. S. C. thermogram of 13O.8.

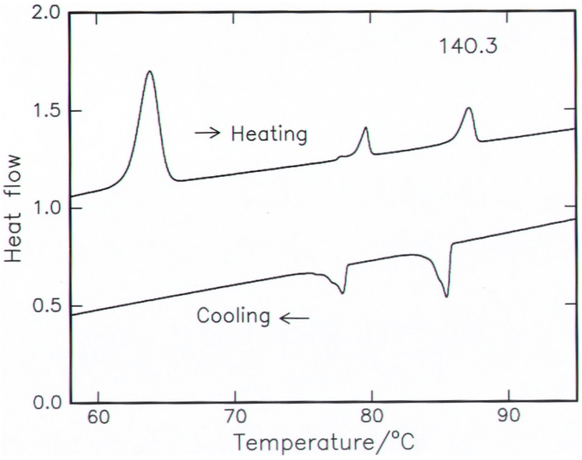


Fig. 2. D. S. C. thermogram of 14O.3.

However, in the case of other compounds this texture on further cooling shows transient transition bars across the fans which disappear slowly and transform to a smooth focal conic fan texture at 63.8, 75.8, 70.3, 81.8, 82.8, and 85.1 °C for the compounds with $m = 2$ to 7 respectively. The appearance of transient transition bars across the fans and the formation of a smooth focal conic fan texture infers [7] that this phase transition is from smectic-A to smec-

Table 1. Transition temperatures (in °C) from Thermal Microscopy and Differential Scanning Calorimetry (enthalpy values in J/g are in parentheses) for 13O.*m* compounds.

13O.*m*	Method	Phase variant	Iso. - S_1	S_1 - S_2	S_1/S_2 - S_3	$S_1/S_2/S_3$ - Crystal.
13O.1	T.M.	A	76.3			61.0
	D.S.C. (h)		(Σ)			84.75 (134.17)
	(c)		76.54 (18.37)			64.42 (104.47)
13O.2	T.M.	AB	75.0	63.8		60.0
	D.S.C. (h)		78.95 (18.20)	(#)		74.63 (97.08)
	(c)		74.71 (18.75)	64.97 (6.98)		56.57 (87.60)
13O.3	T.M.	AB	84.8	75.8		61.0
	D.S.C. (h)		85.97 (12.20)	76.29 (4.44)		62.47 (62.09)
	(c)		82.96 (12.36)	72.97 (5.57)		(*)
13O.4	T.M.	ABG	84.5	70.3	69.5	57.0
	D.S.C. (h)		85.43 (19.73)	75.77 (9.43)	72.76$^{\#}$	61.97 (81.53)
	(c)		81.52 (20.59)	72.24 (9.17)	71.19$^{\#}$	(*)
13O.5	T.M.	ABG	89.1	81.8	80.1	56.1
	D.S.C. (h)		91.98 (7.89)	84.66 (4.41)	(\$)	60.53 (28.19)
	(c)		89.25 (7.96)	81.98 (4.45)	(\$)	(*)
13O.6	T.M.	AB	85.5	82.8		55.0
	D.S.C. (h)		86.75 (20.58)	82.08 (14.72)		57.81 (82.91)
	(c)		83.14 (21.19)	81.6 (14.69)		(*)
13O.7	T.M.	AB	88.6	85.1		54.0
	D.S.C. (h)		89.87 (16.89)	86.47 (11.26)		59.21 (70.65)
	(c)		86.16 (16.66)	82.92 (11.51)		(*)
13O.8	T.M.	AF	89.0	86.2		59.0
	D.S.C. (h)		87.24 (4.75)	86.01 (4.81)		59.98 (52.20)
	(c)		86.16 (5.61)	85.02 (4.94)		(*)
13O.9	T.M.	FG	88.2	87.3		58.0
	D.S.C. (h)		89.67 (10.16)	(\$)		59.85 (104.9)
	(c)		86.64 (9.63)	(\$)		(*)
13O.10	T.M.	F	86.2			62.0
	D.S.C. (h)		89.28 (26.14)			63.90 (83.92)
	(c)		83.47 (26.49)			(*)
13O.12	T.M.	FG	89.7	87.2		76.0
	D.S.C. (h)		87.44 (22.62)	(\$)		72.35 (87.87)
	(c)		85.95 (24.67)	85.32$^{\#}$		(*)
13O.14	T.M.	FG	87.9	87.0		74.1
	D.S.C. (h)		87.57 (30.26)	(\$)		76.74 (107.9)
	(c)		83.91 (31.78)	(\$)		56.01 (97.04)
13O.16	T.M.	FG	85.2	81.1		75.0
	D.S.C. (h)		85.01 (9.53)	(\$)		78.13 (93.29)
	(c)		82.97	79.95		46.97 (76.23)

$^{\Sigma}$ merged in the crystal peak, $^{\$}$ peaks are not observed, $^{\#}$ peaks are not well resolved, * super cooled to below room temperature.

tic-B. In the case of the compound 13O.8, the cooling produces a phase S_2 which exhibits both broken focal conic fan and schlieren mosaic textures from the focal conic fan texture and homeotropic textures of smectic-A phase, respectively, at 86.2 °C. These textures are similar to those observed [10 – 12] for the smectic-F phase in the compounds 9O.4, 9O.6, 9O.8, 10O.12, and 10O.16 of the *n*O.*m* series. Therefore, this S_2 phase is confirmed as smectic-F. On further cooling, these liquid crystalline phases transform to a solid crystalline phase, indicating that these compounds exhibit a bi phase variant except of the compounds 13O.4 and 13O.5. On cooling the samples of 13O.4 and 13O.5, the smooth focal conic fan texture in the homogeneous region transformes into a striped broken focal conic fan texture at 69.5 and 80.1 °C, respectively. It is also observed that the phase is similar to that noted [10] for the smectic-G phase of N-(*p*-*n*-octyloxybenzylidene)-*p*-*n*-pentylaniline, thus characterizing the phase as smectic-G.

The compounds with $m \geq 9$ show only two smectic phases except of the compound with $m = 10$, which exhibits only one smectic phase. In these compounds, a smectic phase S_1 separates from the isotropic melt at 88.2, 86.2, 89.7, 87.9, and 85.2 °C with two different types of optical textures, viz. focal conic fan tex-

Table 2. Transition temperatures (in °C) from Thermal Microscopy and Differential Scanning Calorimetry (enthalpy values in J/g are in parentheses) for 14O.*m* compounds.

14O.*m*	Method	Phase variant	Iso. - S$_1$	S$_1$ - S$_2$	S$_1$/S$_2$ - S$_3$	S$_1$/S$_2$/S$_3$ - Crystal.
14*O*.1	T.M.	A	76.5			68.6
	D.S.C. (h)		(Σ)			82.96 (160.87)
	(c)		76.65 (21.62)			67.27 (129.64)
14*O*.2	T.M.	AB	76.0	68.0		53.0
	D.S.C. (h)		78.0 (16.76)	($)		71.6 (86.52)
	(c)		75.8 (15.93)	67.6 (7.64)		52.9 (74.0)
14*O*.3	T.M.	ABG	87.0	79.6	76.3	64.0
	D.S.C. (h)		87.1 (3.92)	79.6 (2.04)	77.7 (0.98)	63.8 (22.15)
	(c)		85.5 (4.42)	77.8 (2.30)	77.1[#]	(*)
14*O*.4	T.M.	AB	84.0	76.1		58.6
	D.S.C. (h)		84.4 (20.25)	76.5 (12.10)		60.2 (84.49)
	(c)		82.4 (20.69)	74.5 (11.75)		(*)
14*O*.5	T.M.	ABG	89.3	83.7	76.2	58.0
	D.S.C. (h)		90.6 (12.64)	84.9 (7.76)	78.1 (0.05)	57.44 (42.45)
	(c)		88.9 (12.66)	83.2 (7.62)	75.5 (0.07)	(*)
14*O*.6	T.M.	ABG	86.1	82.9	81.8	57.0
	D.S.C. (h)		88.4 (22.31)	85.2 (16.52)	($)	56.4 (58.14)
	(c)		86.6 (19.92)	83.4 (15.41)	82.50[#]	(*)
14*O*.7	T.M.	AB	90.1	88.0		49.0
	D.S.C. (h)		91.9 (14.48)	90.2 (11.03)		48.7 (37.10)
	(c)		89.9 (14.88)	88.1 (10.81)		(*)
14*O*.8	T.M.	F	88.4			57.2
	D.S.C. (h)		90.5 (30.49)			59.8 (78.37)
	(c)		88.8 (24.98)			(*)
14*O*.9	T.M.	F	92.1			60.0
	D.S.C. (h)		92.6 (34.19)			59.8 (65.78)
	(c)		90.4 (34.60)			(*)
14*O*.10	T.M.	F	91.5			66.0
	D.S.C. (h)		91.4 (19.79)			66.2 (53.52)
	(c)		89.5 (20.13)			(*)
14*O*.12	T.M.	F	90.2			68.0
	D.S.C. (h)		92.1 (29.05)			72.1 (84.45)
	(c)		90.1 (29.72)			(*)
14*O*.14	T.M.	FG	88.3	87.2		74.4
	D.S.C. (h)		90.6 (21.50)	($)		79.1 (59.80)
	(c)		88.3 (19.00)	($)		56.9 (44.30)
14*O*.16	T.M.	FG	87.5	86.1		73.0
	D.S.C. (h)		87.6 (20.19)	($)		73.0 (65.65)
	(c)		85.9 (18.61)	($)		(*)

[Σ] merged in the crystal peak, [$] peaks are not observed, [#] peaks are not well resolved, * super cooled to below room temperature.

ture (with the appearance of spherulites and lancets) and the droplet texture leading to the normal mosaic pattern of the smectic-F phase. These textures are similar to those observed [2, 11] in the case of 10O.14 and other *n*O.*m* compounds which exhibit a direct smectic-F phase from the isotropic melt on cooling. On further cooling, the smectic-F phase transforms into another smectic phase, except in 13O.10 with a broken or striped focal conic fan texture at 87.3, 87.2, 87.0, and 81.1 °C in 13O.9, 13O.12, 13O.14, and 13O.16, respectively. This texture is similar to that observed [11] for smectic-G of the 10O.14 compound. Thus the phase is characterised as smectic-G. The smectic-F phase observed in 13O.10 transforms to solid on further cooling.

The textural observations concur with the results obtained in the other *n*O.*m* compounds [7, 8, 11] which exhibit the same phase sequence.

The transition temperatures (in °C) from optical thermal microscopy (cooling) and differential scanning calorimetry along with the enthalpy values (in J/g) are given in Table 1. The DSC thermogram (both heating and cooling cycles with two different scan rates) for the compound 13O.8 is depicted in Fig. 1 as a representative case. It is observed that the two phases are well resolved with low scan rate.

Table 3. Transition temperatures (in °C) from Thermal Microscopy and Differential Scanning Calorimetry (enthalpy values in J/g are in parentheses) for 16O.*m* compounds.

16O.*m*	Method	Phase variant	Iso. - S_1	S_1 - S_2	S_1/S_2 - Crystal.
16O.2	T.M.	AB	68.2	63.0	60.2
	D.S.C. (h)		(Σ)	(Σ)	75.87 (60.64)
	(c)		(Σ)	(Σ)	64.51 (49.40)
16O.3	T.M.	AB	84.4	78.5	69.4
	D.S.C. (h)		86.84 (9.57)	80.70 (5.00)	71.77 (48.77)
	(c)		83.10 (9.12)	77.34 (4.39)	54.27 (50.39)
16O.4	T.M.	AB	82.4	75.9	66.3
	D.S.C. (h)		83.88 (9.31)	78.28 (4.76)	69.02 (45.04)
	(c)		80.39 (10.35)	74.89 (5.29)	49.47 (40.48)
16O.5	T.M.	AF	84.0	81.8	62.8
	D.S.C. (h)		90.07 (19.82)	$86.28^{\#}$	65.94 (55.99)
	(c)		84.33 (21.73)	$82.35^{\#}$	43.85 (49.10)
16O.6	T.M.	F	84.1		61.4
	D.S.C. (h)		87.91 (8.21)		65.03 (17.41)
	(c)		85.14 (8.26)		(*)
16O.7	T.M.	F	87.1		59.0
	D.S.C. (h)		91.55 (33.65)		66.85 (79.04)
	(c)		85.34 (43.14)		(*)
16O.8	T.M.	F	85.4		56.0
	D.S.C. (h)		92.04 (38.90)		67.52 (105.65)
	(c)		88.58 (41.24)		(*)
16O.9	T.M.	FG	83.4	82.8	57.0
	D.S.C. (h)		86.75 (13.17)	($)	61.67 (38.62)
					53.03 (7.70)$^{\Delta}$
	(c)		82.97 (7.82)	(#)	(*)
16O.10	T.M.	F	82.6		69.0
	D.S.C. (h)		87.06 (19.56)		70.18 (69.86)
	(c)		83.25 (16.39)		(*)
16O.12	T.M.	FG	90.8	89.1	65.0
	D.S.C. (h)		93.17 (34.64)	$88.71^{\#}$	75.68 (94.15)
	(c)		91.71 (35.22)	$89.99^{\#}$	(*)
16O.14	T.M.	FG	87.9	86.7	79.9
	D.S.C. (h)		93.31 (38.29)	(#)	80.07 (107.74)
	(c)		88.41 (41.26)	(#)	47.49 (51.17)
16O.16	T.M.	FG	80.2	77.4	63.4
	D.S.C. (h)		(Σ)	(Σ)	84.22 (99.19)
					65.90 (12.76)$^{\Delta}$
	(c)		$80.20^{\#}$	$77.25^{\#}$	62.60 (45.87)

$^{\Sigma}$ merged in the crystal peak, $^{\Delta}$ crystal-crystal transition, $^{\#}$ peaks are not well resolved, * super cooled to below room temperature.

Characterization of the liquid crystalline phases of N-(p-n-tetradecyloxybenzylidene)-p-n-alkylanilines (14O.m)

The 14O.*m* compounds exhibit five different types of phase variants, viz. two different types of single phase variants, two different double phase variants and one triple phase variant. It is observed that the compounds with alkyl chain length $m \leq 7$ exhibit mainly orthogonal smectic phases. Moreover, in some cases the tilted smectic phase exists along with the orthogonal phases. However, in case of the compounds with $m \geq 8$ tilted phases are found [7] to occur on quenching the orthogonal smectic phases. This observation is similar to that observed in the case of 13O.*m* and other higher homologues of *n*O.*m* series with short alkyl chain length $m \leq 7$ or 8.

On cooling the samples, viz. 14O.1, 14O.2, 14O.3, 14O.4, 14O.5, 14O.6 and 14O.7 from the isotropic liquid, the mesomorphic phase S_1 appears in the form of batonets at 76.5 °C, 76.0, 87.0, 84.0, 89.3, 86.1, and 90.1 °C, respectively. On further cooling, these batonets coalesce to form a focal conic fan texture along with a homeotropic pseudo isotropic texture, indicating that it is an orthogonal phase, as is found in the compounds of the 13O.*m* series, which exhibit a

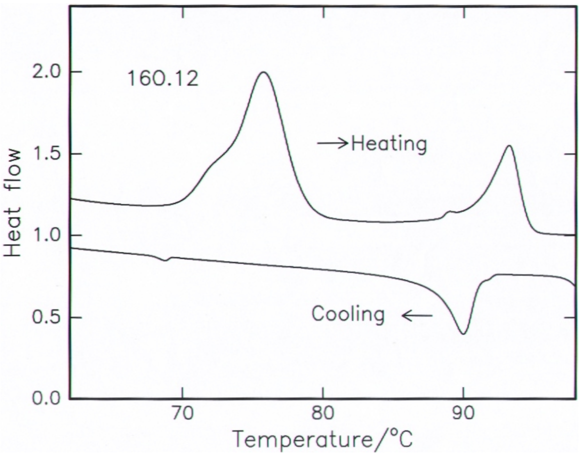


Fig. 3. D. S. C. thermogram of 16O.12.

smectic-A phase. On further cooling, as in the case of 13O.*m* series, compounds with $m = 2$ to 7, the smectic-A phase transforms into another smectic phase S_2 at 68.0, 79.6, 76.1, 83.7, 82.9, and 88.0 °C. The transition is evidenced by the appearance of the transient transition bars across the focal conic fans of the smectic-A phase. These transient transition bars slowly disappear after the completion of the transition, leading to a smooth focal conic fan texture. This texture is different from that observed in smectic-A, and the appearance of transient transition bars across the phase boundary (on the fans) further characterises the present S_2 phase (in analogy with those observed in case of 13O.2, 13O.3, 13O.4, 13O.5 and 13O.6) as smectic-B phase. On further cooling, the smectic-B phase in the compounds with $m = 3$, 5, and 6 transforms to another smectic phase with the appearance of striped broken focal conic fan texture similar to that observed in 13O.5 characterizing it as smectic-G phase. However, the smectic-B phase texture in case of the compounds 14O.2, 14O.4, and 14O.7 is observed to transform into a crystalline solid on further cooling.

The compounds with $m = 8$ to 12 show only one smectic phase, and the compounds with $m = 14$ and 16 exhibit two smectic phases. In the compounds 14O.8, 14O.9, 14O.10, 14O.12, 14O.14 and 14O.16 a smectic phase S_1 separates from the isotropic melt at 88.4, 92.1, 91.5, 90.2, 88.3, and 87.5 °C with two different types of optical textures during cooling, viz. a focal conic fan texture (with the appearance of spherulites and lancets) and the droplet texture leading to the normal mosaic pattern (as that has been observed in 13O.10 and other compounds, which show [11] direct by the smectic-F phase from the isotropic liquid). On further cooling, the smectic-F phase transforms into another smectic phase with a striped or broken fan texture in the case of 14O.14 and 14O.16 at 87.2 and 86.1 °C, indicating it as a smectic-G phase. However, the smectic-F phase observed in 14O.8 to 14O.12 transforms to solid on further cooling.

The transition temperatures from thermal microscopy and DSC along with the enthalpy values are given in Table 2. The DSC thermogram for the compound 14O.3 (both on heating and cooling) is depicted in Fig. 2 as a representative case.

Characterization of the liquid crystalline phases of N-(p-n-hexadecyloxybenzylidene)-p-n-alkylanilines (16O.m)

These compounds show three different bi phase variants and a unique mono phase variant. Unlike the case of 13O.*m* and 14O.*m* compounds, the 16O.*m* compounds exhibit only mono and bi phase variants. The tri phase variance, present in the other lower and higher homologous series of *n*O.*m* compounds, viz. $n = 10$, 11, 12, 13, 14, 15, and 18, is absent. Further, it has been observed that the manifestation of a single phase variant is predominant and conspicuously with the tilted smectic-F phase. Quenching of liquid crystalline nature is observed in the case of 16O.1, where the solid crystalline phase melted directly to isotropic liquid without showing any mesophase.

On cooling the isotropic phase, the compounds with $m = 2$, 3, 4, and 5 show a similar type of phase behaviour as observed for the lower homologues of the 14O.*m* compounds and the same texture, viz. the onset of batonets and the transformation of these into a focal conic fan texture and characterizing it as smectic-A phase. These transformations occur at 68.2, 84.4, 82.4, and 84.0 °C for compounds with $m = 2$, 3, 4, and 5, respectively. On further cooling this phase shows transient transition bars across the fans, which smoothen out to exhibit a smooth focal conic fan texture except in 16O.5. This observation is similar to that noted for the lower homologues of the other two series, viz. 13O.*m* and 14O.*m*, and this result characterises the phase as smectic-B. The compound with $m = 5$, on further cooling the smectic-A phase transformed into a broken focal conic fan texture at 81.8 °C in the homogeneous regions, and in the pseudo isotropic regions the schlieren texture is observed. It is also observed that the textural changes are similar to those reported [12] for 9O.4

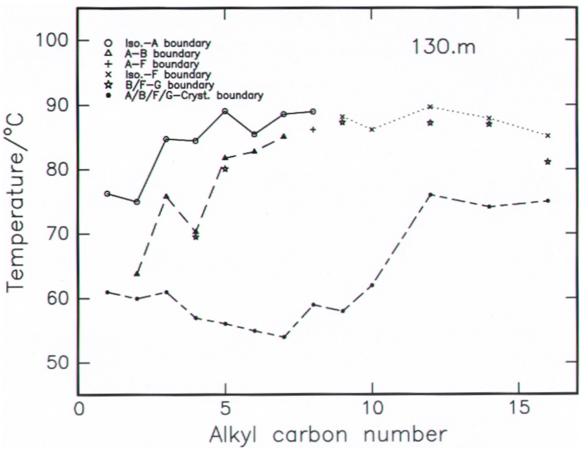


Fig. 4. Phase diagram of 13O.*m* compounds.

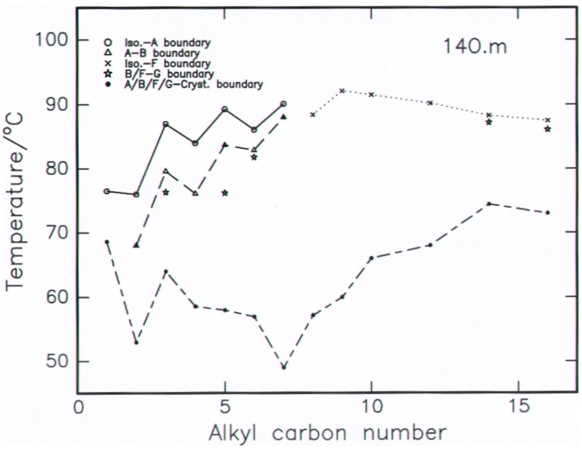


Fig. 5. Phase diagram of 14O.*m* compounds.

of the *n*O.*m* series. Thus, this phase is characterized as smectic-F phase.

The cooling of the isotropic phase of the compounds with $m = 6$ to 10, 12, 14, and 16 shows two different types of optical textures, viz. the focal conic fan texture (with the appearance of spherulites and lancets) and the droplet texture leading to the normal mosaic pattern of smectic-F phase as that having been observed [11] in 13O.10, 14O.10, 15O.10. The compounds with $m = 6$ to 8 and 10, on further cooling transform to the solid crystal state, while the other four compounds exhibit a striped focal conic fan texture characterizing it as smectic-G phase (similar to that observed in 14O.12 and other compounds which show the FG phase sequence).

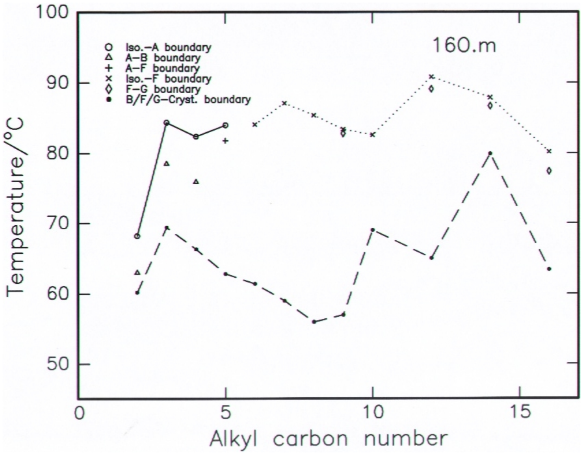


Fig. 6. Phase diagram of 16O.*m* compounds.

The thermal data from the optical polarizing microscopy and differential scanning calorimetry for this series of compounds is given in Table 3. The DSC thermogram for the compound 16O.12 (both heating and cooling cycles) is depicted in Fig. 3 as a representative case. The phase diagrams of the 13O.*m*, 14O.*m* and 16O.*m* series are given in Figs. 4, 5, and 6, respectively.

The following table depicts the liquid crystalline phase variants in the three series.

n/m	1	2	3	4	5	6	7	8	9	10	12	14	16
13	A	AB	AB	ABG	ABG	AB	AB	AF	FG	F	FG	FG	FG
14	A	AB	ABG	AB	ABG	ABG	AB	F	F	F	F	FG	FG
16	–	AB	AB	AB	AF	F	F	F	FG	F	FG	FG	FG

The comparison of these results regarding the phases of the higher homologues of the *n*O.*m* compounds with $n \geq 10$ reveals that the compounds with shorter alkyl chains favour two dimensional orthogonal phases rather than tilted phases. The body of the data shows that the compounds with a total number of carbon atoms > 22 in the flexible end chains of *n*O.*m* compounds exhibit the tilted phase directly from the isotropic melt on cooling. The minimum number of carbon atoms in the alkoxy and alkyl chains required for the manifestation of the single phase variant (smectic-F) is $n = 13$ and $m = 10$. It has been observed that the smectic-F phase in combination with other phases (both orthogonal and tilted) occurs also in other compounds, not with standing the fact that it is being found more coexistent with the smectic-G phase.

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