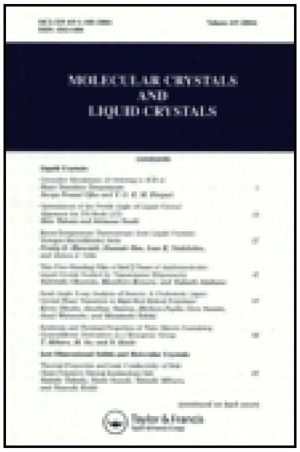

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Mesomorphic Homologous Series 4-Formylphenyl 6-n-Alkoxy-2-Naphthalenecarboxylates (I) and 2-Acetylnaphthalen-6-yl 4-n-Alkoxybenzoates (II)

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Mesomorphic Homologous Series

4-Formylphenyl 6-*n*-Alkoxy-2-Naphthalenecarboxylates (I) and 2-Acetylnaphthalen-6-yl 4-*n*-Alkoxybenzoates (II)

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Two homologous series of naphthalene derivatives have been synthesized and the mesomorphic behaviour of their members has been studied. In series I the first nine members are enantiotropic nematic, the decyl derivative exhibits a reentrant nematic phase and enantiotropic smectic and nematic phases while the remaining members are enantiotropic smectic. In series II the first seven members exhibit nematic, the octyl derivative exhibits monotropic smectic and enantiotropic nematic phases and the remaining members are enantiotropic smectic and nematic or only smectic. The thermal stability of these series is compared with the corresponding homologous series of coumarin derivatives.

1. INTRODUCTION

Trivedi and Thaker[1] presented the two mesomorphic heterocyclic homologous series 4-formylphenyl 7-alkoxy-2-oxo-2*H*-1-benzopyran-3-carboxylates (III) and 3-acetyl-2-oxo-2*H*-1-benzopyran-7-yl 4 alkoxybenzoates (IV). We report here the synthesis and the study of mesomorphic behaviour of the two corresponding homologous series 4-formylphenyl 6-*n*-alkoxy-2-naphthalenecarboxylates (I) and 2-acetylnaphthalen-6-yl 4-*n*-alkoxybenzoates (II) and the comparison of their thermal stabilities with those of the corresponding coumarin series.

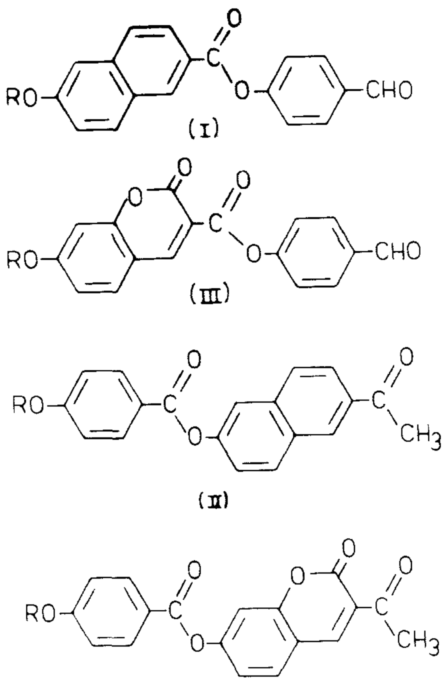

FIGURE 1

2. RESULTS

Series I: 4-formylphenyl 6-*n*-alkoxy-2-naphthalenecarboxylates

Melting points and transition temperature of the compounds synthesized are compiled in Table I. The first nine members exhibit an enantiotropic nematic phase. The smectic phase commences with the decyl derivative which exhibits both smectic and nematic enantiotropic phases and a reentrant nematic phase. The rest of the members are enantiotropic smectic. All the compounds adopt homeotropic textures when heated. When the nematic–isotropic transition points are plotted against the number of carbon atoms in the alkyl chain, they show the usual odd-even effect. The smectic–isotropic and nematic–isotropic transition points merge with one another. (Figure 2).

The thermal stabilities of the compounds of series I are compared with those of 4-formylphenyl 7-alkoxy-2-oxo-2*H*-1-benzopyran-3-carboxylates in Table III.

TABLE I

4-Formylphenyl 6-*n*-alkoxy-2-naphthalenecarboxylates (I)

	Transition temperatures (°C)				
Compound	Alkyl group	Reentrant	Smectic	Nematic	Isotropic
1	Methyl	—	—	130.0	159.5
2	Ethyl	—	—	135.5	167.5
3	Propyl	—	—	101.5	137.5
4	Butyl	—	—	107.5	144.5
5	Pentyl	—	—	106.5	128.0
6	Hexyl	—	—	108.0	134.0
7	Heptyl	—	—	83.5	127.5
8	Octyl	—	—	75.5	125.5
9	Nonyl	—	—	82.0	123.5
10	Decyl	55.0	76.5	102.5	123.0
11	Dodecyl	—	89.0	121.0	123.0
12	Tetradecyl	—	91.5	—	125.0
13	Hexadecyl	—	84.5	—	125.5
14	Octadecyl	—	93.0	—	126.0

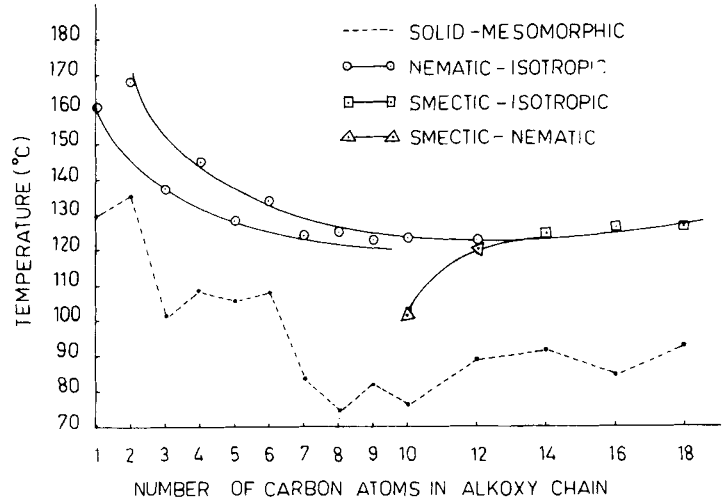

FIGURE 2 Transition temperatures of 4-formylphenyl 6-*n*-alkoxy-2-naphthalenecarboxylates.

Series II: 2-acetylnaphthalen-6-yl 4-*n*-alkoxybenzoates

Melting points and transition temperatures of the compounds of this series are compiled in Table II. The first seven members are enantiotropic nematic. The smectic phase commences with the octyl derivative which exhibits smectic monotropic and nematic enantiotropic phases. The nonyl and decyl derivatives exhibit both smectic and nematic enantiotropic phases. The remaining members are enantiotropic smectic. All the members adopt homeotropic textures when heated. The nematic–isotropic points, when plotted against the number of carbon atoms in the alkyl group, show a descending tendency. The

TABLE II

2-Acetylnaphthalen-6-yl 4-*n*-alkoxybenzoates (II)

Compound	*n*-Alkyl group	Transition temperature (°C)		
		Smectic	Nematic	Isotropic
15	Methyl	—	190.0	197.5
16	Ethyl	—	179.0	199.5
17	Propyl	—	142.5	175.0
18	Butyl	—	140.5	173.5
19	Pentyl	—	118.5	163.5
20	Hexyl	—	117.0	163.5
21	Heptyl	—	113.0	156.0
22	Octyl	(107.5)	111.5	156.5
23	Nonyl	109.5	134.5	150.0
24	Decyl	110.5	142.0	151.5
25	Dodecyl	105.0	—	149.0
26	Tetradecyl	105.5	—	153.5
27	Hexadecyl	108.0	—	155.0
28	Octadecyl	109.5	—	156.5

Values in the parenthesis indicate monotropy.

TABLE III

Average transition temperatures of series I–IV (°C)

		I	II	III	IV
(i)	Nematic–isotropic	139.9	—	165.5	144.2
(ii)	Smectic–isotropic	125.5	156.0	151.4	155.5
(iii)	Smectic–Nematic	102.5	—	128.8	142.0
(iv)	Commencement of smectic phase	C_{10}	C_8	C_6	C_5

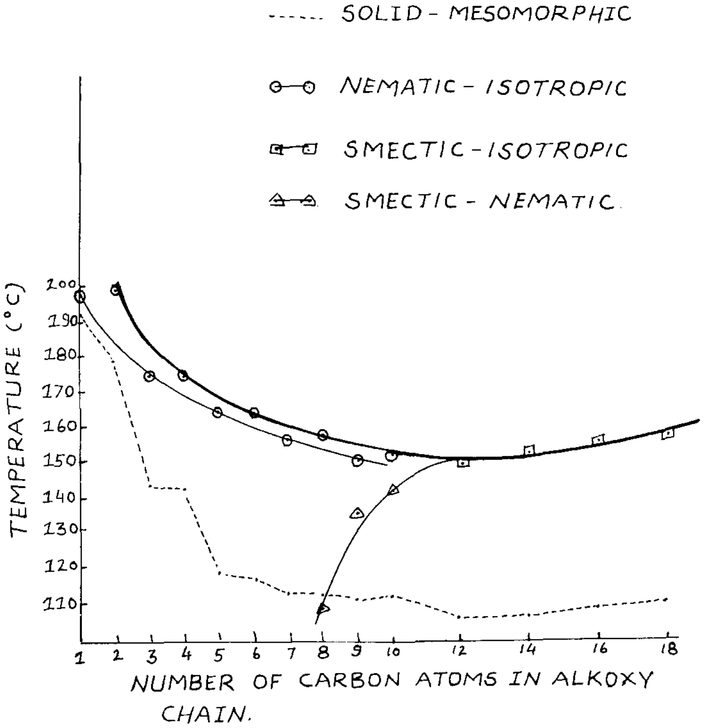

FIGURE 3 Transition temperatures of 2-acetylnaphthalen-6-yl 4-*n*-alkoxybenzoates.

The nematic–isotropic points, when plotted against the number of carbon atoms in the alkyl group, show a descending tendency. The

The thermal stabilities of the members of series (II) are compared with those of 3-acetyl-2-oxo-2*H*-1-benzopyran-7-yl 4-alkoxybenzoates in Table III.

Structural formulae of the two series are shown in Figure 1. The mesophases of series I are thermally less stable than those of series III (Table III). The molecules of series III contain a coumarin nucleus whereas the molecules of series I contain a naphthalene nucleus. The presence of a lactone ring in the coumarin nucleus creates a permanent dipole across the major axis of the molecules giving rise to greater nematic thermal stability. Secondly, in series I the polarizability effect is only along the major molecular axis, whereas in series III it is along the major molecular axis as well as in the lateral direction. Therefore, the smectic thermal stability of series III will be greater and the nematic thermal stability smaller.

TABLE IV

Transition temperature of compound number 10
(4-formylphenyl 6-*n*-decyloxy-2-naphthalenecarboxylate)

Heating (°C)		Cooling (°C)	
Solid–Smectic	76.5	Isotropic–Nematic	123.0
Smectic–Nematic	102.5	Nematic–Smectic	102.5
Nematic–Isotropic	123.0	Smectic–Reentrant nematic	55.0
		Reentrant–Solid	50.5

NEMATIC REENTRANT PHASE

The reentrant nematic phase (the phase occurring below the smectic phase) was first reported by Cladis.[2-3] Recently there have been reports that molecules containing terminal —CHO, —CN and —NO_2 groups have a tendency to exhibit the reentrant nematic phase.

The decyl derivative of the 4-formylphenyl ester of 6-*n*-alkoxy-2-naphthoic acid exhibits a reentrant nematic phase. On cooling the isotropic liquid of this derivative the normal nematic phase appeared at 123°, the smectic phase at 102.5° and before it was supercooled to the solid, the reentrant nematic phase appeared at 55° (Table IV). The reentrant nematic phase was identified by the typical Schlieren textures and the mobility of this phase when the cover slip is displaced.

The thermal stabilities of series II and IV are almost equal (Table III) because their molecules are almost identical in length. Furthermore, the lateral attractions due to the C=O group of the lactone ring in series IV is less effective as it operates almost at the end of the molecules and renders the close packing of molecules rather difficult. The lateral intermolecular attractions are weaker.

The smectic phase in series I and II commences later compared to series III and IV, respectively.

EXPERIMENTAL

Melting points and transition temperatures were determined using a Leitz Ortholux Polarizing Microscope equipped with a heating stage. In the neighbourhood of each phase transition, the temperature was raised at the rate of 0.5° per minute.

PREPARATION OF COMPOUNDS

Series – I

1. 6-Acetyl-2-methoxynaphthalene was prepared according to Robinson and Rydon.[4]

2. 6-Methoxy-2-naphthoic acid, 6-Hydroxy-2-naphthoic acid, 6-*n*-Alkoxy-2-naphthoic acid and 6-*n*-Alkoxy-2-naphthoyl chlorides were prepared according to Gray and Jones.[5]

3. 4-Formylphenyl 6-*n*-alkoxy-2-naphthalenecarboxylates: 6-*n*-Alkoxy-2-naphthoyl chlorides (0.005 mol) and p-hydroxybenzaldehyde (0.005 mol) were dissolved in 10 ml dry pyridine and heated on a water bath for 2 hr. The reaction mixture was left overnight and was then poured into cold diluted HCl. The solid product obtained was

TABLE V

Analytical values

Compound	Molecular formula	% Calculated		% Found	
		C	H	C	H
1	$C_{19}H_{14}O_4$	74.50	3.98	74.09	4.46
2	$C_{20}H_{16}O_4$	75.01	5.00	74.66	4.96
3	$C_{21}H_{18}O_4$	75.46	5.39	75.54	5.74
4	$C_{22}H_{20}O_4$	75.86	5.74	76.12	5.59
5	$C_{23}H_{22}O_4$	76.25	6.07	75.83	6.10
6	$C_{24}H_{24}O_4$	76.60	6.38	76.18	6.34
7	$C_{25}H_{26}O_4$	76.91	6.66	76.68	6.24
8	$C_{26}H_{28}O_4$	77.23	6.93	76.78	6.62
9	$C_{27}H_{30}O_4$	77.50	7.17	77.04	7.12
10	$C_{28}H_{32}O_4$	77.76	7.40	77.36	7.31
11	$C_{30}H_{36}O_4$	78.26	7.82	78.25	7.59
12	$C_{32}H_{40}O_4$	77.50	7.17	77.04	7.12
13	$C_{34}H_{44}O_4$	79.11	8.52	78.70	8.12
14	$C_{36}H_{48}O_4$	79.41	8.82	78.97	8.34
15	$C_{20}H_{16}O_4$	75.01	5.00	74.94	4.64
16	$C_{21}H_{18}O_4$	75.44	5.38	75.01	5.21
17	$C_{22}H_{20}O_4$	75.86	5.74	75.42	5.30
18	$C_{23}H_{22}O_4$	76.25	6.07	75.80	5.84
19	$C_{24}H_{24}O_4$	76.60	6.38	76.22	5.94
20	$C_{25}H_{26}O_4$	76.91	6.66	76.55	6.40
21	$C_{26}H_{28}O_4$	77.22	6.93	76.88	6.67
22	$C_{27}H_{30}O_4$	77.50	7.17	77.03	7.28
23	$C_{28}H_{32}O_4$	77.80	7.40	78.24	7.51
24	$C_{29}H_{34}O_4$	78.03	7.62	77.59	7.41
25	$C_{31}H_{38}O_4$	78.47	8.01	78.04	8.01
26	$C_{33}H_{42}O_4$	78.89	8.36	78.42	7.88
27	$C_{35}H_{46}O_4$	79.23	8.68	78.75	8.21
28	$C_{37}H_{50}O_4$	79.58	8.92	79.14	8.48

collected, washed with 10% NaOH followed by H_2O. Crystallisation from petroleum ether gave colourless flakes. Yield 48%.

The structure of the 4-formylphenyl 6-ethoxy-2-naphthalenecarboxylate (No. 2) is confirmed by the NMR spectrum ($CDCl_3$) 1.5 (t, 3 H, $—CH_3$ group of ethoxy chain), 4.2 (q, 2 H, $—CH_2—O$ of ethoxy chain), 7.15–8.2 (m, 6 H, Arom Protons of Naphthalene), 7.45 (d, $J = 9$ Hz, 2 H, C_1 and C'_6 protons), 7.85 (d, $J = 9$ Hz, 2 H, C'_3, and C'_5 protons), 8.65 (m, 1 H, C_4, of —CHO group).

Analyses are recorded in Table V.

Series - II

1. 6-Hydroxy-2-acetylnaphthalene was prepared according to Desai and Desai.[6]

2. p-*n*-Alkoxybenzoic acids and p-*n*-Alkoxybenzoyl chlorides were prepared as described by Dave and Vora.[7]

3. 2-Acetylnaphthalen-6-yl 4-*n*-alkoxybenzoates: p-*n*-Alkoxybenzoyl chlorides (0.005 mol) and 6-hydroxy-2-acetyl-naphthalene (0.005 mol) were dissolved in 10 ml dry pyridine and refluxed for 10 minutes. The mixture was left overnight and poured into ice-cold dil. HCl. The product, collected by filtration, was washed with 10% NaOH and H_2O. Colourless needles were obtained by crystallisation from petroleum ether or ethanol (charcoal). Yield 43%.

The structure of the 2-acetylnaphthalen-6-yl 4-*n*-decyloxybenzoate (No. 23) is confirmed by the NMR spectrum. ($CDCl_3$) 0.90 (t, 3 H, terminal CH_3 group of decyloxy chain), 1.2–2.2 (m, 16 H, $—(CH_2)_2$ —of the decyloxy chain), 2.7 (s, 3 H, $—COCH_3$), 4.05 (t, 2 H, $—CH_2$ —O of decyloxy chain), 7.0 (d, $J = 9$ Hz, 2 H, C_3, and C'_5, proton), 7.32–8.05 (m, 5 H, Aromatic protons of naphthalene), 8.15 (d, $J = 9$ Hz, C'_2, and C'_6 protons), 8.45 (s, 1 H, C_1 proton).

Analyses are recorded in Table V.

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