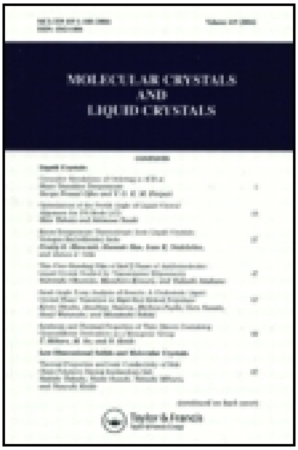

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Effect of Chain Branching on Mesomorphism in Broad Molecules†

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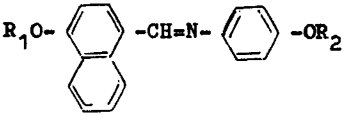
Two new homologous series of Schiff's bases having the structure



where R_1 = *n*-alkyl; R_2 = *n*-C_5H_{11} (I), *i*-C_5H_{11} (II) were synthesised. The method of preparation and the liquid crystalline properties of these compounds are described. Both series are nematogenic; the smectic phase is absent even in higher members of the series. In series I, the C_2 and C_3 homologue exhibit two solid modifications. The influence of branching in the end alkoxy groups of these compounds on the mesomorphism is discussed. The mesomorphic properties of these compounds are compared with those of related compounds.

INTRODUCTION

Terminal substituents play a vital role in imparting liquid crystallinity to a potentially mesomorphic compound. Generally in a liquid crystalline compound, the end groups are alkyl, alkoxy or a compact unit like CN, NO_2, halogen etc. A number of studies are known wherein

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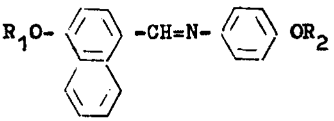
the influence of the end groups on mesomorphism is investigated and terminal group efficiency orders have been deduced.[1-3] However most of these studies were carried out on classical liquid crystalline compounds built of benzene units. In the present study the effect of branching of terminal substituents on broad nematogenic molecules constituting homologous series are investigated.

RESULTS AND DISCUSSION

Two homologous series of liquid crystalline Schiff's bases of general structure I and II were synthesised by condensing 4-*n*-alkoxy-1-naphthaldehydes with the corresponding *p*-alkoxyanilines.



$R_1 = n$-Alkyl $\quad R_2 = n$-C_5H_{11}-I, $\quad i$-C_5H_{11}-II†

The melting points and mesomorphic transition temperatures of these compounds are compiled in Tables I and II.

In series I, the 4-*n*-alkoxy-1-naphthylidene-*p*-*n*-pentyloxyanilines, the methyl, propyl, pentyl, hexadecyl and octadecyl members are non-mesomorphic. The C_4, C_9, C_{12} and C_{14} derivatives exhibit enantiotropic nematic phases, and the others are monotropic nematic. The smectic phase is found to be absent in the series. Two solid-solid modifications C_I and C_{II} are exhibited by the ethyl and propyl derivatives. The stable solid modification C_I has a higher melting temperature than the metastable solid modification C_{II}. In the case of the ethyl derivative, both solid forms on heating give the isotropic liquid which, on cooling, gives the monotropic nematic phase and this on further cooling gives solid modification C_{II} (Fig. 1a). In the case of propyl derivative no nematic phase is obtained by cooling the isotropic liquid which crystallises to give the C_{II} solid modification (Fig. 1b). In both cases, the metastable C_{II} modification on standing transforms to stable C_I modification.

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†i-C_5H_{11} is $(CH_3)_2CHCH_2CH_2$-

TABLE I

4-*n*-Alkoxy-1-naphthylidene-*p*-*n*-pentyloxyanilines
$RO.C_{10}H_6.CH = N.C_6H_4.OC_5H_{11}(n)$

	Alkyl Group *R*	Transition Temperatures (°C) C-N or N-I	C-I or N-I
1	Methyl	—	86.5
2	Ethyl	(61.5)	81.5 (I) 74.5 (II)
3	Propyl	—	78.0 (I) 68.0 (II)
4	Butyl	62.5	64.5
5	Amyl	—	68.5
6	Hexyl	(65.5)	73.5
7	Heptyl	(55.5)	66.0
8	Octyl	(66.0)	80.0
9	Nonyl	55.5	64.0
10	Decyl	(66.0)	73.5
11	Dodecyl	62.5	64.5
12	Tetradecyl	58.0	61.5
13	Hexadecyl	—	71.5
14	Octadecyl	—	58.5

C = crystal, N = nematic, I = isotropic liquid. Values in parentheses indicate monotropy.

TABLE II

4-*n*-Alkoxy-1-naphthylidene-*p*-*i*-pentyloxyanilines
$RO.C_{10}H_6.CH = N.C_6H_4.OC_5H_{11}(i)$

	Alkyl Group *R*	TransitionTemperatures (°C) N-I	C-I
1	Methyl	—	104.5
2	Ethyl	—	102.5
3	Propyl	—	78.0
4	Butyl	(50.0)	68.5
5	Amyl	(40.5)	56.0
6	Hexyl	(51.5)	58.0
7	Heptyl	(43.0)	67.0
8	Octyl	(48.5)	56.5
9	Nonyl	(44.5)	56.5
10	Decyl	(47.5)	53.5
11	Dodecyl	(36.0)	52.0
12	Tetradecyl	—	52.5
13	Hexadecyl	—	72.0
14	Octadecyl	—	80.0

C = crystal, N = nematic, I = isotropic liquid. Values in parentheses indicate monotropy.

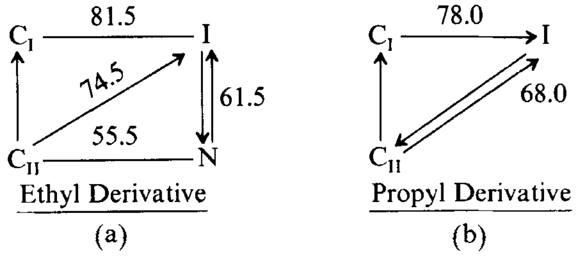


FIGURE 1

When the transition temperatures of the compounds of this series are plotted against the number of carbon atoms in the aldehyde alkoxy chain, the nematic-isotropic transitions lie on two curves exhibiting an odd-even effect which is however apparent for the heptyl and nonyl members only. (Fig. 2). This is because the initial odd members are non-mesomorphic. A unique phenomenon observed

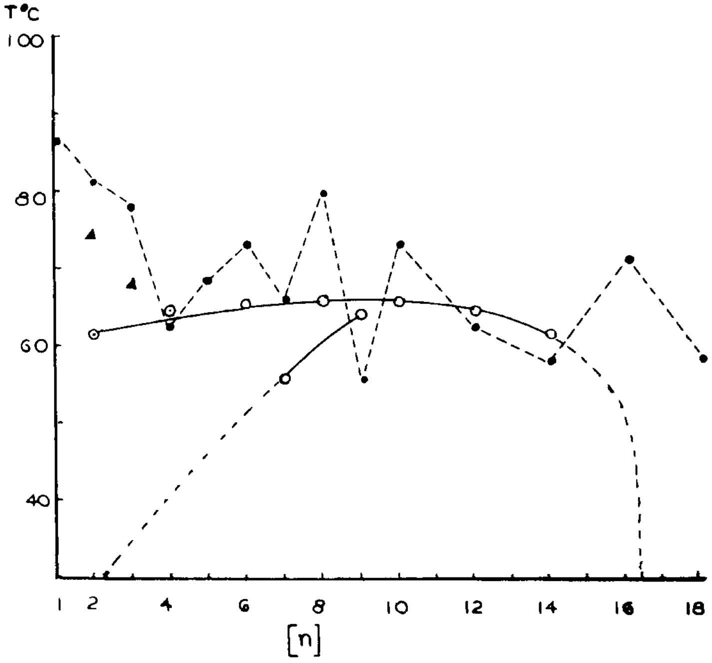


FIGURE 2 Transition temperatures as a function of the number (n) of carbon atoms in the alkoxy chain (R_1) of the 4-*n*-Alkoxy-1-naphthylidene-*p*-*n*-pentyloxyanilines, (●) Solid-Isotropic, (○) Nematic-Isotropic, (▲) Solid-Solid.

in this series is the sudden drop in the curve for the higher members, the last members studied (C_{16} and C_{18}) being non-mesomorphic.

In series II, the 4-*n*-alkoxy-1-naphthylidene-iso-pentyloxyanilines, the methyl, ethyl, propyl, tetradecyl, hexadecyl and octadecyl members are non-mesomorphic. The C_4 to C_{12} derivatives exhibit monotropic nematic phases. The smectic phase is absent in this series also. When the transition temperatures are plotted against the number of carbon atoms in the aldehyde alkoxy chain, the N-I transitions exhibit a marked odd-even effect and lie on two curves which are convex in nature (Fig. 3). In this series also, the even curve falls off steeply after the C_{10} derivative; the higher members are non-mesomorphic.

In the corresponding benzylidene series,[4,5] the initial members are nematic, the middle members are both smectic and nematic and the higher homologues are only smectic. The broad naphthalene moiety

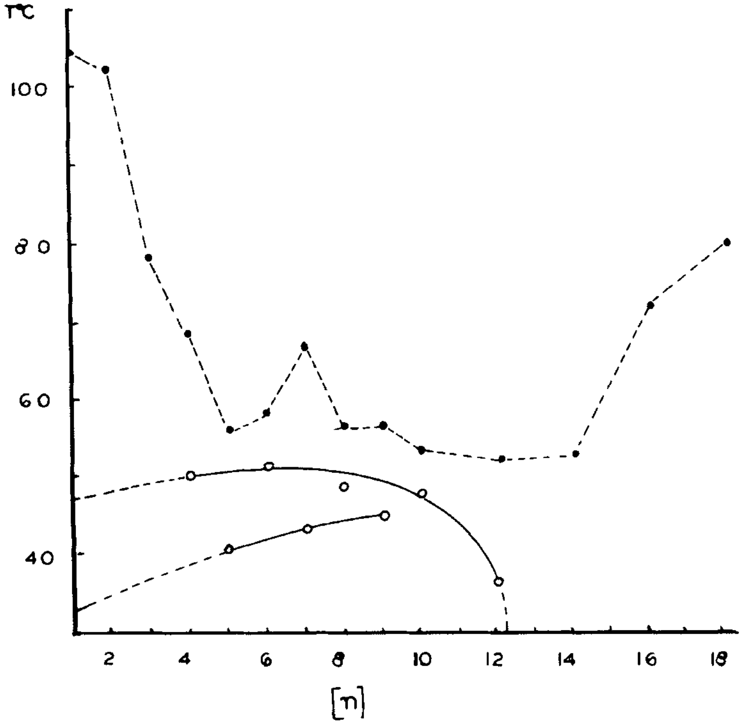
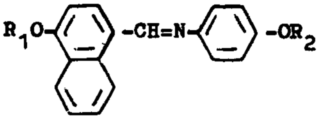


FIGURE 3 Transition temperatures as a function of the number (*n*) of carbon atoms in the alkoxy chain (R_1) of the 4-*n*-Alkoxy-1-naphthylidene-*p*-*i*-pentyloxyanilines, (●) Solid-Isotropic, (○) Nematic-Isotropic.

TABLE III

Average Thermal Stability in °C



Series	R_2	Average N-I(R_1 = C_6 − C_{12})
I	$n-C_5H_{11}$	63.5
II	$i-C_5H_{11}$	45.1
III	$n-C_4H_9$	68.3[7]
IV	$n-C_3H_7$	58.9[7]
V	C_2H_5	71.8[6]

of the present series apparently reduces the lateral attractions to such an extent that the smectic phase is not formed at all. The end to end cohesions are also disrupted in the higher homologues due to the longer alkoxy groups, causing the disappearence of the nematic phase also. This phenomenon is more apparent in the case of the iso-amyloxy series, wherein the end alkoxy group is branched. This appears to cause hindrance to the end to end cohesions, and so the nematic phase disappears earlier and also the N-I thermal stability is reduced considerably.

Table III summarises the average thermal stabilities of the present

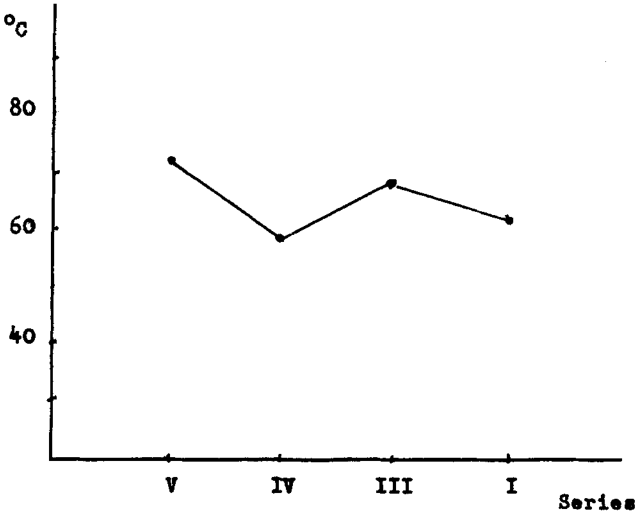


FIGURE 4

series and compares them with related series. All the series compared are similar except for the end alkoxy group R_2. On plotting the average thermal stabilities for these series (I, III, IV, and V) against the number of carbon atoms in R_2, a marked odd-even effect is observed. (Fig. 4). The average thermal stability of series II is the lowest, due to the branching in the end alkoxy group.

EXPERIMENTAL

A. Preparation of compounds

i. *p-Alkoxyanilines* were prepared by the alkylation of *p*-nitrophenol with alkyl bromides followed by reduction of the *p*-alkoxynitrobenzene thus obtained.[4,5]

ii. 4-*n-Alkoxy*-1-*naphthaldehydes* were prepared according to Dave *et al.*[8]

iii. *Schiff's Bases* were prepared by heating equimolecular quantities of the aldehyde and aniline in ethanol under reflux for about one hour. On cooling, the crude product separated out, and was purified by repeated crystallisation from ethanol. The melting points and transition temperatures of these compounds are summarized in Tables I and II. All these compounds gave satisfactory elemental analysis results.

B. Determination of transition temperatures

These were determined with a Leitz Ortholux Polarizing microscope equipped with a Leitz heating stage as described elsewhere.[8]

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