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Influence of Naphthalene Moiety on Mesomorphism†

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Compounds containing naphthalene moiety are synthesized and the liquid crystalline properties studied by texture observations. The mesomorphic properties of these compounds are compared with related compounds to understand the influence of broad units such as naphthalene on mesomorphism. It is observed that there is a limit to which the end alkoxy group can be extended in a mesogen. The method of preparation, and properties of these compounds are given.

INTRODUCTION

Of the large number of liquid crystals known, only a few contain broad molecules such as naphthalene units. Mesomorphism in anisylidene 2,6-, 1,5- and 1,4- diaminonaphthalenes was reported by Wiegand[1] in 1954. Gray and Jones[2] investigated liquid crystalline properties of different alkoxy naphthoic acids. Dave and co-workers studied a variety of liquid crystalline compounds exhibiting smectic, nematic and cholesterol mesomorphism, containing naphthalene moiety such as alkoxybenzoates of 1,5- and 1,4- dihydroxynaphthalene,[3] esters of cholestrol[4,5] and alkoxy naphthylidene Schiff's bases.[6,7,8] The present attempt is to further investigate the imfluence of naphthalene moiety on short liquid crystalline molecules.

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TABLE I

4-n-Alkoxy-1-naphthylidene-4′-ethoxyanilines—RO. $C_{10}H_6 - CH = C_6H_4 - OC_2H_5$

Compound	Alkyl Group (*R*)	Transition Temperatures (°C) Nematic/Isotropic	Solid/Isotropic
1	Methyl	—	102.5
2	Ethyl	(75.0)	116.5
3	Propyl	(54.5)	102.0
4	Butyl	(75.0)	109.5
5	Pentyl	(65.6)	98.0
6	Hexyl	(94.5)	85.0
7	Heptyl	(69.0)	77.0
8	Octyl	(73.5)	76.5
9	Nonyl	(70.0)	78.0
10	Decyl	(72.5)	87.5
11	Dodecyl	(71.0)	74.5
12	Tetradecyl	(68.5)	81.0
13	Hexadecyl	—	87.5
14	Octadecyl	—	87.0

RESULTS AND DISCUSSION

Here we report the mesomorphic behavior of a series 4-*n*-alkoxy-1-naphthylidene-4′-alkoxyanilines.

The transition temperatures of the compounds are given in Table I. All the members of this series are monotropic nematic except the methoxy, hexadecyloxy and octadecyloxy derivatives which are non-mesomorphic. The smectic phase is completely absent in this series.

The transition temperatures *vs* the number of carbon atoms in the alkoxy chain plot of the series is given in Figure 1. The *N–I* curve exhibits a marked odd-even effect; the odd member curve is convex, ascends steeply and flattens out at C_9–derivative. However, it does not merge with the even member curve. The even member curve is almost parallel to the X-axis and shows a tendency to fall towards the end. Similar is the behavior of the *N–I* curves in corresponding series obtained by condensing 4-*n*-alkoxy-1-naphthaldehydes with propoxy, butoxy and pentyloxy anilines.[9] In these cases also the *N–I* curve dips suddenly and last members are non-mesomorphic.

As each methylene unit in the end alkoxy group is increased the polarizable centers of the molecules are forced apart decreasing the terminal cohesions; this leads to the reduction in the nematic stability and a stage will soon be reached wherein the molecules will show no nematic phase. Usually in a normal homologous series the smectic phase appears at this

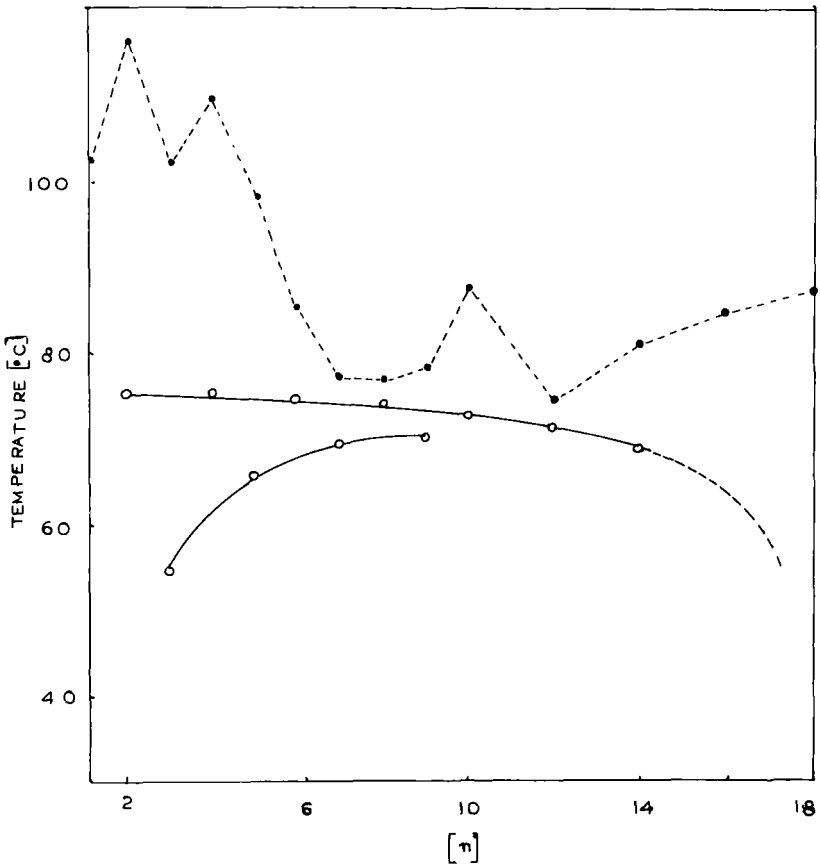

FIGURE 1 Transition temperatures as a function of the number (n) of carbon atoms in the alkyl chain of 4-*n*-alkoxy-1-naphthylidene-4′-ethoxyaniline: (●) Solid-Isotropic; (○) Nematic-Isotropic.

juncture. But in those series wherein the lateral attractions are weak as in the present case due to the broad naphthalene nucleus, the smectic phase fails to appear and results in such type of behavior. This is indicative of the fact that there is a limit to which the terminal alkoxy group can be extended for a nematic liquid crystal.

In the homologous series wherein R_2 is phenyl (4-*n*-alkoxy-1-naphthylidene-4′-aminobiphenyls),[7] the C_1 to C_3 derivatives are non-mesomorphic; C_4 to C_{12} derivatives are monotropic nematic and C_{14} to C_{18} members exhibit enantiotropic nematic mesophase. The C_{18} derivative exhibits an additional smectic phase which is monotropic in nature. It is

TABLE II

Average thermal stabilities in °C—4-*n*-Alkoxy-1-naphthylidene-4′-*n*-alkoxyanilines—$R_1O - C_{10}H_6 - CH = N - C_6H_4 - OR_2$

Series	R_2	Nematic-Isotropic (R_1)
I	OC_2H_5	74.14 ($C_6H_{13} - C_{14}H_{29}$)
II	C_3H_7	57.71 ($C_6H_{13} - C_{14}H_{29}$)
III	C_4H_9	68.64 ($C_6H_{13} - C_{14}H_{29}$)
IV	C_5H_{11}	65.57 ($C_6H_{13} - C_{14}H_{29}$)

interesting to note that by substituting a phenyl group in place of the ethoxy group the molecule becomes more mesomorphic. The phenyl moiety not only increases the polarizability of the molecule but also the length compensating for the breadth increase due to the naphthalene unit.

Compared to the benzylidene series,[10] in the naphthylidene series the nematic phase is thermally less stable. The 1–4 substituted naphthalene unit, which can be considered as a bridge side substitution in the phenylene unit, increases the breadth of the molecule. No doubt the polarizability of the system is also increased with the naphthalene unit. Of the two, the breadth has a greater influence on the mesophase and the nematic stability is lowered. Same is the reason for the absence of the smectic phase in the series.

The average nematic thermal stability of homologous series of naphthylidene Schiff's bases with various p-*n*- alkoxyanilines (ethoxy to pentyloxy) are compiled in Table II. It can be seen that the nematic stabilities in these series vary in an orderly manner. This is due to the odd-even effect of this terminal alkoxy functin; similar observation can be seen in the case of alkoxy-benzylidene-alkoxyanilines studied by Dave and Patel.[10]

Experimental

Preparation of Compounds 4-*n*-Alkoxy-1-naphthylidene-4′-ethoxyanilines were prepared by refluxing equimolecular amounts (0.02 mol) of 4-*n*-alkoxy-1-naphthaldehydes[6] and p-phenetidine (A.R.) in ethanol (25 ml) for 1 hr. The crude product obtained on cooling the reaction mixture is crystallized several times from ethanol to obtain the pure compound (yield 70%). The purity of the compounds is checked by TLC. All the compounds gave satisfactory *C,H,N* analysis. The melting points and transition temperatures of the compounds are given in Table I.

Determination of transition temperatures These were determined in a Leitz Ortholux Polarizing microscope as described elsewhere.[6]

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