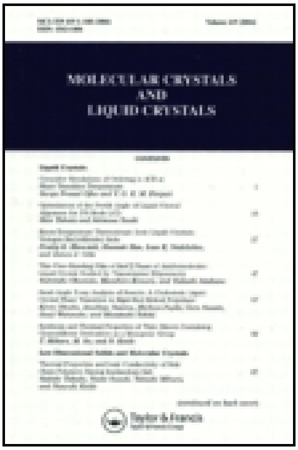

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Mesomorphic Behavior of Some New Fluorene Compounds

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MESOMORPHIC BEHAVIOR OF SOME NEW FLUORENE COMPOUNDS*

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Several new fluorene derivatives have been synthesized and their liquid crystalline polymorphic behavior examined. Specifically, 2-fluorenylmethylidene-4'-n-alkylanilines with different alkyl groups are compared with corresponding compounds wherein the alkyl groups have been replaced either by the alkoxy or other different groups. In addition, some of the 4-alkyl and alkoxybenzylidene-2-aminofluorenes have also been prepared for comparison. Many of these compounds show not only the nematic phase but also two smectic phases. The presence of a lateral substituent in analogous compounds decreases the nematic-isotropic transition by about 60°C.

1. INTRODUCTION

In order to obtain compounds more suitable for NMR studies, we have synthesized several new fluorene derivatives which exhibit liquid crystal polymorphism. When the fluorene group is fully deuterated it allows the NMR

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experiments to obtain the maximum achievable information regarding the orientational ordering of the molecule. The fluorene group is one of only a few such groups in nature which has this feature. This results from the group being rigid and containing five inequivalent and resolvable time averaged deuterium quadrupole interactions. Five such interactions from a group of known structure (in the absence of overall molecular symmetry) are necessary to fully determine the elements of the Maier-Saupe order matrix.[1]

A number of 2-fluorenylmethylidene-4'-n-alkylanilines have been synthesized where the chain length in the alkyl group is C_1-C_{10}, C_{12} and C_{14}. The transition temperatures for the various liquid crystal phases are listed in Table I. The phase transition temperatures were determined with a Leitz polarizing microscope using a Mettler FP-2 heating stage. For some of these compounds the phase transition temperatures were also determined by differential scanning calorimetry (Perkin-Elmer DSC IV as shown in Figure 1). The melting points (solid-liquid or solid-liquid crystal transition) are those recorded upon heating. DSC transition temperatures of these compounds matched well with those determined by the polarizing microscope. The error of the temperature measurements is estimated to be smaller than ±2°C.

When the chain length of the compounds in Table I is C_1 the nematic is monotropic, while an enantiotropic nematic phase is observed with carbon chain C_2-C_{10}. The monotropic smectic 1 phase starts appearing with a chain length of C_3-C_5. This phase becomes enantiotropic with a chain C_6-C_{14}. The smectic 2 phase is monotropic and

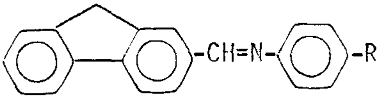

TABLE I 2-Fluorenylmethylidene-4'-*n*-alkylanilines.

R	Transition temperatures, °C, from solid or preceding liquid crystal states to Smectic 1	 Nematic	 Isotropic
CH_3	- - -	- - -	157 149[a]
C_2H_5	- - -	124.5	144
C_3H_7	- - -	138 110[b]	165
C_4H_9	- - -	141 123[b] 98[c]	156.5
C_5H_{11}	- - -	147.5 129[b] 92.5[c]	164
C_6H_{13}	125.5 92.5[c]	135	154.5
C_7H_{15}	125 88.5[c]	140.5	157
C_8H_{17}	119 85.5[c]	145.5	151
C_9H_{19}	123 74[c]	144	149.5
$C_{10}H_{21}$	119 68.5[c]	143.5	145.5
$C_{12}H_{25}$	118	- - -	141
$C_{14}H_{29}$	117.5	- - -	136.5

[a] Transition from monotropic nematic.
[b] Transition from monotropic smectic 1.
[c] Transition from monotropic smectic 2.

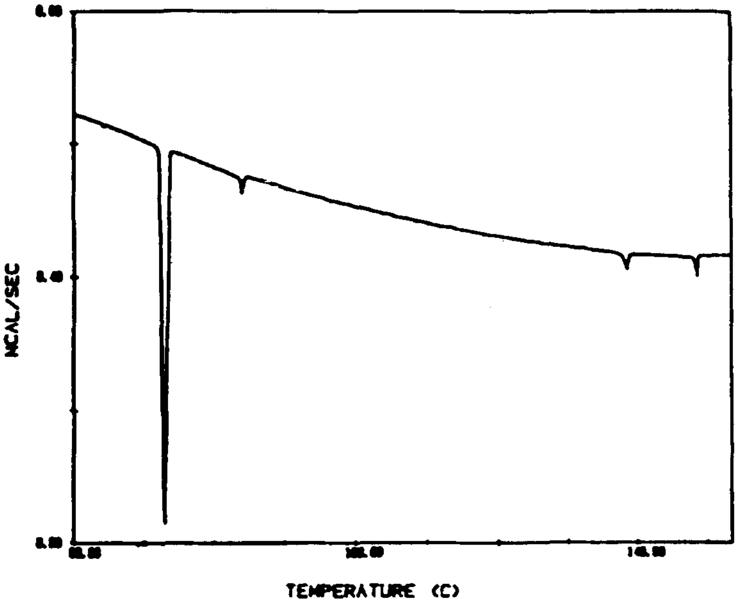

FIGURE 1 DSC cooling curve for the material, 2-fluorenylmethylidene-4'-n-octylaniline (F.8) showing the I-N, N-S_A, S_A-S_2, and S_2-K transitions. The data were acquired on the Perkin-Elmer DSC-IV.

starts with carbon chain C_4-C_{10}. In Figure 2, various transition temperatures have been plotted against the number of carbon atoms in the alkyl chain. A glance of the plot indicates the usual alternation of the nematic-isotropic transition temperatures with increasing chain length.[2]

The smectic 1 phase has a focal-conic structure often containing fans and homeotropic areas. This smectic phase may be regarded as smectic A by the textures reported from Sackmann and Demus.[3] It is difficult to say anything definite about the nature of the smectic 2. Its identification is under investigation and will be published elsewhere.

Since these materials appear to form the orthogonal smectic phases it was of interest to examine their miscibility with materials which contain the smectic C phase. Figure 3 shows the resulting phase diagram of a mixture of 2-fluorenylmethylidene-4'-n-octylaniline with heptyloxyazoxybenzene. This phase diagram is typical of such mixtures and shows a reluctance of these fluorene derivatives to form a tilted structure.

The transition temperatures of 2-fluorenylmethylidene-4'-n-alkoxyanilines are given in Table II. These transition temperatures are also plotted, against the number of carbon atoms in the alkyl chain (see Figure 4). The even-odd alternation of the nematic-isotropic transition temperatures has an opposite trend to what is observed (Figure 2) in the case when the group is alkyl instead of alkoxy chain. This type of behavior has been observed in other series.[4] The smectic 1 phase in the case of these compounds appears to be S_A while the smectic 2 phase

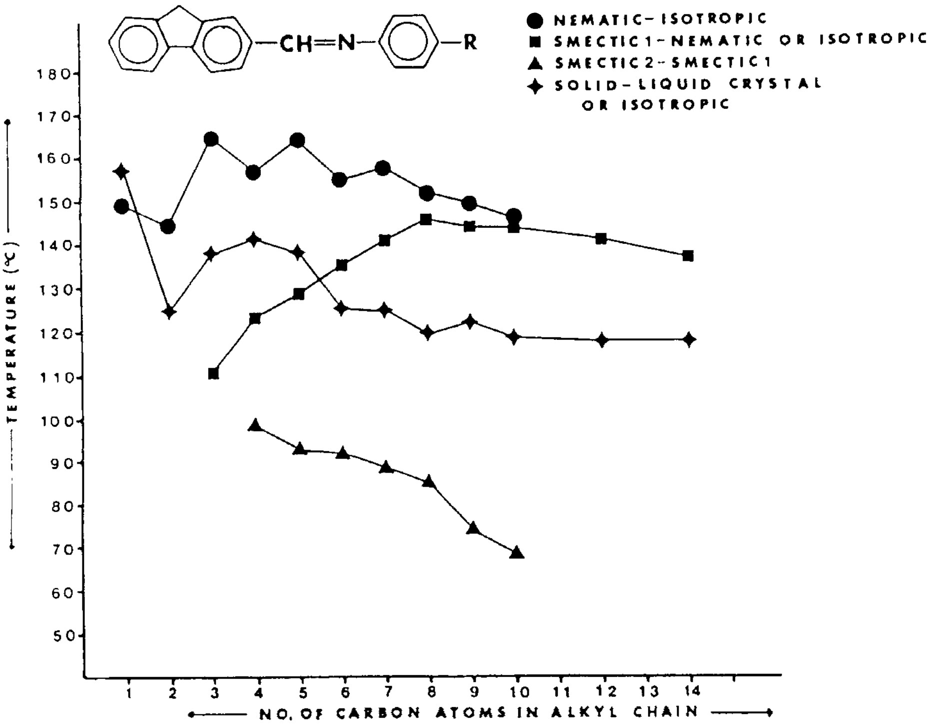

FIGURE 2 Transition temperatures of 2-fluorenylmethylidene-4'-n-alkylanilines plotted against the number of carbon atoms in the alkyl chain.

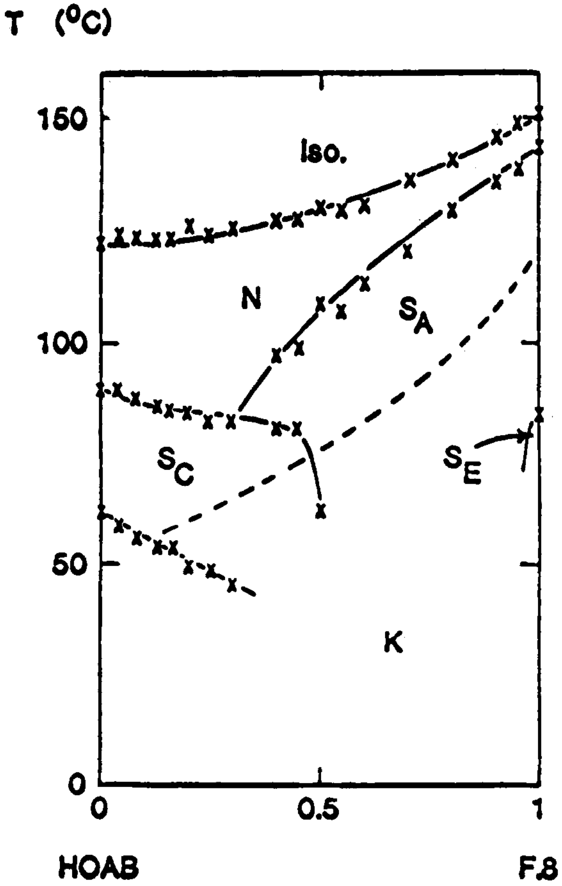

FIGURE 3 Phase diagram resulting from a binary mixture of 2-fluorenylmethylidene-4'-n-octylaniline (F.8) and 4,4'-bis-n-heptyloxyazoxybenzene (HOAB). We tentatively identified smectic 2 as smectic E (S_E) however more work is in progress to be definite about the identification.

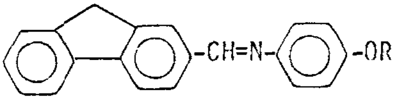

TABLE II. 2-Fluorenylmethylidene-4'-n-alkoxyanilines.

	Transition temperatures, °C, from solid or preceding liquid crystal states to		
RO	Smectic 1	Nematic	Isotropic
H_3CO	- - -	172	202.5
H_7C_3O	- - -	159	195
H_9C_4O	- - -	154	200
$H_{11}C_5O$	- - -	149 144.5[a]	190.5
$H_{13}C_6O$	145 127[b]	152	190
$H_{15}C_7O$	139 125[b]	159	184
$H_{17}C_8O$	135	163	182.5
$H_{19}C_9O$	132	166.5	178
$H_{21}C_{10}O$	129.5	167	174.5
$H_{25}C_{12}O$	127	168	169.5
$H_{29}C_{14}O$	126	- - -	164.5

[a] Transition from monotropic smectic 1.
[b] Transition from monotropic smectic 2.

was observed only in carbon chains C_6 and C_7 because crystallization takes place quite rapidly in this series of compounds. Also the identical liquid crystal transition temperatures of this series are higher by 20-50°C when compared with those of the analogous compounds listed in Table I. This can be easily explained by the

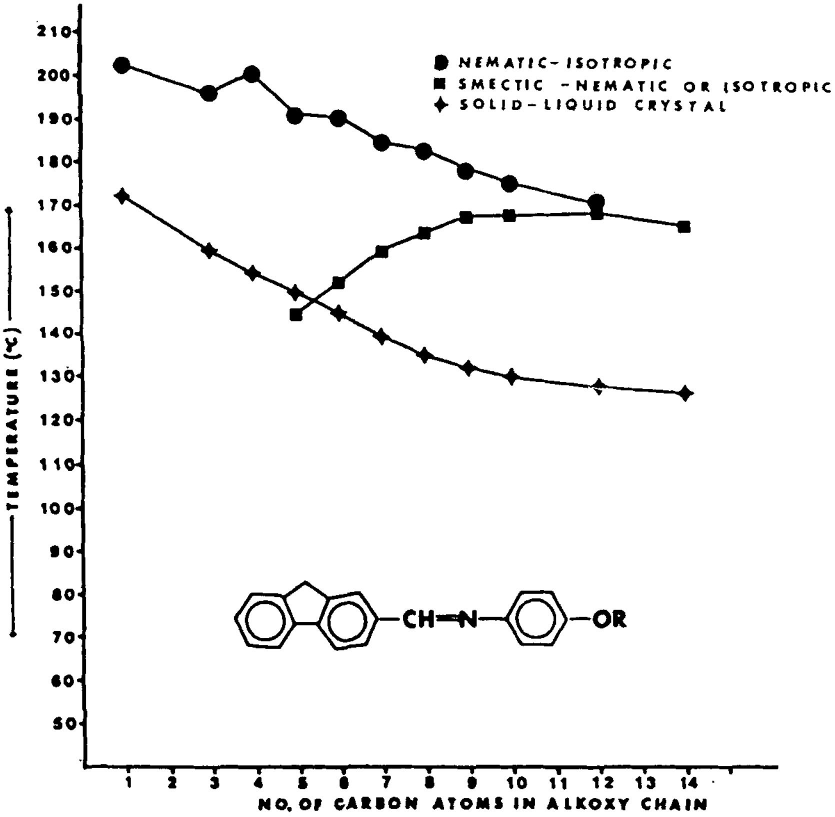

FIGURE 4 Transition temperatures of 2-fluorenylmethylidene-4'-n-alkoxyanilines plotted against the number of carbon atoms in the alkoxy chain.

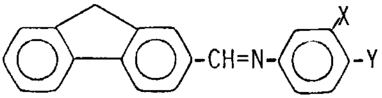

Table III. 2-Fluorenylmethylidene-3'-X-4'-Y-anilines.

		Transition temperatures, °C, from solid or preceding liquid state to	
X	Y	Nematic	Isotropic
H	OCH_3	172	202.5
Cl	OCH_3	- -	164 144[a]
H	CH_3	- -	157 149[a]
Cl	CH_3	- -	153

[a] Transition from monotropic nematic.

fact that the alkoxy group produces a permanent dipole.

The transition temperatures of 4-fluorenylmethylidene-3-chloro-4-Y-anilines are given in Table III. When 'Y' is the methoxy group a monotropic nematic phase is observed. The N-I transition is lower by 59° when compared with the nonlaterally substituted compound. This lowering of nematic to isotropic transition can be attributed to the lateral broadening of the molecule.[5,6] When 'Y' is the methyl group a liquid crystal phase is not formed. However, if the chain length is increased liquid crystal phases may be observed.

Table IV lists the transition temperatures of anils wherein the imine linkage (-CH=N-) is reversed. It is interesting to observe that the analogous compounds of

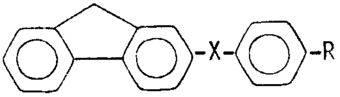

TABLE IV. Effect of reversing the central imine linkage.

R	X	Transition temperatures, °C, from solid or preceding liquid crystal states to Smectic 1	Nematic	Isotropic
n-C_7H_{15}	-CH=N-	125 88.5[a]	140.5	157
n-C_7H_{15}	-N=CH-	107 90[a]	137	162.5
n-$C_7H_{15}O$	-CH=N-	139	159	184
[b]n-$C_7H_{15}O$	-N=CH-	117	156	189
n-$C_8H_{17}O$	-CH=N-	135	163	182.5
[b]n-$C_8H_{17}O$	-N=CH-	113.5	169	187
n-$C_{10}H_{21}O$	-CH=N-	129.5	167	174.5
[b]n-$C_{10}H_{21}O$	-N=CH-	115	162	183

[a] Transition from monotropic smectic 1.
[b] Reported by Gray et al., J. Chem. Soc. 4359 (1955).

2-fluorenylmethylidene-4'-R-anilines have lower N-I transition temperatures when compared with the N-I transition temperatures of the compounds of 4-R-benzylidene-2'-aminofluorenes.[6] These differences in the N-I transition temperatures may be due to a twist about the imine linkage between the terminal fluorene and benzene rings, thereby reducing the coplanarity of the molecule. This in turn may affect the mutual conjugation along the entire molecule, thereby changing the polarizability.[8]

Recently Coates[9] and Griffin[10] have prepared compounds having a trifluoromethyl terminal group. We therefore prepared some 2-fluorenylmethylidene-4'-R-anilines, where R is either trifluoromethyl or other terminal substituents. The transition temperatures for the compounds of this series are given in Table V. It is observed at a glance of this table that all compounds of this series show a nematic phase except when the terminal group is trifluoromethyl. This may be due to the large size of CF_3 as suggested by Coates,[9] and may in turn cause a broadening of the molecule thus reducing forces essential for the formation of the liquid crystal phases. As expected when the terminal group is CN the N-I transition is highest.

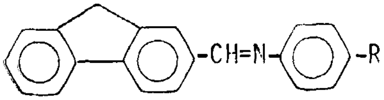

TABLE V. 2-Fluorenylmethylidene-4'-R-anilines

R	Transition temperatures, °C, from solid or preceding liquid crystal states to Nematic	 Isotropic
CH_3	- -	157 149[a]
OCH_3	172	202.5
NO_2	191	203
CN	151.5	216
$COCH_3$	183.5	198.5
CF_3	- -	199

[a] Transition from monotropic nematic.

2. PREPARATION OF MATERIALS

2-Fluorenecarboxyaldehyde, and 2-aminofluorene are commercially available and pure enough for the synthesis of the final products.

Most of the substituted anilines and benzaldehydes required for our work were available commercially. Many of these starting materials were purified either by recrystallization or distillation under reduced pressure.

2.1 2-Fluorenylmethylideneanilines were prepared by refluxing the equimolecular quantities of the 2-fluorenecarboxyaldehyde and the appropriate substituted aniline in absolute alcohol with a few drops of glacial acetic acid for 5-6 hours. After isolation the product was recrystallized several times from suitable solvents until the transition temperatures remained constant.

2.2 Benzylidene-2-aminofluorenes were similarly prepared as the anils of 2-fluorenecarboxyaldehyde.

For purified compounds the transition temperatures between mesophases and from the isotropic liquid to the mesophase were sharp and reversible. Microscopic determination of such temperatures during the heating and cooling of a pure compound in most of the cases were, within a fraction of a degree, equal to temperatures for these transitions.

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