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Nematic Mesophases in 9-Methyl and 9-Bromo-2-Fluorenyl 4-Alkoxybenzoates

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The esters, 9-methyl-2-fluorenyl 4-alkoxybenzoates with C_5 , C_7 , C_9 , C_{11} , and C_{14} chain lengths were synthesized in order to determine the effect of the 9-substituent in the fluorene rings on their mesomorphic properties. Their structures were determined by spectroscopic methods including 1H -NMR, ^{13}C -NMR, and 2D-COSY-NMR. All these compounds showed a nematic phase with a nematic–isotropic transition temperature between 74–100°C. The nematic phase in these materials could be supercooled to room temperature. The nematic phase also appeared in the corresponding 9-bromo esters but at higher temperatures and was enantiotropic only in one homolog, C_9 . Comparisons were also made with the 7-bromo-2-fluorenyl 4-alkoxybenzoates with C_7 , C_9 , and C_{14} chain lengths. These compounds all yielded the smectic A phase with the nematic phase only appearing in the C_7 homolog. The presence of bromine in the 7-position of the fluorenyl esters increased the liquid crystal isotropic transition temperature to about 200°C.

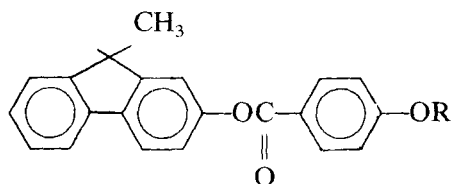
INTRODUCTION

The use of liquid crystal compounds in display devices has generated considerable interest in the synthesis of room temperature nematic mesogens with wide temperature ranges.¹ The biphenyls have been very useful in display devices because of their high stability, low (below 100°) nematic–isotropic transition temperatures, large positive anisotropy in the dielectric constant and large birefringence. The highly conjugated biphenyl core is one of the structural features which

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provide these desirable properties. An interesting variant to the biphenyl core is fluorene. This group is more planar, also is highly conjugated and gives more flexibility in molecular design. Gray et al.¹ prepared 2-butyl-7-cyanofluorene and found that it gave only a monotropic nematic transition (at -23°). The compound 2-hexyloxy-7-cyanofluorene was found to yield no nematic phase at all. Further investigation of these compounds was done by Davison et al.² They found that the melting points were in general higher even though the nematic clearing points were slightly lower than those of the biphenyl variety. Overall, several studies of mesomorphic behavior of compounds containing the fluorene moiety have been done using different molecular environments such as anils,^{3,4} ketones,⁵ and esters.^{6,7} These compounds in their pure form show the nematic (*N*) phase but most often the smectic *A* (*S_A*) phase at $\sim 100^\circ\text{C}$ or above. Recently, we reported that an induced nematic phase was formed in mixtures of the fluorene aniline with halogeno-terminally substituted Schiff bases,⁸ which presents another approach to obtaining a wide range, low temperature *N* phase.

It is known that unsubstituted fluorene has a much higher melting point than that substituted with a methyl group in the 9-position. Some investigations on 9-methyl-2,7 disubstituted fluorene with alkyl and ketone substituents was done by Billard et al.⁹ but the nematic phase which appeared below room temperature was only monotropic. In order to obtain enantiotropic nematic phases with lower temperatures, we synthesized a number of 9-methyl-2-fluorenyl alkoxybenzoates as well as 9-bromo substituted esters,



We found that the presence of the methyl group decreases the nematic–isotropic, *N–I*, transition temperature to below 100° , yielding a nematic range of about 20°C which can be supercooled to room temperature. The 9-bromo substituent also decreases the *N–I* transition temperature but not as much as the methyl substituent and gives primarily a monotropic nematic phase. The 7-bromo substituted fluorene esters were also prepared; they showed a smectic *A* phase over a longer temperature range with the clearing point always above 200°C .

SYNTHESIS AND STRUCTURAL CHARACTERIZATION

The substituted 2-fluorenyl 4-*n*-alkoxybenzoates **4** were prepared from the ketone **1** according to the method shown in Figure 1. The esters **2** were prepared by oxidizing the ketone **1** with *m*-chloroperbenzoic acid using the method of Jones et al.¹⁰ Hydrolysis of the ester **2a** and **2c** was done using K_2CO_3 in methanol–water,¹¹ while the ester **2b** was hydrolyzed using hydrobromic acid in acetone. An attempt to hydrolyze this acetate with hydrochloric acid¹² caused an exchange of the bromine with the chlorine ion as shown by the difference in the 1H NMR chemical shifts of $\delta = 5.9$ for the bromide compared to $\delta = 5.1$ for the chloride. The reaction time affected the bromide/chloride ratio as one would expect.

The ketones **1** were prepared as shown in Figure 2. Treatment of fluorenone **5** with methylmagnesium iodide according to the method of Badger¹³ gave 9-methyl-9-hydroxyfluorene **6** which was reduced

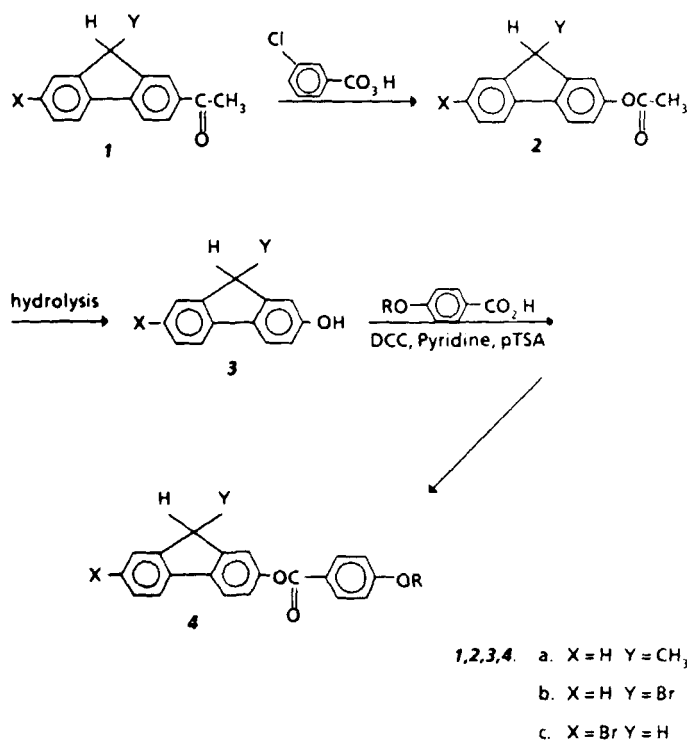


FIGURE 1 Synthetic method for the 7- and 9-substituted-2-fluorenyl 4-alkoxybenzoates, **4**.

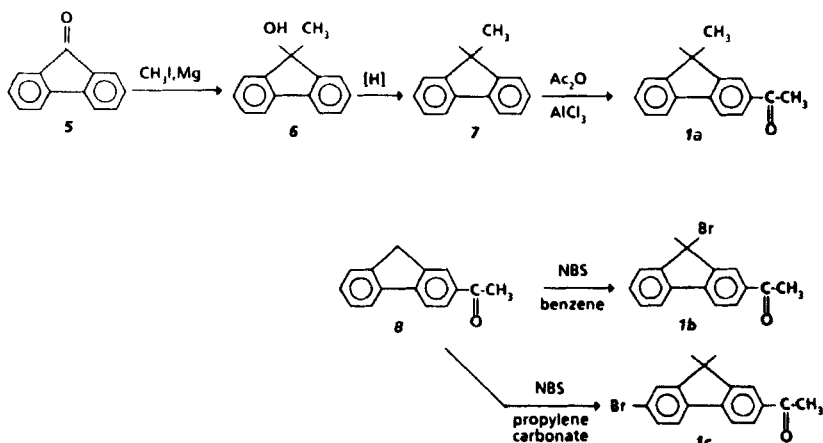


FIGURE 2 Synthetic method for ketones 1a, 1b, and 1c.

to the 9-methylfluorene 7.¹⁴ Acetylation of this compound using the method of Ray and Rievasch¹⁵ gave the 9-methyl-2-acetylfluorene 1a. Bromination of the ketone 8 with NBS in benzene according to the method of Ross et al.¹⁶ gave the 9-bromo-2-acetylfluorene 1b, while bromination in propylene carbonate (1,2 propanediol cyclic

TABLE I
Data for Compounds Prepared

Compd. #	Purified Yield (%)	m.p. (°C, solvent)	TLC R_f	IR (cm ⁻¹)	NMR, δ ppm (multiplicity, H_f -assignment, J in Hz)
1a	81	119-120 CH_2Cl_2 -hexane	0.48	1660 (C=O)	8.1-7.1 (m, 7, fluorene), 4.0 (q, 1, CH_2 , J = 7), 2.65 (s, 3, CH_3 , C(O)), 1.55 (d, 3, CH_3 , J = 7)
1b	51	120-122 CHCl_3 -MeOH	0.41	1660 (C=O)	8.3-7.2 (m, 7, fluorene), 6.0 (s, 1, CH), 2.63 (s, 3, CH_3 , C(O))
1c	54	129-131 CHCl_3 -MeOH	0.36	1660 (C=O)	8.2-7.2 (m, 6, fluorene), 3.88 (s, 2, CH_2), 2.62 (s, 3, CH_3 , C(O))
2a	80	94-96 MeOH	0.59	1725 (C=O)	7.8-6.7 (m, 7, fluorene), 3.95 (q, 1, CH), 2.25 (s, 3, CH_3 , C(O)), 1.48 (d, 3, CH_3 , J = 7)
2b	74	124-125 CHCl_3 -hexane	0.55	—	7.8-7.0 (m, 7, fluorene), 5.91 (s, 1, CH), 2.26 (s, 3, CH_3 , C(O))
2c	75	88-92 CHCl_3 -hexane	0.51	—	7.8-6.8 (m, 7, fluorene), 3.82 (s, 2, CH_2), 2.26 (s, 3, CH_3 , C(O))
3a	91	129-130 CHCl_3 -hexane	0.21	3300 (OH)	7.7-6.7 (m, 7, fluorene), 6.2 (broad s, 1, OH), 3.85 (q, 1, CH), 1.45 (d, 3, CH_3 , J = 7)
3b	48	decomposition above 115 column chrom. CHCl_3 -hexane	0.26	3300 (OH)	7.6-6.8 (m, 7, fluorene), 5.9 (s, 1, CH), 5.0 (s, 1, OH)
3c	94	175-178 column chrom. CHCl_3 -hexane	0.25	3300 (OH)	7.7-6.7 (m, 6, fluorene), 4.8 (s, 1, CH), 3.75 (s, 2, CH_2)
6	85-90	172-174 benzene	0.24	3400 (OH)	7.7-7.0 (m, 8, fluorene), 2.0 (s, 1, OH), 1.65 (s, 3, CH_3)
7	42-45	45 MeOH	0.82	2900, 1600 1440 (CH)	7.9-7.2 (m, 8, fluorene), 3.88 (q, 1, CH_2 , J = 7), 1.48 (d, 3, CH_3 , J = 7)

*Literature m.p. 174-5° given in Ref. 17.

carbonate) gave 7-bromo-2-acetylfluorene **1c**. Characterization data for these compounds are given in Table I. The structure of **4a** was confirmed by elemental analysis, MS, TLC, IR (see Experimental), and by ^1H NMR, ^{13}C NMR and ^1H homonuclear 2D-COSY NMR.

The ^1H -NMR signals of **4a** were completely assigned using model compounds such as 2-fluorenol, 2,7-disubstituted fluorene,¹⁰ proton decoupling, and the first use of 2D-COSY NMR. Downfield aromatic signals are complex and their assignments are based on the following arguments. Signals from H_a and H_b , 8.16 and 6.96 respectively, were assigned by integration and irradiation experiments. Proton signals arising from the fluorene ring (87.1 to 7.8 ppm) were resolved by off diagonal peak connectivities in the ^1H homonuclear 2D-COSY NMR (Figure 3). The ^{13}C NMR signals of **4a** (Table II) were assigned using model compounds including 2-fluorenol, fluorene, 9-oxofluorene-4-

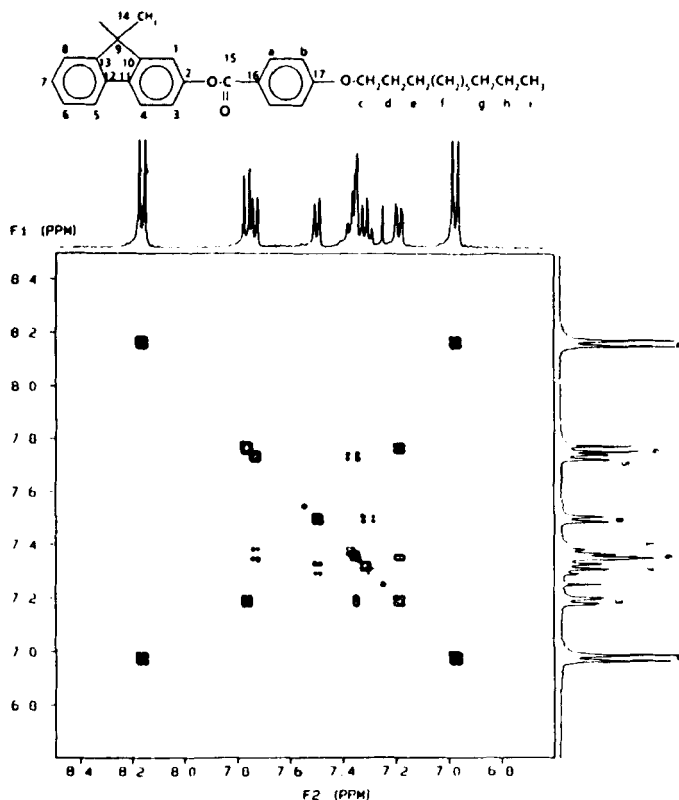
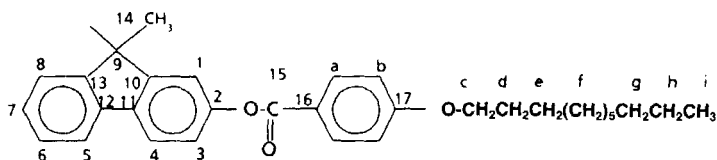


FIGURE 3 ^1H Homonuclear 2D-COSY-NMR of the aromatic region of **4a**.

TABLE II
 ^1H and ^{13}C NMR Data for **4a**



No	^1H -NMR			^{13}C -NMR	
	δ [ppm]	number of protons	multiplicity	3J [Hz]	δ [ppm]
1	7.34	1	d	*1.8	117.7
2	--	--	--	--	**150.4
3	7.18	1	dd	8.2; *1.8	119.7
4	7.75	1	d	8.2	120.3
5	7.72	1	d	7.4	120.3
6	7.35	1	m	7.4; 7.2	123.9
7	7.30	1	m	7.2; 7.3	126.8
8	7.49	1	d	7.3	127.0
9	3.96	1	q	7.3	42.6
10	--	--	--	--	150.4
11	--	--	--	--	138.1
12	--	--	--	--	139.8
13	--	--	--	--	149.1
14	1.52	3	d	7.3	18.1
15	--	--	--	--	165.2
16	--	--	--	--	121.7
17	--	--	--	--	**163.5

carboxylic acid heptyl ester (Sadtler Research Laboratories) and using chemical shift calculations and selective irradiation experiments.

Mesomorphic Properties

Transition temperatures (obtained from microscopic studies) for the 9-methyl-2-fluorenyl 4-*n*-alkoxybenzoates **4a** are given in Table III. A plot of the transition temperatures vs alkyl chain length (Figure 4)

TABLE II

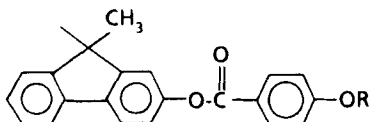
(continued)

No	$^1\text{H-NMR}$			$^{13}\text{C-NMR}$	
	δ [ppm]	number of protons	multiplicity	3J [Hz]	δ [ppm]
a	8.16	2	d	8.8	132.2
b	6.96	2	d	8.8	114.3
c	4.03	2	t	6.5	68.4
d	1.81	2	m	--	29.1
e	1.47	2	m	--	26.0
f	1.2-1.4	10	m	--	29.4-29.6
g	1.2-1.4	2	m	--	31.9
h	1.2-1.4	2	m	--	22.7
i	0.88	3	t	7.0	14.1

*4J

**Tentative assignment

TABLE III

Transition Temperatures ($^{\circ}\text{C}$) for 4a

R	C	S_A -N	C-N or I	N-I
C_5	30		117.2-118.0	(98.9)
C_7	42		89.0-90.0	97.0
C_9	30		78.4-79.0	94.7
C_{11}	22	(40.1)	74.4-75.1	92.4
C_{14}	55.8	(55.8)	81.8-82.8	90.5

C-crystallization temperature observed on cooling at $2^{\circ}/\text{min}$. S_A -smectic A, N-nematic, I-isotropic liquid.

()-indicates a monotropic transition.

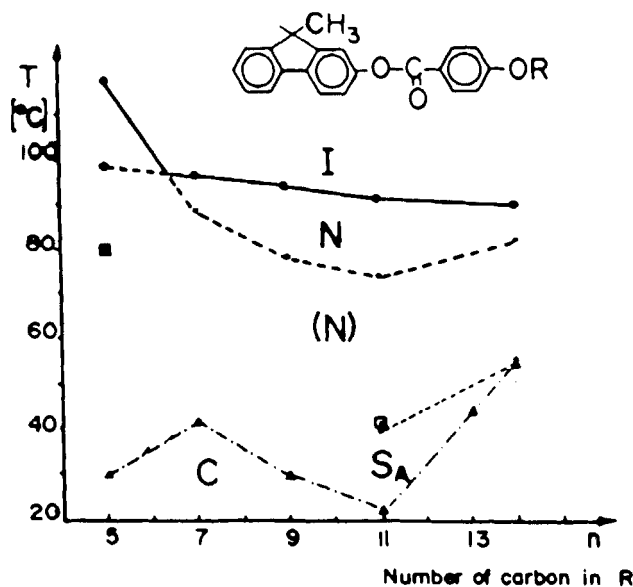
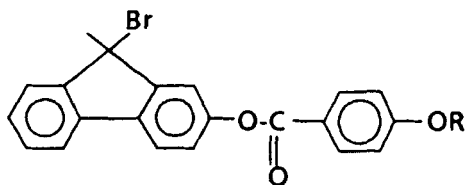


FIGURE 4 Transition temperatures of 4-methyl-2-fluorenyl 4-*n*-alkoxybenzoates vs number of carbon atoms in the alkyl chain.

shows that the clearing points to the isotropic liquid occur between 90 and 97°C with a slight decrease with increasing chain length. For the C_5 homolog this temperature (the m.p.) is higher (118°) but a monotropic nematic phase appears at 99°. The melting points occur between 74°C and 118°C, falling to a minimum for $R = C_{11}$. For the C_{11} homolog, a monotropic smectic A phase was observed at 22°C. The S_A phase was observed to be very short for C_{14} as crystallization occurs at almost the same temperature as the $N-S_A$ transition. No other smectic phases were observed. There is also a minimum in the crystallization curve as one would expect at C_{11} which falls to room temperature (22°). Similarly for the C_9 homolog, crystallization occurs almost at room temperature giving a near room temperature nematic phase in the cooling cycle. The C_5 homolog has a higher melting point but in the cooling cycle gives a long-range (70°) monotropic nematic phase. A crystal-crystal transition was observed for the C_5 and C_{11} esters (\square in Figure 4).

Replacing the methyl group with a bromine, as shown in Table IV, for compounds **4b** increases the isotropic liquid crystal transition temperatures from 99 to 125°C, as well as the crystallization points. Only the C_9 homolog has a 20° range enantiotropic nematic phase. Both

TABLE IV
Transition Temperatures (°C) for **4b**



R	C	C-N or I	N-I
C ₇	91.0	125.0-125.2	(121.0)
C ₉	63.0	100.8-102.2	119.2
C ₁₄	50.5	98.7-99.3	(92.6)

C—crystallization temperature observed on cooling at 2°/min.

N—nematic

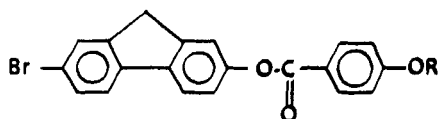
I— isotropic liquid

() indicates a monotropic transition.

C₇ and C₁₄ homologs have monotropic nematic phases with 30° to 42° ranges on cooling.

The presence of bromine in the 7-position of the 2-fluorenyl 4-*n*-alkoxybenzoates **4c** (Table V) yields materials which have a tendency to form smectic *A* phases with transition temperatures to the isotropic

TABLE V
Transition Temperature (°C) for **4c**



R	C	C-S _A	S _A -N	S _A or N-I
C ₇	97.4	122.0-122.3	207.8-208.3	215.3
C ₉	77.1	118.2	---	208.7-210.3
C ₁₄	75.2	116.9	---	201.5-202.8

C—crystallization temperature observed on cooling at 2°/min.

S_A—smectic A

N—nematic

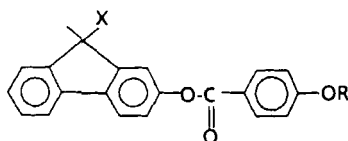
I— isotropic liquid

liquid at 202–215°C. Only the C₇ homolog appears to be a nematic with a short temperature range of 7°. The esters show a long range (~100°C) smectic A phase which is stabilized by the bromine in the 7-position.

DISCUSSION

The esters 9-methyl- and 9-bromo-2-fluorenyl 4-*n*-alkoxybenzoates **4a** and **4b** have much lower transition temperatures than their unsubstituted homologs, as shown in Table VI. The nematic phase appears at lower temperatures for the 9-methyl substituted esters and supercools to nearly room temperature. The methyl group in the 9-position of the fluorene core breaks the planar symmetry of this part of the molecule, introducing a chiral center. This change in the sym-

TABLE VI
Effect of Exchange of X Substituent in 9-Position in 2-Fluorenyl 4-*n*-Alkoxybenzoates on Transition Temperatures (C°) for



R	X*	C	C-S _A	S _A -N	C-N or I	N-I
C ₅	H			---	152.2	156.0
	CH ₃	30		---	117.2-118.0	(98.9)
C ₇	H			---	123.0	152.7
	CH ₃	42.0		---	89.0-90.0	97.0
	Br	91.0		---	125.1	(121.0)
C ₉	H	76		(98.8)	109.0	146.7
	CH ₃	30		(40.1)	78.4-75.1	94.4
	Br	63		---	100.8-102.2	119.2
C ₁₄	H	84.6	105.0	124.6	---	136.1
	CH ₃	55.8		(55.8)	81.8-82.8	90.5
	Br	50.5		---	(92.6)	98.7-99.3

*For X = H transition temperatures were taken from Ref. 6.

C—crystallization temperature observed on cooling at 2°/min.

S_A—smectic A

N—nematic

I— isotropic liquid

metry could be the main cause of decreasing transition temperatures. The bromine in the 9-position showed the same tendency; however, these esters are less suitable for application because of their yellow colors.

Substitution by a 7-bromo-substituent in the fluorene core stabilizes the smectic *A* phase and raises the transition temperatures above 200°C as listed in Table V.

EXPERIMENTAL

A Perkin-Elmer model 700 IR, a Varian A-60 and a Bruker WM 360 MHz NMR spectrometer were used as analytical tools. Melting points were determined using a Thomas Hoover melting point apparatus at a heating rate of 2°/min. TLC was done on silica gel GMLF (Analtech) plates using CHCl₃ as the solvent. Transition temperatures were determined using a polarizing microscope equipped with a calibrated Mettler heating stage ramped at a rate of 2°/min. The smectic *A* phase was identified using aligned samples under conoscopic viewing.

9-Methyl-2-hydroxyfluorene, **3a**

To a methanolic solution (120 ml) containing 2.35 g (0.01 m) of **2a** was added K₂CO₃ (7.9 g) in 50 ml of H₂O at room temperature. The solution was allowed to stand 30 min at room temperature; then it was acidified with 60 ml 10% HCl and shaken with ether. The extracts were washed with H₂O, dried over MgSO₄ and the solvent removed. Recrystallization of the crude product from CHCl₃-hexane gave 1.8 g (91%) of 9-methyl-2-hydroxy fluorene, **3a** (Table I).

9-Bromo-2-hydroxyfluorene, **3b**

To an acetone soln (15 ml) containing 820 mg (2.7 mmol) of **2b** was added 0.1 ml HBr (48% soln) and the solution was refluxed for 2 hr then concentrated to a ~5 ml volume. Ethyl ether (50 ml) was added and the reaction mixture washed with H₂O, dried over MgSO₄, filtered, and solvent removed. Purification on silica gel column chromatography with hexane-CHCl₃ as eluent (gradient concentration) gave 340 mg (48%) of 9-bromo-2-hydroxy fluorene, **3b** (Table 1).

2-Fluorenyl 4-*n*-alkoxybenzoates, **4** were prepared using a standard method according to Holmberg and Hansen.¹⁸ A typical procedure is given for **4a**, *R* = C₁₁.

9-Methyl-2-fluorenyl 4-undecyloxybenzoate, 4a ($R = C_{11}$)

To 4-undecyloxybenzoic acid 584 mg (2.0 mmol) dissolved in 5 ml of pyridine was added 392 mg (2.0 mmol) 9-methyl-2-hydroxyfluorene, **3a**, 20 mg of *p*-toluenesulfonic acid (*p*TSA) and 412 mg (2.0 mmol) 1,3-dicyclohexylcarbodiimide (DCC). The reaction mixture was stirred at room temperature for 1 hr and heated to 70°C for 12 hr and then cooled to room temperature. The precipitated *N,N'*-dicyclohexylurea (DCU) was removed by filtration and washed with 5 ml CH_2Cl_2 . The solvent was removed under vacuum; the crystals were dissolved in $CHCl_3$ and then purified on silica gel (60–100 mesh, Type 60A) column using hexane- CH_2Cl_2 as eluent. Recrystallization from ethanol gave a pure product 170 mg (18%) of **4a** ($R = C_{11}$). The transition temperatures are shown in Table III. TLC showed one spot $R_f = 0.72$ (R_f for **3a** = 0.21), IR ($CHCl_3$) 1725 cm^{-1} (str C = O), and 360 MHz NMR data ($CDCl_3$ TMS) are shown in Table II. MS (70 eV) *m/e* (relative intensity): 470 (M^+ , 5.8), 275(100), 195(11.7), 152(7.8), 121(82.1).

Analysis for $C_{32}H_{38}O_3$ Found: C–81.53, H–8.15, Required: C–81.66, H–8.14.

Acknowledgments

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