Synthesis and Liquid Crystal Phase Behaviour of 2-(4-Cyanophenyl)-7-*n*-alkylfluorenes: Luminescent Mesogens

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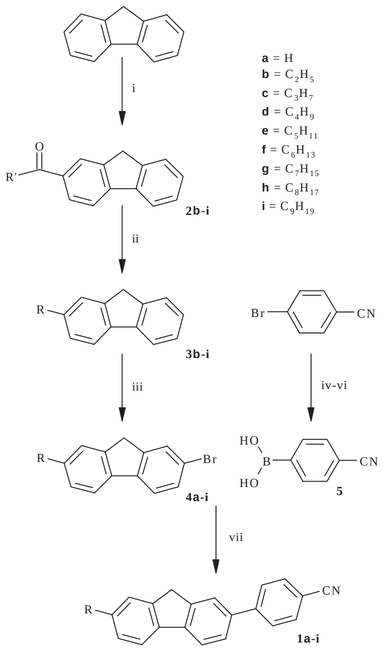
(Received September 17, 2001; CL-010922)

A new range of nematic liquid crystals containing the 2-phenylfluorene core has been prepared which may be considered as a model system for luminescent mesogens, which have potential interest as new display materials.

Fluorene containing materials are used as electroluminescent materials for a new generation of flat panel displays,[1] which are capable of displaying coloured images at speeds compatible with their use as TV monitors. The poly(dialkylfluorene)s used in such displays are electroluminescent, and, by suitable chemical modification, they can be made to luminesce at red, green and blue wavelengths.[2] Liquid crystalline luminescent materials are the subject of current research, since they may offer new possibilities for light emitting elements in flat panel displays.[3]

Mesogens containing biphenyl and terphenyl as core units have been extensively used as components of liquid crystal display mixtures.[4] The fluorene moiety differs from a biphenyl unit in being flat and slightly bent in the plane of the rings. Previous work on fluorene containing mesogens showed them to exhibit mainly smectic phases or very short nematic ranges.[5] Lengthening the fluorene core by addition of a *p*-cyanobenzene ring results in a wider mesophase range, and addition of suitable terminal substituents yields stable nematic mesophases.

The 2-(4-cyanophenyl)-7-alkylfluorenes **1b**-**i** have been prepared *via* the five step convergent synthesis outlined in Scheme 1. Fluorene was monoacylated by a Friedel-Crafts procedure using a mixture of the appropriate acid chloride, aluminium chloride and 1,1,2,2-tetrachloroethane to give the products **2b**-**i** in 69-85% yield.[6] The 2-acylfluorenes **2b**-**i** were then reduced using the Huang-Minlon modification of the Wolff-Kishner reduction.[7] Heating the compounds strongly with a mixture of hydrazine hydrate, potassium hydroxide and diethylene glycol gave the 2-alkylfluorene **3b**-**i** in 38-89% yield. In some cases sodium carbonate was used in place of potassium hydroxide, as the strong caustic base led to unwanted side reactions by deprotonation of the methylene bridge.[8] Bromination of the alkyl compounds **3b**-**i** was effected by slow addition of a solution of bromine in chloroform. The products **4b**-**i** were obtained in crude yields of 52-83%. In some cases this material was contaminated with up to 20% unbrominated starting material. It was found that the impure samples could be carried forward to the next step of the synthesis with no detrimental effects, as the unbrominated material was inactive under the reaction conditions. Pure material could, however, be isolated by subsequent recrystallizations, but at the expense of yield.[9] The parent compound **4a** was prepared by direct bromination of fluorene in 32% yield.[10] Treatment of 4-bromobenzonitrile with *n*-butyllithium at low temperature gave the aryllithium intermediate, which was then quenched with triisopropylborate to give the borate ester. Hydrolysis of the ester in dilute acid was followed by precipitation from alkaline solution to give 4-cyanobenzoboronic acid **5** in 66% yield. The aryl bromide and boronic acid were coupled using the Suzuki procedure.[11] A mixture of **4**, **5**, tetrakistriphenylphosphine palladium(0), sodium carbonate solution and 1,2-dimethoxyethane was heated at reflux. The coupled products **1a**-**i** were purified by filtration through a plug of silica followed by recrystallization. In the early stages of this work the yields for this final step were low, 3-21%. Refinements to the procedure resulted in much improved yields of up to 57%.



Scheme 1. Reagents and conditions: i, R′COCl, $AlCl_3$, $CHCl_2CHCl_2$, 0 °C; ii, $NH_2NH_2.xH_2O$, KOH or Na_2CO_3, $(HOCH_2CH_2)_2O$, reflux; iii, Br_2, $CHCl_3$, 0 °C then reflux; iv, *n*-BuLi, THF, −100 °C; (v) $(i\text{-PrO})_3B$, THF, −100 °C; vi, H_3O^+, rt; vii, Na_2CO_3, $Pd(PPh_3)_4$, H_2O, DME, reflux.

The liquid crystal phase behaviour of the compounds prepared is summarized in Table 1. Members of the series **1b**-**i** exhibited enantiotropic nematic phases, which were identified by polarized optical microscopy. The heptyl (**1g**), octyl (**1h**) and nonyl (**1i**) homologues also exhibited a smectic phase, identified as smectic A from X-ray scattering experiments. Calorimetric data on the materials obtained using a Perkin Elmer DSC 7 is also reported in Table 1. The transition temperatures are compared with the structurally related 4-*n*-alkyl-4″-cyano-*p*-terphenyls[12] in the final column of Table 1. Both homologous series exhibit smectic A phases for the longer alkyl chain lengths. The low values of the nematic to isotropic transitional entropy changes recorded for the phenylfluorene series are consistent with the bent shape of the molecules, which may have a tendency for local biaxial ordering.

X-ray measurements were carried out on 2-(4-cyanophenyl)-7-octylfluorene **1h** using a Marr Research Image Plate Detector, and a standard Cu Kα X-ray source. The sample was contained in a Lindemann tube, and the smectic layers aligned partially as concentric cylinders in the sample tube. At 130 °C, the measured layer spacing was 39 Å, with a very weak scattering feature corresponding to a spacing of 22.8 Å along the smectic layer normal. A calculation of the molecular length (Cerius,[2] MSI) gave a value of 23.2 Å for the all trans extended

Table 1. DSC and POM thermodynamic data for the 2-(4-cyanophenyl)-7-*n*-alkylfluorenes.

	R	Transition	Temperature/ °C		ΔH/ kJ mol^{-1}	ΔS/R	CT
			DSC	POM[a]			T_{trans}/ °C
1a	H	Cr → I	229.6	232	19.53	4.68	198
1b	C_2H_5	Cr → N	201.3	201	11.2	2.79	-
		N → I	247.1	248	0.46	0.11	-
1c	C_3H_7	Cr → N	186.6	188	15.77	4.13	182
		N → I	239.6	241	0.4	0.09	258
1d	C_4H_9	Cr → N	157.9	154	18.92	5.28	154
		N → I	219.6	216	0.41	0.1	242
1e	C_5H_{11}	Cr → N	128.6	130	14.54	4.35	131
		N → I	216.3	218	0.43	0.11	240
1f	C_6H_{13}	Cr → N	114.2	118	18.5	5.7	125
		N → I	203.3	203	0.41	0.1	228
1g	C_7H_{15}	Cr → SmA	117.5	122	19.85	6.07	134
		SmA → N[b]	–	152	–	–	126
		N → I	201.8	201	0.49	0.12	222
1h	C_8H_{17}	Cr → SmA	114.5	114	21.14	6.56	86
		SmA → N[b]	177.9	160	0.55	0.15	197
		N → I	193.3	187	0.41	0.11	214
1i	C_9H_{19}	Cr → SmA	113.0	118	21.87	6.77	87
		SmA → N[b]	181.9	186	0.93	0.11	206
		N → I	189.4	194	1.72	0.21	212

Transition temperatures for 4,4''-alkylcyanoterphenyls (nCT) are included for comparison.

[a] Measured temperatures from the polarising microscope have been corrected by calibration with standard materials.

[b] This weak transition was not detected by DSC.

Table 2. Luminescence data for the 2-(4-cyanophenyl)-*n*-alkylfluorenes.

	R	λ_{ex}/nm	λ_{em}/nm	Δλ/nm
Fluorene	H	266	304	38
1a	H	318	376	58
1e	C_5H_{11}	324	391	67
1i	C_9H_{19}	324	395	71
5CT	C_5H_{11}	303	378	75

Comparison with fluorene and 5CT.

chain conformation. Comparison of the measured layer spacing with the molecular length suggests an interdigitated SmA_d phase, similar to those observed for smectic A phases of alkyl cyanobiphenyls. The weak feature detected is consistent with an incommensurate periodicity of about one molecular length, showing that not all the molecules are paired in the interdigitated layers.

In order to investigate the potential of these new mesogens as luminescent liquid crystals, preliminary experiments were carried out on on dilute solutions of fluorene, **1a**, **1e**, **1i** and 4-*n*-pentyl-4″-cyano-*p*-terphenyl (5CT) in dichloromethane using a Perkin Elmer LS 50B luminescence spectrometer. The solution was excited at the absorption maximum as determined by UV-VIS spectroscopy (Shimadzu 1601 UV-Visible spectrophotometer). In all three cases, strong fluorescence was observed. The addition of a methylene bridge to 5CT, giving **1e**, results in a significant bathochromic shift of 21 nm for the absorption maximum. The extinction coefficient for **1e** is also larger (ε/dm^{3}mol^{-1}cm^{-1} 61400 *vs* 42900 for 5CT). These results are consistent with the greater delocalization of electrons over the two coplanar aromatic rings in **1e**. 5CT displays a slightly larger red shift on fluorescence, but the emission maximum for **1e** is still at a longer wavelength. These results are summarized in Table 2.

Financial support from Hitachi Limited is gratefully acknowledged, as is the help of Dr. G. Ungar, University of Sheffield, who carried out the X-ray measurements.

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