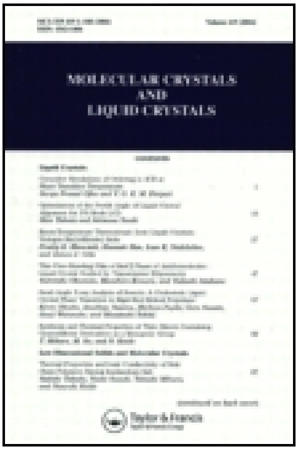

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Fluorene Analogues of Biphenyls: Comparison of Mesogenic Behaviour

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Fluorene Analogues of Biphenyls: Comparison of Mesogenic Behaviour†

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(*Received December 29, 1984*)

A variety of 2,7-disubstituted fluorenes has been synthesised including 2-alkyl-7-cyanofluorenes, 2-pentyl-7-fluorenyl esters and esters of 7-pentyl-2-fluorenecarboxylic acid. Transition temperatures have been determined and are compared with those of analogous biphenyl compounds: it is found that the melting points are higher and the nematic clearing points slightly lower than those of the biphenyl analogues. Suitable mixtures have been used to determine other physical properties.

All of the fluorene esters prepared have a phenyl or cyclohexane ring incorporated in the structure to promote wide mesophase temperature ranges and higher melting points. Some of the esters also give smectic phases.

INTRODUCTION

The effect of replacing biphenyl by fluorene in compounds giving nematic and smectic liquid crystal phases is of considerable interest in the study of the influence of molecular shape on mesogenic properties. The —CH_2— bridge in fluorene (1, X = Y = H) makes the

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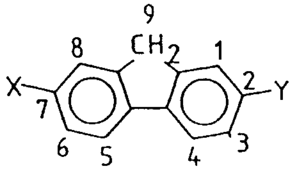
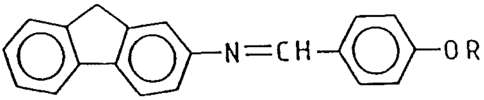
†Presented at the Tenth International Liquid Crystal Conference, York, July 15–21, 1984.

molecule planar,[1,2] which is favourable to mesogenic stability but, conversely, the bridge both broadens the molecule and brings the ring-X and ring-Y bonds out of collinearity, the molecule being bent through an angle[1] of *ca.* 24°.



(1)

A number of fluorene compounds with mesogenic properties are already known. 2-Alkoxyazomethines and 2,7-bisalkoxyazomethines of both fluorene [e.g. (2)] and fluorenone give liquid crystals[3] and so do 2-alkoxyfluorene-7-carboxylic acids and their n-propyl esters[4] (3). The acids exist as dimers and have high transition temperatures. A number of 2-alkyl-7-acylfluorenes are smectogenic[5] and recently some smectogenic and nematogenic esters of 2-bromo- or 2-cyano-7-hydroxyfluorene have been described.[6]



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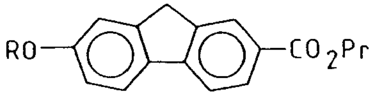


(3)

Gray *et al.*[7] prepared 2-butyl-7-cyanofluorene and found that, unlike the alkylcyanobiphenyls, it gave only a monotropic N → I transition (at −23°C); with 2-cyano-7-hexyloxyfluorene they were unable to observe a nematic phase.

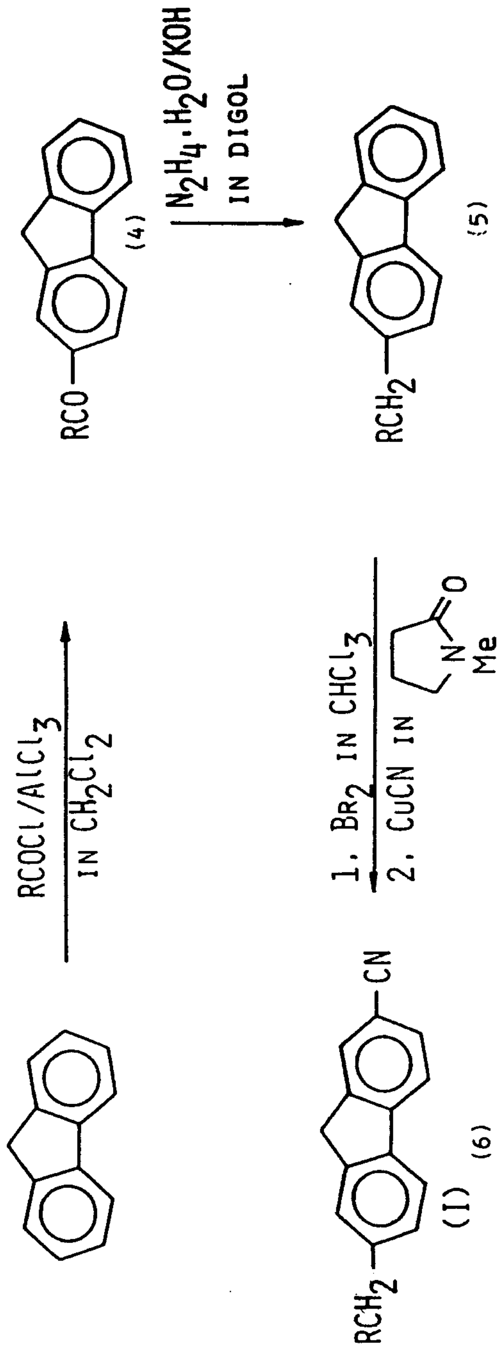
We have now prepared a series of alkylcyanofluorenes and a number of other 2,7-disubstituted fluorenes in a search for nematogens suitable for use in electro-optic displays.

RESULTS AND DISCUSSION

Alkylcyanofluorenes

These were made as shown in Scheme 1.

Melting points and transition temperatures for four alkylcyanoflu-



SCHEME 1 Synthesis of 2-alkyl-7-cyanofluorenes.

TABLE I

Transition temperatures (°C) for 4-alkyl-4'-cyanobiphenyls[7] and 2-alkyl-7-cyanofluorenes (6)

	Alkylcyanobiphenyls			Alkylcyanofluorenes	
Alkyl-	C → N, S	S → N	N → I	C → I	(N → I)
n-C_5H_{11}	22.5	—	35	66	(17.5, 24.5[a])
n-C_6H_{13}	13.5	—	27	50	(14, 21[a])
n-C_7H_{15}	28.5	—	42	51	(29.5)
n-C_8H_{17}	21	32.5	40	55, 58	(33)

[a] Virtual transitions. C = crystal; N = nematic; S = smectic; I = isotropic

orenes are given in Table I, with values for the corresponding alkylcyanobiphenyls for comparison.

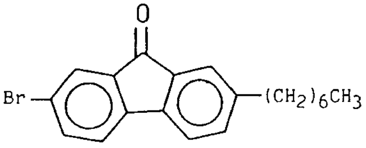
The octyl compound [6; R = $(CH_2)_6CH_3$] is dimorphic: all the crystals appear similar but at 54–55°C the higher melting crystals, which are in the minority, undergo a solid phase transition giving opaque crystals which are easily distinguished from the rest. None of the compounds gives enantiotropic mesophases; initially, only the octyl compound showed a monotropic transition and therefore virtual (N → I) transition temperatures were determined for the other three compounds. In each case two mixtures were used for each compound and the two values obtained for the pentyl and hexyl compounds are shown in Table I. The relatively high values (28.5 and 31°C) for the heptyl compound encouraged further attempts at supercooling its isotropic melt and finally a monotropic phase change was observed.

The —CH_2— bridge in fluorene gives an average reduction in N → I transition temperatures of *ca.* 11°C but causes large increases in melting points (20 to 40°C) which militates against the formation of enantiotropic mesophases. This increase in melting point is observed for mixtures also (cf. Tables III and V).

Oxidation to fluorenones

An attempt was made to produce fluorenone analogues of the 2-alkyl-7-cyanofluorenes *via* dichromate oxidation, but unfortunately this process proved to be inefficient and unselective; oxidation of the side chain to the alkanoyl compound occurred as readily as oxidation of the methylene bridge. Thus 2-bromo-7-heptylfluorene with sodium dichromate in glacial acetic acid gave the unchanged fluorene (23%), the desired compound (7) (11%), 2-bromo-7-heptanoylfluorenone

(7%) and another compound (8%) which was probably 2-bromo-7-heptanoylfluorene.

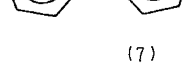


(7)

Physical measurements on an alkylcyanofluorene mixture and comparison with an analogous biphenyl material

A ternary eutectic mixture of alkylcyanofluorenes was prepared with the composition C_5 43%, C_7 30% and C_8 27% by weight. The melting point of the mixture was *ca.* 17–24°C and this lack of a sharp C → I transition can probably be attributed to the polymorphism displayed by some of the compounds.

In order to raise the N → I transition temperature to produce an ambient temperature mesophase for the material, it was necessary to add a high clearing point compound to this eutectic mixture. Hence 20% by weight of BiCH5 [(8), N → I 229°C] was added to the mixture giving a material which will be referred to as the fluorene mixture F1; the composition of F1 is given in Table II. The properties of F1 (transition temperatures, birefringence and viscosity) are given in Table III. An equivalent mixture of 4-alkyl-4′-cyanobiphenyls was also prepared which will be referred to as the biphenyl mixture B1;



(8)

TABLE II

Composition of fluorene mixture F1

Materials			Composition
	Alkyl chain	Composition	
2-Alkyl-7-	C_5	43%	80%
cyanofluorene	C_7	30%	
mixture	C_8	27%	
BiCH5			20%

TABLE III

Transition temperatures, birefringence and viscosity of fluorene mixture F1

C → N/°C	12–22
N → I/°C	62–67
Birefringence	0.208
Viscosity/cSt	325

TABLE IV

Composition of biphenyl mixture B1

Materials			Composition
	Alkyl chain	Composition	
4-Alkyl-4'-cyanobiphenyl mixture	C_5 C_7 C_8	43% 30% 27%	80%
BiCH5			20%

the composition of this mixture is given in Table IV while its properties are given in Table V. A comparison of F1 and B1 shows that the fluorene mixture has the higher melting point but a lower clearing point. The birefringences of the two mixtures are similar but the viscosity of F1 is nearly an order of magnitude greater than that of B1. This large increase in viscosity produced by incorporating a methylene bridge into the biphenyl moiety of the compounds is remarkable.

TABLE V

Transition temperatures, birefringence and viscosity of biphenyl mixture B1

C → N/°C (upper limit of range)	7
N → I/°C	69–74
Birefringence	0.212
Viscosity/cSt	41

Electro-optic threshold sharpness measurements on fluorene mixture F1 and comparison with the analogous biphenyl mixture B1

Sharpness of the voltage threshold can be expressed by the ratios M_{20} and M'_{20} which are defined as follows:

$$M_{20} = \frac{V_{10,0,20}}{V_{90,45,20}} \quad \text{and} \quad M'_{20} = \frac{V_{50,10,20}}{V_{90,45,20}}$$

where $V_{x,\alpha,T}$ are the voltages required to produce $x\%$ transmission of a light beam through a twisted nematic cell at a viewing angle α to the normal at temperature T (°C). $V_{90,45,20}$ is essentially a threshold voltage while $V_{10,0,20}$ is a saturation voltage. A sharp threshold implies low values of M_{20} and M'_{20} with values of threshold and saturation voltages that are close together. For each nematic mixture tested, two different cells were constructed and the voltage readings from the pair were generally within ±0.02 V of one another. The average measurements on the fluorene and biphenyl mixtures (F1 and B1) are given in Table VI along with the merit values M_{20} and M'_{20}. The ratio V_{10}:V_{90} is essentially a measure of V_{ON}/V_{OFF}. A comparison of the values shows that the fluorene mixture has lower threshold voltages and a slightly sharper threshold than the biphenyl mixture.

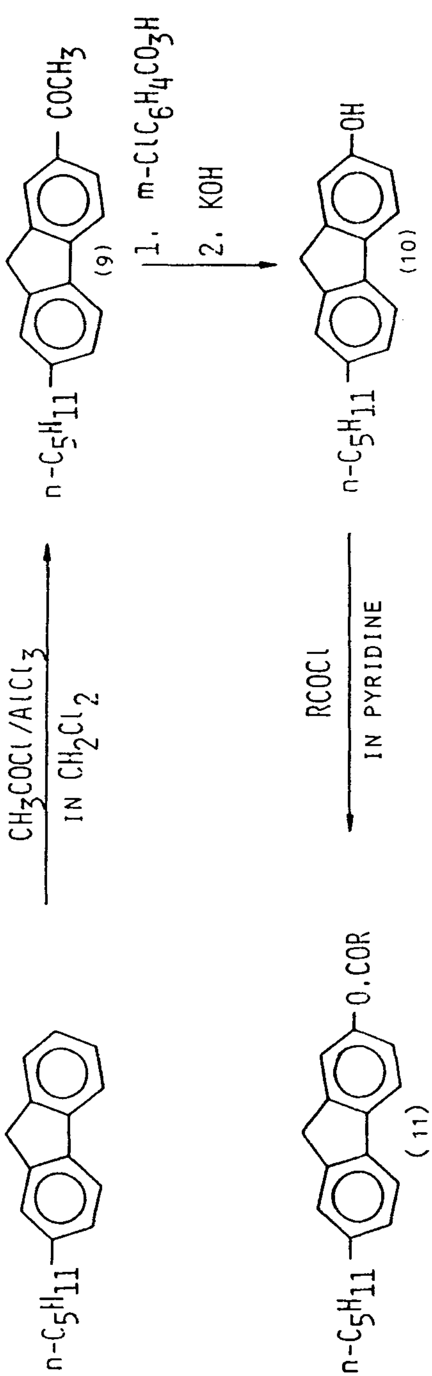
Esters of 2-hydroxy-7-pentylfluorene and 7-pentylfluorene-2-carboxylic acid

Esters of 2-hydroxy-7-pentylfluorene were made as shown in Scheme 2, and Table VII lists the R groups for (11) (which consist of 4-substituted phenyl and 4-substituted cyclohexane moieties) along with

TABLE VI

Electro-optic threshold measurements on F1 and B1

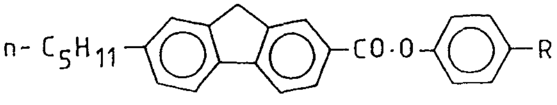
Threshold parameter	F1 voltages	B1 voltages
$V_{10,0,20}$	1.90	2.11
$V_{90,0,20}$	1.42	1.57
$V_{50,10,20}$	1.44	1.59
$V_{90,45,20}$	1.09	1.15
V_{10}:V_{90}	1.34	1.34
M_{20}	1.74	1.83
M'_{20}	1.32	1.38



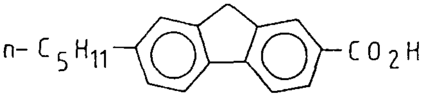
SCHEME 2 Synthesis of esters of 2-hydroxy-7-pentylfluorene.

the transition temperatures of these esters. Alkylation of (10) with bromopentane in the presence of potassium carbonate gave 2-pentoxy-7-pentylfluorene which has a high melting point (115–116°C); the isotropic melt could not be supercooled by more than a few degrees. The virtual N-I transition temperature, determined by the use of mixtures, is 39°C and there is thus little chance of observing nematic mesophases in the 2-alkoxy-7-alkylfluorene series.

Esters of general structure (12) were also sought which required the synthesis of 7-pentylfluorene-2-carboxylic acid (13).

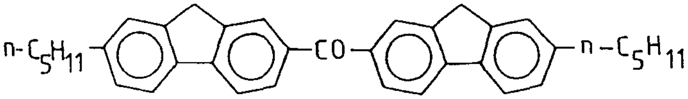


(12)



(13)

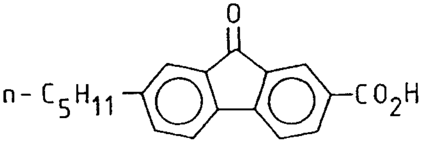
An attempt was made to prepare the acid chloride of (13) by treating 2-pentylfluorene with oxalyl chloride under the conditions used by Neubert and Fisher[8] who synthesised 4-alkylbenzoyl chlorides from 4-alkylbenzenes. The only product that could be separated was a trace (*ca.* 1/2% yield) of (14) which has presumably resulted from acylation of 2-pentylfluorene by the acid chloride of (13) formed in the reaction mixture.



(14)

An attempt was then made to obtain the required acid (13) from 2-acetyl-7-pentylfluorene by oxidation of the acetyl group with sodium hypochlorite solution. However, a four component mixture was obtained which probably consisted (spectroscopic evidence) of the starting material and the required acid (13) along with compounds

(15) and (16) since the methylene bridge of the fluorene core is known[9] to be susceptible to oxidation by sodium hypochlorite.



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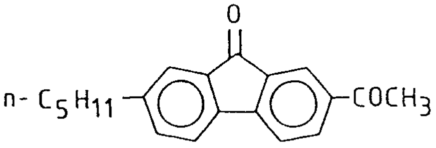
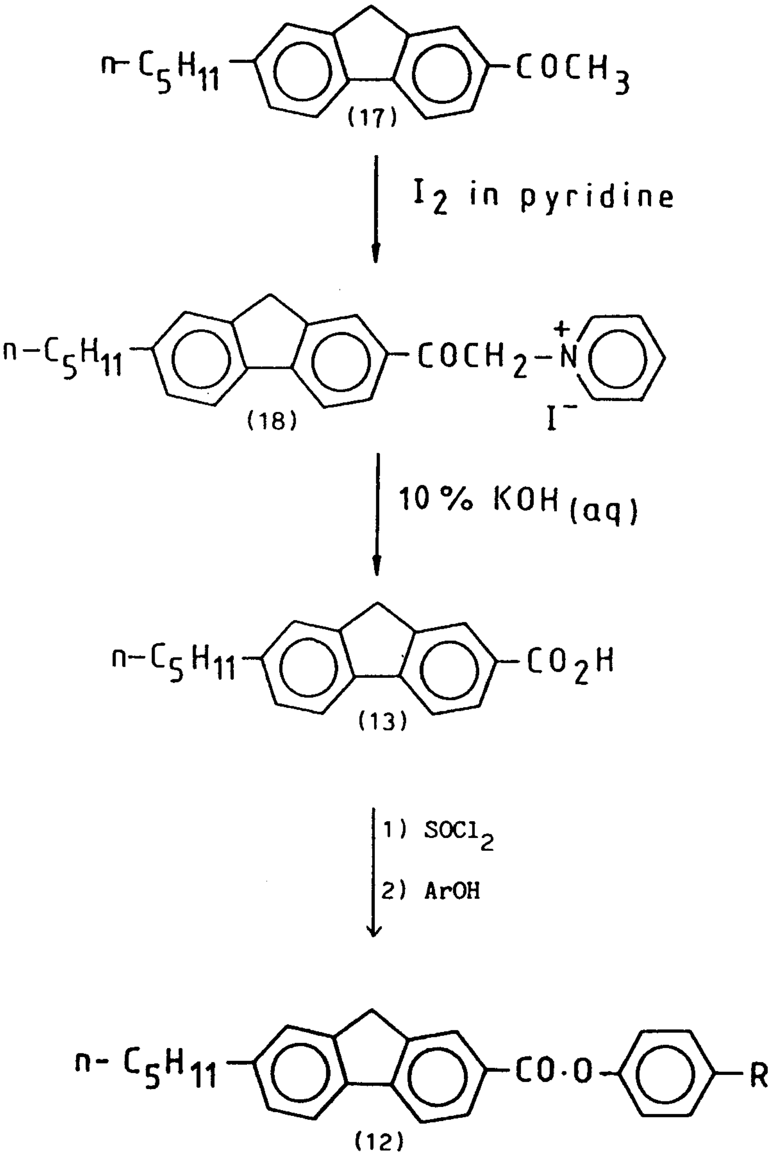


(16)

Another approach to the preparation of the acid (13) was investigated where 2-cyano-7-pentylfluorene was treated with sulphuric acid in order to hydrolyse the cyano group. This hydrolysis did not proceed to completion and the acid amide of (13) was obtained. This amide was hydrolysed with sodium hydroxide in aqueous ethanol to give the required acid (13), but the most convenient route to (13) was ultimately found to be the pathway given in Scheme 3. It was unnecessary to separate the intermediate (18) from the reaction mixture, so the transformation from (17) to (13) was completed in one experiment. The conditions used are similar to those used by Iida[10] in converting 2-acetamido-7-acetyl-9,10-dihydrophenanthrene into 2-acetamido-7-(9,10-dihydro)phenanthroic acid, and the best yield obtained was 48%. The acid (13) was subsequently converted into the acid chloride from which two esters (12) were prepared.

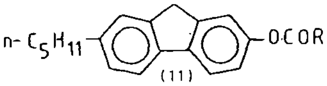
Table VIII gives the transition temperature of the acid (13) and its esters (12). The acid (13) is a nematogen with a fairly wide mesophase temperature range (*ca.* 50°C) having relatively high transition temperatures. The mesophases of the esters (12) are slightly more thermally stable than those of the analogous esters (11) of 2-hydroxy-7-pentylfluorene. The effect of reversing the ester linkage between the fluorene core and the phenyl ring is minimal in terms of shape, but perhaps more extensive conjugation is possible when the carbonyl moiety is bonded directly to the fluorene core giving greater polarisability to the molecule. This effect would be expected to give a



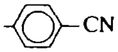
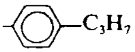
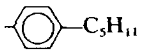
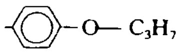
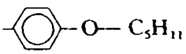
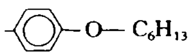
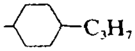
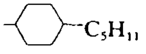
SCHEME 3 Preparation of 7-pentylfluorene—2-carboxylic acid and its esters.

TABLE VII

Esters of 2-hydroxy-7-pentylfluorene: transition temperatures (°C)



(11)

(11), R =	C → N, S	S → N	N → I
 —CN	138–139	173–174	208–209
 —C_3H_7	108–109	—	173–174
 —C_5H_{11}	97–98	—	162–163
 —O— C_3H_7	139–140	—	196–197
 —O— C_5H_{11}	120–121	—	186–187
 —O— C_6H_{13}	115–116	—	183–184
 —C_3H_7	107–108	146–147	171–172
 —C_5H_{11}	87–88	166–167	179–180

C = crystal; N = nematic; S = smectic; I = isotropic

TABLE VIII

7-Pentylfluorene-2-carboxylic acid and its esters: transition temperatures (°C)

Compounds	C → N, S	S → N	N → I
(13)	203-204	—	254-255
(12), R = CN	141-142	—	214-215
(12), R = n-C_5H_{11}	113-114	175-176	178-179

greater nematic thermal stability to the esters (12) of 7-pentylfluorene-2-carboxylic acid (13) as observed (Tables VII and VIII). The esters (11) and (12) with a terminal cyano group have a greater mesophase thermal stability than those with other terminal substituents, a trend which is well documented for many other mesogens. The enhanced mesophase stability of biphenyl mesogens with a terminal cyano group has been partially attributed to the anti-parallel pairing of the molecules.[11] It is therefore virtually certain that similar effects are occurring in the case of the cyano-substituted fluorene mesogens. The esters (11) of hydroxypentylfluorene incorporating an alkoxy substituent on the phenyl ring have higher transition temperatures than the analogous alkyl substituted compounds. This is the expected trend, probably arising from conjugation of the lone pair of the oxygen atom with the phenyl ring giving an enhanced axial polarisation for the alkoxy compounds.

Large increases in viscosity resulted from dissolving esters (11) of hydroxypentylfluorene in room temperature nematic mixtures. Since the fluorene mixture F1 (containing alkylcyanofluorenes) also has an anomalously large viscosity, this confirms that the fluorene core produces viscous materials.

EXPERIMENTAL

Physical measurements and purity of materials

Transition temperatures of single substances were determined on a Kofler block mounted on a Kyowa SDZ-PL polarising microscope. Transition temperatures of mixtures were measured on a Vickers polarising microscope (M72C) with a Mettler FP52 hot stage and Mettler FP5 temperature controller.

Birefringence measurements were made with an Abbé refractometer illuminated with a sodium lamp.

Viscosity measurements were made with a calibrated Ostwald viscometer, the temperature of which was maintained at 20°C in a glycerol/water bath.

The purities of the compounds synthesized and of intermediates were checked by t.l.c. and structures were confirmed by infrared and nuclear magnetic resonance spectroscopy.

Preparation of materials

2-Alkanoylfluorenes (4). The alkanoyl chloride (0.33 mole) was added to a filtered solution of fluorene (0.3 mole) in dichloromethane (300 ml). This mixture was added to a stirred mixture of aluminum chloride (0.33 mole) in dichloromethane (200 ml) and the whole stirred at room temperature for 2–3 hr. and then heated until no more fumes were evolved (*ca.* 1.5 hr.). Normal work up gave a solid which was either dissolved in benzene-dichloromethane and chromatographed on silica gel with benzene as eluant or purified by crystallisation (Table IX).

2-Alkylfluorenes (5). The alkanoylfluorene (0.22 mole) was stirred in diethylene glycol (700 ml) at 100–110°C until an almost clear solution was obtained. Potassium hydroxide (0.5 mole) was added and stirring continued until it had dissolved. The mixture was cooled to *ca.* 95°C and hydrazine hydrate (0.44 mole) was added. The mixture

TABLE IX

2-Alkanoylfluorenes (4)

Compound (4) R (Molecular formula)	Purification	Yield %	M.p. °C	Elemental analysis: Found (%) (required)	
				C	H
n-C_4H_9 ($C_{18}H_{18}O$)	Chromatography C_6H_6 on SiO_2	75	109–110	85.8 (86.35)	7.2 (7.25)
n-C_5H_{11} ($C_{19}H_{20}O$)	Cryst. (Me_2CO)	42	117–118	85.9 (86.3)	7.6 (7.6)
n-C_6H_{13} ($C_{20}H_{22}O$)	Chromatography C_6H_6 on SiO_2 then cryst. (Me_2CO)	78	110–112	86.2 (86.3)	8.0 (8.0)
n-C_7H_{15} ($C_{21}H_{24}O$)	Cryst. (Me_2CO)	62	99–100	86.1 (86.3)	8.3 (8.3)

TABLE X

2-Alkylfluorenes (5)

Alkyl group (Molecular formula)	Yield %	M.p. °C	Elemental analysis: found (%) (required) C	H
Pentyl	70	61-63	90.7	8.5
($C_{18}H_{20}$)			(91.45)	(8.5)
Hexyl	64	64-65	91.3	8.9
($C_{19}H_{22}$)			(91.15)	(8.85)
Heptyl	84	58-60	91.1	9.3
($C_{20}H_{24}$)			(90.9)	(9.15)
Octyl	60	64-66	91.0	9.4
($C_{21}H_{26}$)			(90.6)	(9.4)

was kept at 100–110°C for 20 min. and then at reflux temperature (*ca.* 165°C) for 1 hr. Some liquid was distilled off until the temperature reached 180–190°C and this temperature was maintained for a further 3 hr. After cooling, water was added and the product extracted into ether. The solid obtained after removal of ether was purified by chromatography on silica gel using light petroleum (b.p. 60–80°C) as eluant (Table X).

2-Alkyl-7-bromofluorenes

Bromine (95% of theoretical amount) was added dropwise to a stirred solution of the alkylfluorene in chloroform. The mixture was stirred at room temperature for 3 hr. and at reflux temperature (in the dark) for 2 hr. The solution was washed (aq. $NaHCO_3$, H_2O) and dried, the solvent was removed and the product crystallised (EtOH). Table XI.

2-Alkyl-7-cyanofluorenes

A suspension of cuprous cyanide (2.6 g, 1.5 equivalents) in *N*-methylpyrrolidone (80 ml) was stirred and heated and a little solvent distilled off under slightly reduced pressure to remove any water present. The alkylbromofluorene was added and the mixture was heated under reflux for 2.5 hr. The mixture was then stirred with $FeCl_3$—HCl—H_2O at 60–70°C for 20 min. and, after cooling, was extracted into light petroleum (b.p. 40–60°C). The extract was washed

TABLE XI

2-Alkyl-7-bromofluorenes

Alkyl group (Molecular formula)	Yield %	M.p. °C	Elemental analysis: found % (required)	
			C	H
Pentyl,			68.9	6.1
($C_{18}H_{19}Br$)	41	95–96	(68.6)	(6.1)
Hexyl,			69.6	6.4
($C_{19}H_{21}Br$)	48	90–92	(69.3)	(6.4)
Heptyl,			70.4	6.8
($C_{20}H_{23}Br$)	54	87–89	(70.0)	(6.75)
Octyl			71.4	7.2
($C_{21}H_{25}Br$)	60	83–85	(70.6)	(7.05)

and dried and then yielded crystals on cooling, these were recrystallised from the same solvent. Table XII.

2-Acetyl-7-pentylfluorene

This was prepared from 2-pentylfluorene in 69% yield by Friedel-Crafts acetylation. It had m.p. 92–93°C after crystallisation (EtOH) (Found: C, 85.8; H, 8.0, $C_{20}H_{22}O$ requires C, 86.3; H, 8.0%).

2-Hydroxy-7-pentylfluorene

m-Chloroperoxybenzoic acid (28 g of 80% acid) was added in portions to a stirred solution of 2-acetyl-7-pentylfluorene (36 g), kept at *ca.*

TABLE XII

2-Alkyl-7-cyanofluorenes

Alkyl group (molecular formula)	Yield %	M.p. °C	Elemental analysis: found (%) (required)		
			C	H	N
Pentyl	24	66–67	86.9	7.3	5.0
($C_{19}H_{19}N$)			(87.3)	(7.3)	(5.4)
Hexyl	23	50–51	87.8	7.7	5.2
($C_{20}H_{21}N$)			(87.2)	(7.7)	(5.1)
Heptyl	21	51–52	87.0	8.0	4.8
($C_{21}H_{23}N$)			(87.15)	(8.0)	(4.8)
Octyl	22	55–56	86.5	8.3	4.7
($C_{22}H_{25}N$)		58–59	(87.1)	(8.3)	(4.6)

0°C and protected from light. The mixture was allowed to warm to ambient temperature and stirred thus for 3 days. The resulting suspension was washed with aqueous sodium bicarbonate and water and the chloroform solution dried. Solvent was removed and the residual acetate was hydrolysed with aqueous ethanolic potassium hydroxide. The hydroxy compound was obtained after acidification in a finely divided state and was extracted into chloroform before purification by chromatography (SiO_2 gel, $CHCl_3$) and crystallisation (cyclohexane). Yield 8.6 g (26%), m.p. 156–158°C (Found: C, 86.1; H, 7.9. $C_{18}H_{20}O$ requires C, 85.7; H, 8.0%).

Isolation and purification of the acetate, m.p. 105–107°C, (Found: C, 81.1; H, 7.4. $C_{20}H_{22}O_2$ requires C, 81.6; H, 7.5%), before hydrolysis decreases the yield slightly.

Esters of 2-hydroxy-7-pentylfluorene

The acid chloride was added gradually to a stirred solution of 2-hydroxy-7-pentylfluorene in pyridine and stirring was continued for *ca.* 20 hr. at room temperature. The mixture was poured into water and the solid collected, washed and dried, and crystallised (Table XIII).

7-Pentylfluorene-2-carboxylic acid

2-Acetyl-7-pentylfluorene (30.98 g, 0.111 mole) and iodine (28.88 g, 0.114 mole) were suspended in dry pyridine (175 ml) and the mixture was stirred at *ca.* 100°C for 2 hr. 10% Potassium hydroxide solution (420 ml) was added to the mixture which was then heated under reflux for 5 hr. The source of heat was removed and stirring continued while concentrated hydrochloric acid was added to the hot solution to pH 1. A brown precipitate was obtained which was filtered off when cool, washed with water and allowed to dry. Two crystallisations from benzene (charcoal) gave 7-pentylfluorene-2-carboxylic acid (14.91 g, 48%), C → N 203–204°C. (Found: C, 81.6; H, 7.15. $C_{19}H_{20}O_2$ requires C, 81.4; H, 7.2%).

Esters of 7-pentylfluorene-2-carboxylic acid

The acid was converted into its chloride by heating it with thionyl chloride under reflux overnight. Excess of thionyl chloride was removed and the residue was crystallized from light petroleum (b.p. 60–80°C). Yield 79% m.p. 75–76°C (Found: C, 77.65; H, 6.5. $C_{19}H_{19}ClO$ requires C, 76.4; H, 6.4%). The phenol dissolved in pyr-

TABLE XIII

Esters of 2-hydroxy-7-pentylfluorene

(11), R (molecular formula)	Crystallisation solvent	Yield %	Elemental analysis: Found % (required)	
			C	H
NC C_6H_4 C → S 138–139°C $C_{26}H_{23}NO$	GAA[a]	52	81.7 (81.85)	6.1[d] (6.1)
n-$C_3H_7C_6H_4$ C → N 108–109°C ($C_{28}H_{30}O_2$)	LP[b]	42	84.05 (84.4)	7.6 (7.6)
n-$C_5H_{11}C_6H_4$ C → N 97–98°C ($C_{30}H_{34}O_2$)	EtOH	51	84.95 (84.5)	7.9 (8.0)
n-$C_3H_7OC_6H_4$ C → N 139–140°C ($C_{28}H_{30}O_3$)	[c]	31	81.3 (81.1)	7.3 (7.3)
n-$C_5H_{11}OC_6H_4$ C → N 120–121°C ($C_{30}H_{34}O_3$)	EtOH	30	81.5 (81.4)	7.75 (7.8)
n-$C_6H_{13}OC_6H_4$ C → N 115–116°C ($C_{31}H_{36}O_3$)	LP[b]	52	81.2 (81.5)	7.8 (7.95)
n-$C_3H_7C_6H_{10}$ C → S 107–108°C ($C_{28}H_{36}O_2$)	EtOH	29	83.1 (83.1)	9.0 (9.0)
n-$C_5H_{11}C_6H_{10}$ C → S 87–88°C ($C_{30}H_{40}O_2$)	EtOH	37	83.3 (83.3)	9.3 (9.3)

[a] glacial acetic acid, [b] light petroleum (b.p. 60–80°C), [c] purified by chromatography (SiO_2 gel, $CHCl_3$), [d] Found, N, 3.7, Required N, 3.7%

idine was added to a solution of the acid chloride in pyridine and the mixture was stirred overnight at *ca*. 70°C and then poured into water. Solid was collected, washed and dried and crystallised (EtOH).

p-Pentylphenyl ester: (Found: C, 85.0; H, 8.0. $C_{30}H_{34}O_2$ requires C, 84.5; H, 8.0%).

p-Cyanophenyl ester: (Found: C, 82.05; H, 6.1; N, 3.6. $C_{26}H_{23}NO_2$ requires C, 81.85; H, 6.1; N, 3.7%).

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