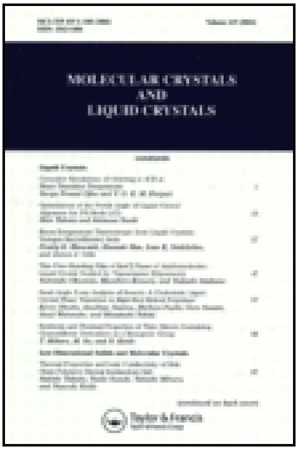

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# Synthesis of Some New Fluorene Esters with Mesomorphic Behavior

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# Synthesis of Some New Fluorene Esters with Mesomorphic Behavior†

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A number of 2-fluorenyl 4′-alkylbenzoates and 4′-alkoxybenzoates have been synthesized to study the effects of the central ester linkage on their mesomorphic behavior. These compounds typically show nematic (N) and the uniaxial smectic phases. Many isomeric fluorene esters with reversed ester linkage were also prepared, but no major differences were observed. The presence of a lateral substituent in the phenyl ring decreases the nematic-isotropic (N-I) temperature by about 28°C. Replacement of phenylene by trans-cyclohexylene has the unusual effect of increasing the N-I transition temperature by about 21°C. The presence of a nitro group at position (7) of the fluorene ring increases N-I temperature by about 66°C and stabilizes the $S_A$.

## INTRODUCTION

Prior to 1975 there appeared in the literature several studies and reviews on the mesomorphic behavior of compounds containing the fluorene moiety.[1,2] In general it was learned that this moiety had the effect of providing stability to the smectic A phase. When compared to the cyanobiphenyls the fluorenes appeared to give less desirable properties for display applications such as high solid-nematic melting points and short temperature range nematic phases. It is perhaps for this reason that studies of these materials were dropped.

Recently, we have started a new study of these materials brought on by the desireable features of this moiety for NMR studies,[3] its high thermal stability and its tendency to form uniaxial smectic phases.[2,4]

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‡On leave from the Institute of Physics, Technical University of Lodz, Poland.

Our initial work on 2-fluorenylmethylidene-4′-R-anilines[5] led us to investigate the effect of replacing the central imine linkage with that of an ester. Thus a number of 2-fluorenyl 4′-R-benzoates were synthesized. In this program a number of effects were studied which include that of the reversed ester linkage; a lateral chloro group in the phenyl ring; with and without a nitro group at position (7) of the fluorene ring; the replacement of the 1,4-phenylene ring with that of the trans-1,4-cyclohexylene; and finally we prepared an analogous ester of cyclohexylene with a nitro group at position (7) of the fluorene.

## RESULTS AND DISCUSSION

We start with the 2-fluorenyl 4′-*n*-alkylbenzoates (Table I) which show the onset of monotropic nematic phase when the chain length is two or four carbons long. On increasing the chain length from $C_5$-$C_{12}$ only a nematic phase is formed.

The nematic-isotropic (N-I) transition temperatures for these compounds have been plotted versus the number of C-atoms in the alkyl chain (Figure 1). The usual alternation of the N-I transition temperatures is observed with increasing chain length.[5,6]

The transition temperatures of 2-fluorenyl 4′-*n*-alkoxybenzoates are given in Table II, and a plot of their transition temperatures versus number of C-atoms of the alkoxy chain is shown in Figure 2. The odd-even alternation of the N-I transition temperatures has the usual effect of what has been observed for the alkyl and alkoxy chains.[5,7]

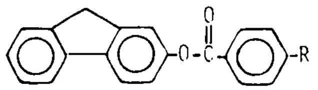
A monotropic smectic phase starts to appear with a chain $C_8$-$C_9$. This phase becomes enantiotropic with a chain $C_{10}$-$C_{16}$. The nematic phase, however, continues to appear even when the number of C-atoms are $C_{16}$ in the alkoxy chain. The smectic phase has a focal-conic texture often accompanied with fans and homeotropic areas. This smectic phase may be regarded as smectic A by the textures reported from Sackman and Demus.[8] In many members of this series both the nematic phase and smectic phase have a very strong tendency to become homeotropic.

As expected the N-I transition temperatures of this series are higher by 22 – 55°C when compared with those of the analogous fluorenyl alkylbenzoates (Table I).

Another observation is the absence of a smectic phase in the case of 2-fluorenyl 4′-*n*-alkylbenzoates (Table I) when compared to the analo-

TABLE I

Transition temperatures (°C)
of 2-fluorenyl 4′-*n*-alkylbenzoates



| R | C-N or I | N-I |
|---|---|---|
| C | 175.1 | — |
| $C_2$ | 152.0 | 130.0[a] |
| $C_4$ | 135.0 | 130.3[a] |
| $C_5$ | 119.9 | 138.7 |
| $C_6$ | 111.6 | 121.7 |
| $C_7$ | 113.7 | 129.6 |
| $C_8$ | 114.1 | 123.3 |
| $C_9$ | 111.5 | 124.0 |
| $C_{10}$ | 113.8 | 118.2 |
| $C_{12}$ | 109.7 | 115.6 |

[a] Transition from monotropic N.

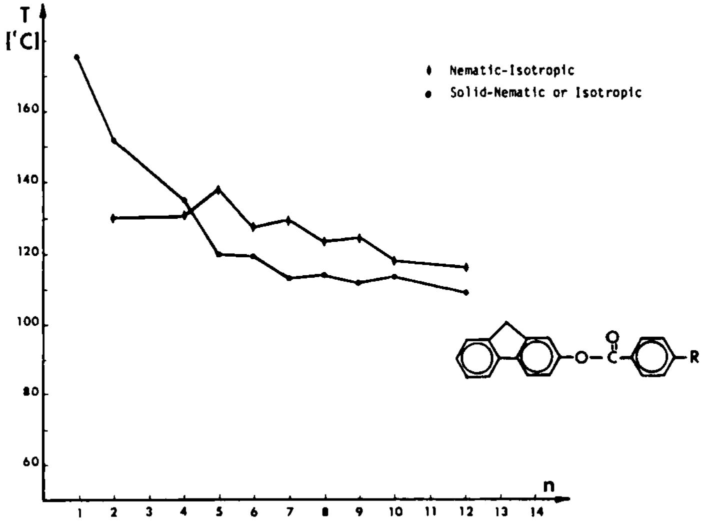


FIGURE 1 Transition temperatures of 2-fluorenyl 4′-*n*-alkylbenzoates plotted versus the number of carbon atoms in the alkyl chain.

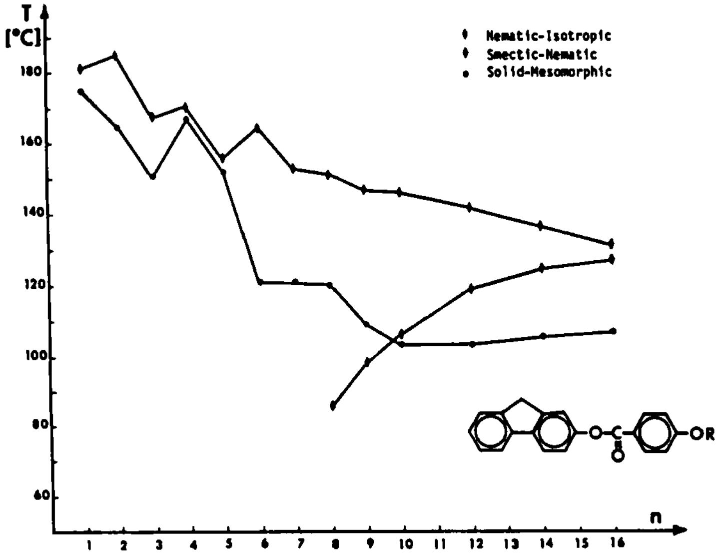
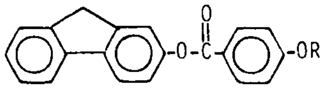


FIGURE 2 Transition temperatures of 2-fluorenyl 4′-*n*-alkoxybenzoates plotted versus the number of carbon atoms in the alkoxy chain.

TABLE II
Transition temperatures (°C) of
2-fluorenyl 4′-*n*-alkoxybenzoates

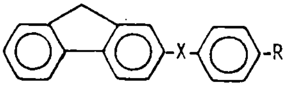


| R | C-$S_A$ or N | $S_A$-N | N-I |
|---|---|---|---|
| C | 174.2 | — | 181.4 |
| $C_2$ | 165.0 | — | 185.1 |
| $C_3$ | 150.5 | — | 167.8 |
| $C_4$ | 167.4 | — | 170.7 |
| $C_5$ | 152.2 | — | 156.0 |
| $C_6$ | 115.5 | — | 159.3 |
| $C_7$ | 123.0 | — | 152.7 |
| $C_8$ | 120.2 | 86.1[a] | 151.3 |
| $C_9$ | 109.0 | 98.8[a] | 146.7 |
| $C_{10}$ | 103.6 | 106.8 | 145.8 |
| $C_{12}$ | 101.8 | 118.5 | 142.9 |
| $C_{14}$ | 105.0 | 124.6 | 136.1 |
| $C_{16}$ | 106.4 | 126.6 | 131.3 |

[a] Transition from monotropic $S_A$.

## TABLE III

Effect of exchange of "X" linkage in 2-fluorenyl 4′-*n*-alkylbenzoates on the transition temperatures (°C)

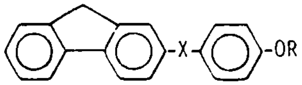


| R | X | C-$S_B$, $S_A$, N or I | $S_B$-$S_A$ | $S_A$-N or I | N-I |
|---|---|---|---|---|---|
| $C_4$ | OOC | 135.0 | — | — | 130.3[a] |
| | CH = N | *141.0 | 98.0[c] | 123.0[b] | 156.5 |
| $C_6$ | OOC | 111.6 | — | — | 121.7 |
| | CH = N | *125.5 | 92.5[c] | 135.0 | 154.5 |
| $C_9$ | OOC | 111.5 | — | — | 124.0 |
| | CH = N | *123.0 | 74.0[c] | 144.0 | 149.5 |
| $C_{10}$ | OOC | 113.8 | — | — | 118.2 |
| | CH = N | *119.0 | 68.5[c] | 143.5 | 145.5 |
| $C_{12}$ | OOC | 109.7 | — | — | 115.6 |
| | CH = N | *118.0 | — | 141.0 | — |

[a] Transition from monotropic N.
[b] Transition from monotropic $S_A$.
[c] Transition from monotropic $S_B$.
*Ref. 5.

## TABLE IV

Effect of exchange of "X" linkage in 2-fluorenyl 4′-*n*-alkoxybenzoates on the transition temperatures (°C)



| R | X | C-$S_B$, $S_A$ or N | $S_B$-$S_A$ | $S_A$-N or I | N-I |
|---|---|---|---|---|---|
| $C_7$ | OOC | 123.0 | — | — | 152.7 |
| | CH = N | *139.0 | 125.0[b] | 159.0 | 184.0 |
| $C_8$ | OOC | 120.2 | — | 86.1[a] | 151.3 |
| | CH = N | *135.0 | — | 163.0 | 182.5 |
| $C_9$ | OOC | 109.0 | — | 98.8[a] | 146.7 |
| | CH = N | *132.0 | — | 166.5 | 178.0 |
| $C_{10}$ | OOC | 103.6 | — | 106.8 | 145.8 |
| | CH = N | *129.5 | — | 167.0 | 174.5 |
| $C_{14}$ | OOC | 105.0 | — | 124.6 | 136.1 |
| | CH = N | *126.0 | — | 164.5 | — |

[a] Transition from monotropic $S_A$.
[b] Transition from monotropic $S_B$.
*Ref. 5.

gous members of the alkoxybenzoates (Table II). Such a feature has been observed in other materials.[9]

Two features are observed when a comparison is made between selected 2-fluorenyl 4′-R-benzoates and 2-fluorenylmethylideneanilines listed in Tables III and IV. The 2-fluorenylmethylidene-4′-*n*-alkylanilines (Table III) have smectic phases and higher N-I transition temperatures (25–33°C). This feature suggests that the various parts of the molecule viz., the terminal fluorene and benzene rings along with the imine linkage are relatively coplanar with respect to one another.[10] The coplanarity of the molecule will enhance mutual conjugation of the entire molecule and thereby enhance the net polarizability along its major axis.

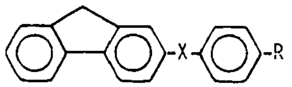
The differences in transition temperatures and the mesomorphic behavior of 2-fluorenyl 4′-*n*-alkoxybenzoates and 2-fluorenylmethylidene-4′-*n*-alkoxyanilines (Table IV) could be explained similarly.

Transition temperatures of the isomeric esters (Table V) in which the central ester linkage is reversed do not show significant changes.

The presence of a nitro group (see Table VI) in the fluorene ring at position (7) in 2-fluorenyl 4′-*n*-heptyloxybenzoate not only produces a smectic phase but also increases the N-I transition temperature by 66°C as one might expect.

TABLE V

Effect of reversing the ester linkage (X) on transition temperature (°C)

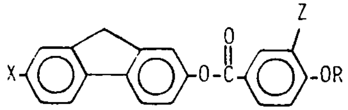


| R | X | C-N or I | N-I |
|---|---|---|---|
| CN | -OOC- | 156.0 | 199.0 |
| | -COO- | 177.2 | 204.4 |
| $CH_3O$ | -OOC- | 174.2 | 181.4 |
| | -COO- | 152.0 | 162.0 |
| $n$-$C_4H_9O$ | -OOC- | 167.4 | 170.7 |
| | -COO- | 151.9 | 166.8 |
| $n$-$C_6H_{13}O$ | -OOC- | 115.5 | 159.3 |
| | -COO- | 119.6 | 159.8 |
| $C_2H_5$ | -OOC- | 152.0 | 130.0[a] |
| | -COO- | 131.4 | — |
| $n$-$C_{10}H_{21}$ | -OOC- | 113.8 | 118.2 |
| | -COO- | 89.2 | 121.0 |

[a] Transition from monotropic N.

TABLE VI

Transition temperature (°C) of 7-X-2-fluorenyl 3′-Z-4′-*n*-alkoxybenzoates



| X | R | Z | C-$S_A$, N or I | $S_A$-N | N-I |
|---|---|---|---|---|---|
| H | $C_7$ | H | 123.0 | — | 152.7 |
| $NO_2$ | $C_7$ | H | 137.2 | 201.0 | 219.1 |
| H | $C_{10}$ | H | 103.6 | 106.8 | 145.8 |
| H | $C_{10}$ | Cl | 132.5 | — | 117.1[a] |

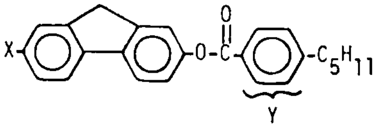
[a] Transition from monotropic N.

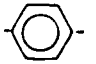
The presence of a chloro group on the benzene ring at position (3) in 2-fluorenyl 3′-chloro-4′-*n*-decyloxybenzoate (Table VI) not only decreases the N-I temperature by about 28°C, but also causes the smectic phase to disappear. This may be attributed to the lateral broadening of the molecule.[7,10,11]

An unexpected result is revealed by Table VII where the 2-fluorenyl 4′-*n*-pentylbenzoate has lower N-I transition temperatures

TABLE VII

Effect of replacing 1,4-phenylene (Y)
with trans-1,4-cyclohexylene in 2-fluorenyl-4′-*n*-pentylbenzoate
on the transition temperatures (°C)



| X | Y | C-N | N-I |
|---|---|---|---|
| H |  | 119.9 | 138.7 |
| H |  | 133.0 | 159.7 |
| $NO_2$ |  | 121.0 | 201.0 |

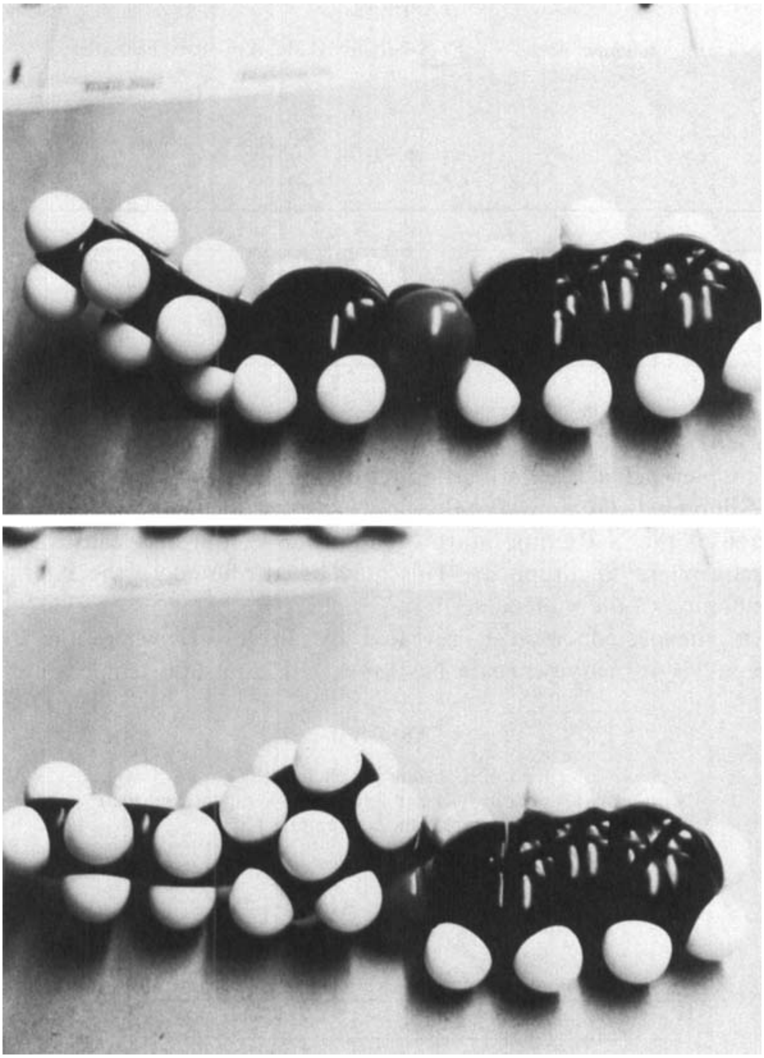


FIGURE 3 Planar structures represented by CPK models of fluorene esters. Top with phenylene; bottom with trans-cyclohexylene.

by 21°C than the analogous compound having trans-1,4-cyclohexylene. Higher N-I temperatures in mesogens having a cyclohexane ring have been observed by others.[12,13] Recently a similar observation to ours has also been made by Demus et al.[14] in 1,4-bis-[4-*n*-hexylcyclohexanoyloxy]-2-ethylbenzene. The higher N-I temperature of this compound has been attributed to repulsive forces.[14]

Space filling models have been used to represent the structures and are also shown in Figure 3 for our materials. It is interesting to note that in the case of 2-fluorenyl 4′-*n*-pentylbenzoate the central ester linkage and the fluorenyl group are not coplanar. This is due to the steric hindrance caused by the 1,3-hydrogens of the fluorene ring to the carbonyl oxygen. This leads to a noncoplanar arrangement between the central ester linkage and the fluorenyl group. This non-coplanarity may cause a decrease in the mutual conjugation at this part of the molecule and consequently a lower N-I transition temperature results. It is seen from Figure 3 that the model for 2-fluorenyl 4′-n-pentylbenzoate was made and does not give a linear molecular structure.

On the other hand the model with trans-1,4-cyclohexylene ring shows coplanarity between the central ester linkage and fluorenyl group which results in a higher degree of conjugation. Further, the terminal cyclohexane ring aligns itself in such a way that on the whole the molecular structure is more linear.

The presence of a nitro group on the fluorene ring at position (7) in an analogous compound with a trans-1,4-cyclohexylene group has a higher N-I temperature. This is easily explained by the presence of a strong dipolar group which increases the net polarizability of the molecule along its major axis. Thus both terminal and lateral intermolecular attraction increases and these in turn increase the N-I transition temperatures.

## EXPERIMENTAL

The phase transition temperatures were determined with a Leitz polarizing microscope using a Mettler FP-2 heating stage. The melting points (solid-liquid or solid-liquid crystal transition) are those recorded from heating. The error of the temperature measurements is estimated to be smaller than ±2°C.

## PREPARATION OF MATERIALS

Most of the starting materials are commercially available and pure enough for the synthesis of the final products. The unavailable p-n-alkoxybenzoic acids were prepared from p-hydroxybenzoic acid and the corresponding alkyl bromide according to the method of Gray and Jones.[15]

*p-n-Alkoxybenzoyl chlorides* were prepared by the usual method of refluxing the appropriate alkoxybenzoic acid (1 mol) and thionyl chloride (1.25 mol) in dry toluene in the presence of anhydrous pyridine. After refluxing, isolated acid chlorides were subsequently used for the preparation of esters.

*Acid chlorides of fluorene-2-carboxylic acid* were identically prepared.

*Fluorene-2-carboxylic acid* was prepared from fluorene according to F. E. Ray and G. Rieveschl.[16]

2-*Hydroxyfluorene* was prepared from 2-acetylfluorene by the method of Jones et al.[17]

*The esters* were prepared by the dropwise addition of the hydroxy compound (1 mol) dissolved in dry toluene and pyridine, to the solution of the corresponding acid chloride (1.1 mol) in dry toluene. After the addition, the reaction mixture was refluxed for 10–12 hr, filtered hot to remove the pyridine hydrochloride, and followed by the removal of the solvent under reduced pressure. The residual solid was cooled and triturated with ethanol to remove the unreacted materials, the product being less soluble in ethanol. For the preparation of some esters instead of toluene and pyridine, methylene chloride and triethylamine were used. In each case the isolated ester was recrystallized several times from an appropriate solvent until the transition temperatures remained constant.

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 heating and cooling of a pure compound in most cases were, within a fraction of a degree, equal to temperatures for these transitions.

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