

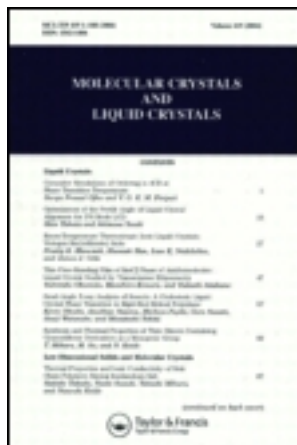
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Mesophase Transition of Series Materials Containing Fluorene, Fluorenone and Biphenyl Structures with Chiral End Groups

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S 2-alkoxyfluorene-7-carboxylic acid 4-(2-methylbutoxy)-phenyl ester and *S* 2-alkoxy-fluorenone-7-carboxylic acid 4-(2-methylbutoxy)-phenyl ester were synthesized and the effects of mesogen modification or substitution of biphenyl with fluorene and fluorenone group in a mesogen core were studied to obtain a wide temperature range for the SmC* phase. It was found that the SmA phase was rather stabilized by a fluorene substitution, though the thermal stability of the SmC* phase decreased in comparison with the data for biphenyl derivatives. On the other hand, by a fluorenone substitution the SmA phase stability decreased markedly and the SmC* phase stability increased. These results could be explained by two factors.

1. Enhancement in attractive intermolecular force by increasing polarizability of fluorene, compared with biphenyl.
2. Enhancement in induction force due to the dipole moment of the carbonyl group in the fluorenone.

1. INTRODUCTION

In recent years, ferroelectric liquid crystals have been the subject of much interest due to their potential advantage in regard to quick response and memory properties in display device application.¹ However, the variety of materials available for those applications is still limited at present, compared with the vast variety of the well-developed nematic liquid crystal materials. Further, the relationship be-

tween the molecular structures and the properties of the chiral smectic C phase has not been fully clarified yet.

However, many of the mesogens of the ferroelectric liquid crystal materials reported so far contain a biphenyl structure² in their mesogens. So, the investigation on the effect of the structural modification of the biphenyl mesogens on the liquid crystalline phase diagram would provide a great deal of information on the relation between the mesogen molecular structure and the mesophase structure.

Among many modification methods, the introduction of the bridge between 2 and 2' positions of the biphenyl group, like fluorene and fluorenone would drastically change the properties of biphenyl mesogens.

The changes introduced by the substitution of fluorene for a biphenyl skeleton could be summarized as follows.

1. The rotational degree of freedom for the C—C bond between the two phenyl rings is killed by the introduction of the bridge. Thus, the fluorene mesogens are completely flat.³ This implies that the delocalization of the electrons would extend to the adjacent aromatic rings and would result in an increase in the polarizability of mesogens, which enhances intermolecular attractive interaction. Thus, the smectic phase would be stabilized.⁴

2. The decrease in the axial ratio for the mesogen group, by the introduction of the "outboard" methylene group, however, would decrease the shape anisotropy for the mesogens and consequently decrease the thermal stability of the smectic phase.

3. The overall shape of the mesogen changes from a linear rod to a banana-like shape, due to the bending of the biphenyl axis with an angle of about 24°. This deformation would also diminish anisotropy and therefore works against smectic phase stabilization.

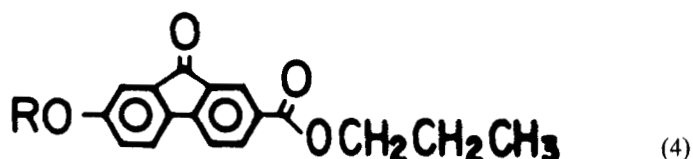
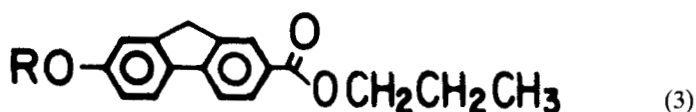
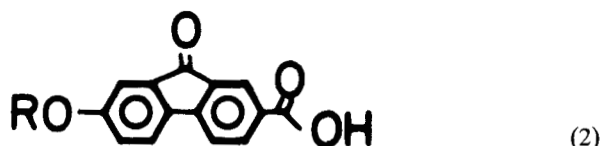
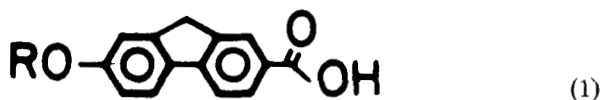
The replacement of biphenyl with fluorenone would add two more changes.

4. The carbonyl group attached perpendicularly to the biphenyl axis further increases the molecule width. Thus, thermal stability for the smectic phase would be further reduced.

5. The permanent dipole moment is introduced into the molecule by the carbonyl group, which was pointed out by van der Meer,⁵ to induce the smectic C phase.

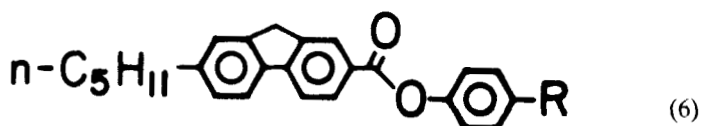
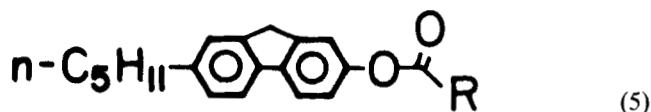
Several liquid crystal materials containing fluorene and fluorenone structures have been reported. Gray and his co-workers⁶ synthesized

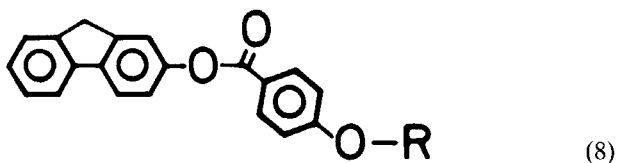
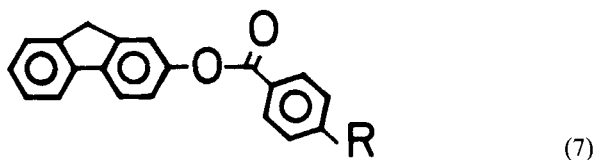
and investigated the 2-alkoxy-7-carboxylic acids and their *n*-propyl esters, which have fluorene or fluorenone structures. (1) ~ (4)



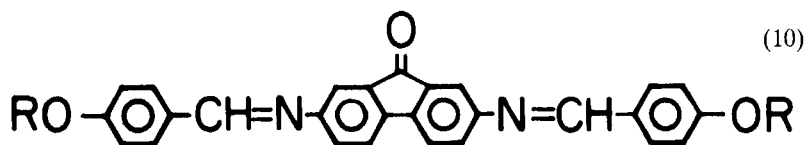
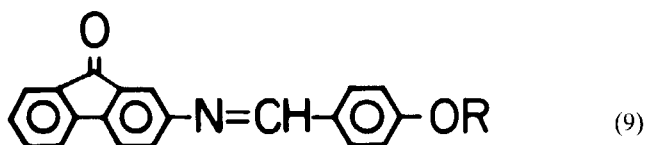
Although fluorene derivatives (1) and (3) showed a smectic (not specified as smectic A, C and other) mesophase in a wide range of temperatures, the fluorenone derivatives (2) and (4) did not show any kind of mesophase.

The fluorene derivatives (5) and (6), and (7) and (8) have been reported by Davidson et al.,⁷ and Arora et al.,⁸ respectively. However, in these fluorene derivatives, the smectic C phase was not identified, though the nematic and smectic A phase were observed. Thus, concerning fluorene derivatives, no stable smectic C phase has been confirmed.

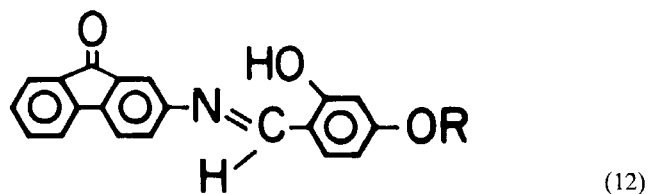
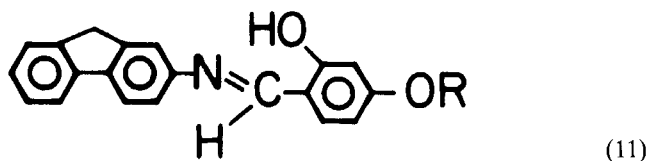




The liquid crystal materials, which have a fluorenone structure, have been the subject of very few reports. Gray et al.,⁹ reported that the fluorenone derivatives (9), (10) showed a stable smectic phase but they did not specify the type of smectic phase in detail.

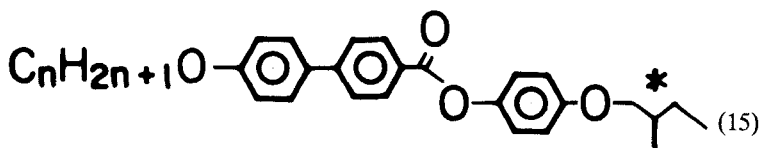
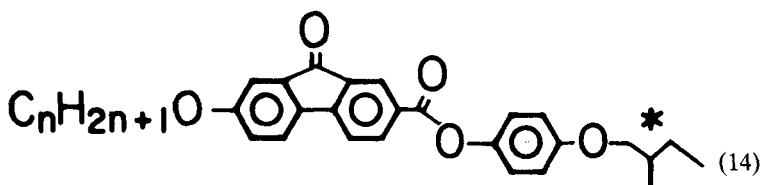
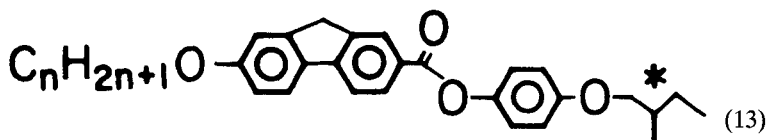


Recently, Kusabayashi et al.,¹⁰ reported the thermal stability of the smectic C phase for the fluorene and fluorenone derivatives (11), (12). They emphasized the importance of the transverse dipole moment, which either resides on the mesogen groups or attaches to the end of them for smectic C phase thermal stability.



Thus, the correlation between the mesophase sequence and molecular structural modification for biphenyl, fluorene and fluorenone has not been fully investigated.

To clarify this problem, and together with the desire to develop new ferroelectric liquid crystal materials having a wide temperature range for the chiral smectic C phase, the authors have synthesized fluorene (13) and fluorenone (14) derivatives having a chiral group



and an alkyl chain with various lengths in a tail of the molecules. By measuring and comparing their mesophase sequence behavior with that for the biphenyl derivatives (15), which is reported in detail by Inukai et al.,¹¹ the structure-mesophase correlation for this class of materials is discussed.

2. RESULT AND DISCUSSION

2.1. Fluorene and fluorenone derivatives syntheses

Starting materials for fluorene derivatives (13) were synthesized according to the method reported by Gray.⁶ The reaction mixtures for the 2-acetyl-7-alkoxyfluorenes oxidation contained a small amount of 2-alkoxyfluorenone-7-carboxylic acids, besides the desired 2-alkoxyfluorene-7-carboxylic acids. The amounts of fluorenone derivatives were about 15% of the fluorene derivatives. These mixtures were esterified with *S* 4-(2-methylbutoxy)-phenol by the usual method. The *S* 2-alkoxyfluorene-7-carboxylic acid 4-(2-methylbutoxy)-phenyl es-

TABLE I

Phase transition temperature ($T/^{\circ}\text{C}$) of *S* 2-alkoxyfluorene-7-carboxylic acid 4-(2-methylbutoxy)-phenyl ester¹³

n	$T_{\text{C-Sc}^* \text{ or SA}}$	$T_{\text{Sc}^* \text{-SA}}$	$T_{\text{SA-I}}$	$T_{\text{Sc}^* \text{-SX}}^a$
6	119	^b (87)	208	
8	117	(109)	201	
10	115	137	194	
12	91	144	187	(80)
14	86	143	183	(81)

^aC: crystal, Sc*: chiral smectic C, SA: smectic A, SX: smectic X (This smectic phase has not been identified yet).

^b(): monotropic transition.

ters (13) and *S* 2-alkoxyfluorenone-7-carboxylic acid 4-(2-methylbutoxy)-phenyl esters (14) were separated from the mixtures through a column chromatographic technique.

2.2. Mesophase transition

The transition temperatures for these materials are listed in Tables I and II and plotted as a function of the alkyl chain length n in Figures 1 and 2 for molecular structures (13) and (14), respectively. In these figures, the values for the transition temperatures of the biphenyl derivatives, published by Inukai and his co-workers (15), having a corresponding terminal alkyl chain, are also indicated with dotted lines.

Fluorene derivatives

The overall mesomorphic behavior is qualitatively similar to that for the biphenyl derivatives, except for an unidentified smectic phase SmX, which appeared below the smectic C* phase in the cooling

TABLE II

Phase transition temperature ($T/^{\circ}\text{C}$) of *S* 2-alkoxyfluorenone-7-carboxylic acid 4-(2-methylbutoxy)-phenyl ester (14)

n	$T_{\text{C-Sc}^*}$	$T_{\text{Sc}^* \text{-SA or I}}$	$T_{\text{SA-Ch or I}}$	$T_{\text{Ch-I}}^a$
6	100	125	157	165
8	101	140	158	
10	112	157	166	
12	104	158	163	
14	95	147		

^aC: crystal, Sc*: chiral smectic C, SA: smectic A, Ch: Cholesteric

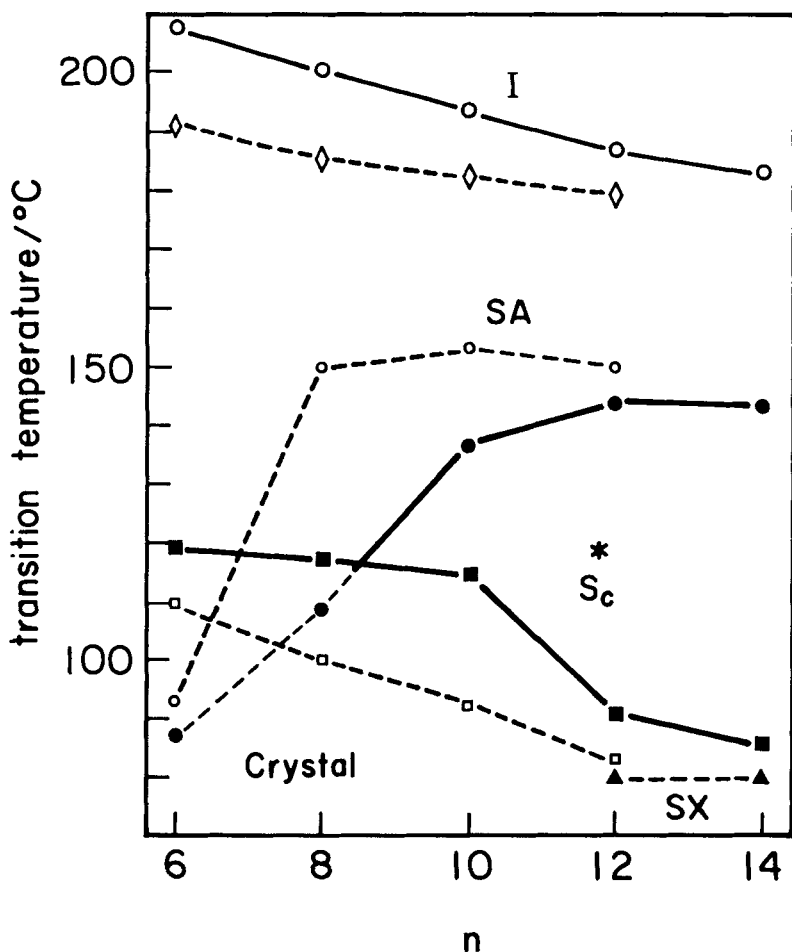


FIGURE 1 Plot showing transition temperatures of fluorene derivatives (13), as a function of the terminal alkyl chain length, with n being $-(CH_2)_nH$. The broken lines indicate the data published for biphenyl derivatives,¹¹ for comparison.

process. For derivatives with $n = 6$ and 8, a thermal hysteresis was observed in the mesophase transition, even with a $5^\circ\text{C}/\text{min}$ cooling and heating rate.

The transition temperature from a smectic A phase to an isotropic phase, T_{SA-I} , was considerably higher in the fluorene derivatives than in the biphenyl derivatives by about 20 degrees.

This could be ascribed to the increase in attractive intermolecular interaction, due to the introduction of the methylene bridge between the adjacent phenyl rings in the biphenyl structure.

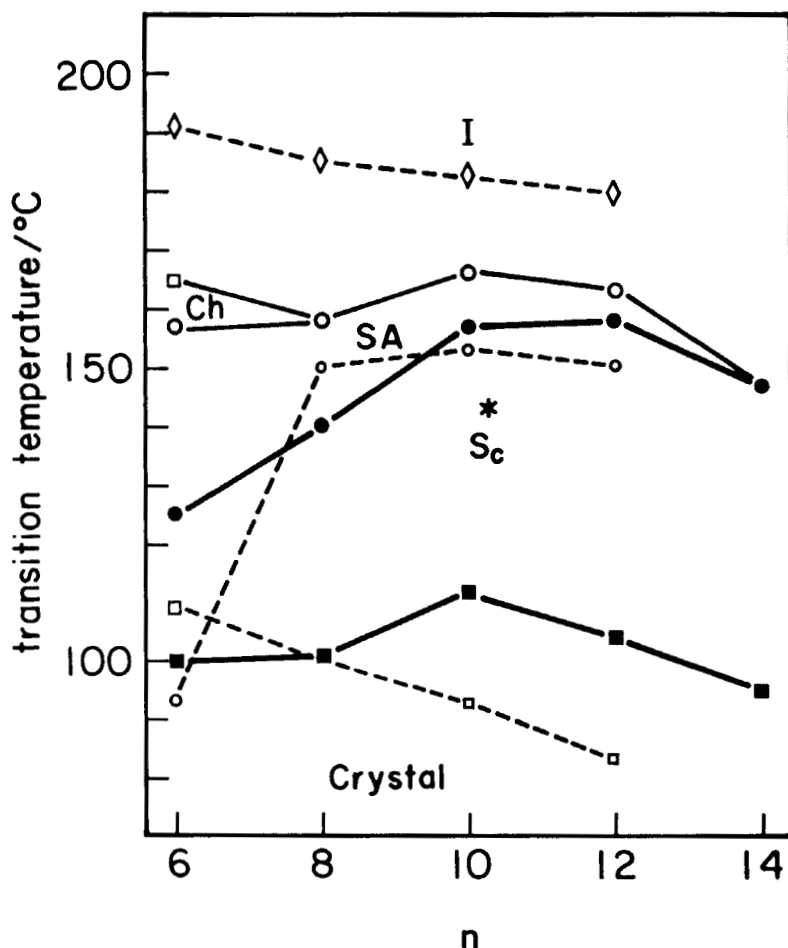


FIGURE 2 Plot showing transition temperature of fluorenone derivatives (14), as a function of the terminal alkyl chain length with n being $-(\text{CH}_2)_n\text{H}$. The broken lines indicate the data published for biphenyl derivatives,¹¹ for comparison.

The electron delocalization effect, due to the planer structure of the fluorene skeleton established by the introduction of the methylene bridge, would much increase the polarizability, which leads to the increase in the attractive dispersion force between molecules. This effect would stabilize a smectic phase, as pointed out by McMillan.⁴

As shown in Figure 1, the curve showing smectic C* to smectic A transition temperatures in relation to the number of carbon atoms in the alkyl chain, has maximum values in both biphenyl and fluorene derivatives. However, the additional methylene group reduces the

thermal stability of the smectic C* phase in the derivatives with $n = 8$ and 10, compared with corresponding biphenyl derivatives.

This effect would be explained as follows. The methylene bridge in the fluorene structure makes the molecule planar, which is favorable to mesogenic stability, as indicated by the increasing T_{SA-I} . However, the bridge broadens the molecule and increases the excluded volume. This reduces the thermal stability of the smectic C phase, because the excluded volume effect works to destabilize the smectic C by packing entropy.⁵

Fluorenone derivatives

As shown in Figure 2, mesomorphic behaviors for fluorenone derivatives (14), are rather different from either of the fluorene and biphenyl derivatives in both smectic A to isotropic phase transitions and smectic C* to smectic A phase transitions. The T_{SA-I} was markedly lower than that for the biphenyl derivatives. In the fluorenone derivatives with $n = 6$, the cholesteric phase was observed between the smectic A phase and the isotropic phase. A comparison with the fluorene derivatives shows that the additional carbonyl group in place of the methylene group for the fluorene derivatives reduces the mesomorphic thermal stability by about 30–50°C.

On the other hand, the T_{SC^*-SA} value was markedly higher than that for the fluorene derivatives and even the biphenyl derivatives by 50°C at $n = 6$. The temperature range for the smectic A phase narrowed with increasing n . At last, the T_{SA-I} and T_{SC^*-SA} merged at $n = 14$, where the smectic A phase disappeared.

The considerable stabilization of a smectic C* phase in the fluorenone derivatives indicates that the molecular force, which inclines the molecular axis in a smectic layer, was much enhanced by the introduction of a carbonyl group having a permanent dipole moment, through the induction energy mechanism proposed by van der Meer and Vertogen.⁵

The transition from the smectic A to smectic C phase is a result of a competition between an attractive induction force and repulsive forces acting between the molecules.⁵ The increase in an attractive induction force is suggested by the fact that the T_{SC^*-SA} rose, in spite of the introduction of the bulky carbonyl group, which works to increase repulsive interaction due to the excluded volume effect.

The cholesteric phase was observed in the fluorenone derivative only with short alkyl chain with $n = 6$. This behavior is consistent with McMillan's theory⁴ which predicts that only the first order tran-

sition from a smectic A to an isotropic phase is observed for longer molecules. For shorter molecules, a transition from a smectic A to a cholesteric phase appears as a first-order phase transition.

3. CONCLUSIONS

The smectic C* phase thermal stability could be increased by an appropriate magnitude of the transverse dipole moment of the carbonyl group for the fluorenone derivatives, even though the mesomorphic stabilities are extremely reduced. Considering the large difference in thermal stabilities for smectic A and C* phases among fluorene, fluorenone and biphenyl derivatives, a transverse permanent dipole with appropriate magnitude is a very important factor for the smectic C* phase formation. The enhancement of the polarizability in the mesogen core is effective to stabilize the smectic A phase.

4. EXPERIMENT

Measurements of transition temperatures and microscopic observations of the textures of mesophases were made, using an Olympus polarizing microscope in conjunction with a Mettler FP82 heating stage and FP80 control unit and a Daini Seikohsha differential scanning calorimeter, model SSC-560s. H-NMR spectra were measured through a JEOL JNM-FX-90 NMR spectrometer for a solution in CDCl₃ with tetramethylsilane as the internal standard. IR spectra were recorded on a KBr disc with a JASCO IRA-2 grating infrared spectrometer. Mass spectrometer data were determined with a JEOL DX300 mass spectrometer. The purity of each sample was checked by HPLC JASCO TWINCLE.

Examples of the preparation of compounds are described below.

Preparations of 2-alkoxyfluorene-7-carboxylic acids

The 2-alkoxyfluorene-7-carboxylic acids were prepared, according to the method reported by Gray and Ibbotson.⁶ The obtained products contained a small amount of 2-alkoxyfluorenone-7-carboxylic acids. The mixed products were used in the next reaction without further separation.

Preparations of S 2-dodecyloxyfluorene-7-carboxylic acid 4-(2-methylbutoxy)-phenyl ester ((13), n = 12) and S 2-dodecyloxyfluorenone-7-carboxylic acid 4-(2-methylbutoxy)-phenyl ester ((14), n = 12)

3.30 g of 2-alkoxyfluorene-7-carboxylic acid, containing a small amount of 2-alkoxyfluorenone-7-carboxylic acid in 25 ml of thionyl chloride, were heated at 70°C for one hour. After evaporating thionyl chloride, 14 ml of dry pyridine was added to the solution. Then, 1.88 g of *S* 4-(2-methylbutoxy)-phenol in 7 ml of dry pyridine solution was added and the mixture was warmed at 70°C for 4 hours. Finally, it was poured into acidic ice water. The brown precipitate was collected. The precipitate was purified by column chromatography. From the first fraction 2.44 g of white needles were obtained after three recrystallizations from the toluene solution, and were identified as *S* 2-dodecyloxyfluorene-7-carboxylic acid 4-(2-methylbutoxy)-phenol ester ((13), $n = 12$) through NMR, MS and IR spectroscopy.

From the second fraction, 420 mg of yellowish needles were obtained after the same purification process and were identified as *S* 2-dodecyloxyfluorenone-7-carboxylic acid 4-(2-methylbutoxy)-phenyl ester ((14), $n = 12$) by the same method.

The following data for dodecyloxy derivatives are typical of the homologous series as a whole:

For (13), ($n = 12$), $m/z556$ (M^+); L_{\max} (KBr) 2900, 2850, 1730, 1610, 1510, 1470, 1280, 1250, 1200, 1160, 1100, 840, 770, 740 (cm^{-1}); δ_{H} (in CDCl_3) 0.81–1.91 (32 H, m, $(\text{CH}_2)_{11}\text{CH}_3$ and $-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$), 3.78 (2H, dd, $\text{ArO}-\text{CH}_2-$), 3.87 (2H, s, fluorene- CH_2), 4.03 (2H, t, $\text{R}-\text{CH}_2-\text{O}$ -fluorene), 7.25–6.87 (6H, m, fluorene (1 and 3) H, $-\text{OArO}-$ (2, 3, 5 and 6)H), 7.74 (2H, d, fluorene (4 and 5)H), 8.20 (1H, d, fluorene 6H), 8.28 (1H, s, fluorene 8H)

For (14), ($n = 12$), $m/z570$ (M^+); L_{\max} (KBr) 2900, 2850, 1730, 1720, 1600, 1510, 1500, 1470, 1300, 1270, 1200, 1140, 1120, 1090, 830, 790, 770, 740 (cm^{-1}); δ_{H} (in CDCl_3) 0.88–1.91 (32H, m, $-(\text{CH}_2)_{11}\text{CH}_3$ and $-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$), 3.78 (2H, dd, $\text{ArO}-\text{CH}_2-$), 4.02 (2H, t, $\text{R}-\text{CH}_2\text{O}$ -fluorene), 6.86–7.25 (6H, m, fluorene (1 and 3)H, $-\text{OArO}-$ (2, 3, 6 and 5)H), 7.50 (2H, d, fluorene (4 and 5)H), 8.29 (1H, dd, fluorene 6H), 8.38 (1H, s, fluorene 8H)

References

1. J. Billard, In "Liquid Crystals of One- and Two-Dimensional Orders," Eds. W. Helfrich and G. Heppke, Springer, Berlin (1980) p. 383
2. (a) J. W. Goodby and T. M. Leslie, *Mol. Cryst. Liq. Cryst.*, **110**, 175 (1984); (b) J. W. Goodby and T. M. Leslie, In "Liquid Crystals and Ordered Fluids," Eds. A. C. Griffin and J. F. Johnson, New York, (1984), Vol. 4, p. 1.
3. (a) D. M. Burns and J. Iball, *Nature*, **173**, 635 (1954); (b) G. M. Brown and M. H. Bortner, *Acta Cryst.*, **7**, 139 (1954).

4. W. L. McMillan, *Phys. Rev. A* **4**, 1238 (1971).
5. B. W. Van Der Meer and G. Vertogen, *J. de Phys.*, **40**, C3-222 (1979).
6. G. W. Gray and A. Ibbotson, *J.*, 3228 (1957).
7. I. R. Davison, D. M. Hall and I. Sage, *Mol. Cryst. Liq. Cryst.*, **129**, 17 (1985).
8. S. L. Arora, B. Ziemnicka and J. W. Doane, *Mol. Cryst. Liq. Cryst.*, **127**, 341 (1985).
9. G. W. Gray, J. B. Hartley, A. Ibbotson and B. Jones, *J.*, 4359 (1955).
10. Y. Shimizu and S. Kusabayashi, *Mol. Cryst. Liq. Cryst.*, **132**, 221 (1986).
11. (a) T. Inukai, K. Furukawa, K. Terashima, S. Saitoh and H. Inoue, *Proceedings of 10th Liquid Crystal Conference in Japan* (1984) p. 164 (in Japanese); (b) T. Inukai, S. Saitoh, H. Inoue, K. Miyazawa, K. Terashima and K. Furukawa, *Mol. Cryst. Liq. Cryst.*, **141**, 251 (1986).