631. *Mesomorphism and Chemical Constitution. Part IX.* The Preparation and Mesomorphic Behaviour of the 7-n-Alkoxy-fluorene- and -fluorenone-2-carboxylic Acids and their n-Propyl Esters.*

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Four *n*-alkyl ethers derived from 7-hydroxy-fluorene- and -fluorenone-2-carboxylic acids together with their *n*-propyl esters have been prepared. As is the case with the 4′-*n*-alkoxydiphenyl-4-carboxylic acids and their *n*-propyl esters,[1] the above fluorene derivatives are mesomorphic, whilst the fluorenone derivatives are not. The relative mesomorphic behaviours of the diphenyl, fluorene, and fluorenone acids and esters are discussed, and the results shown to be in agreement with the general trends [2] for the mesomorphic mono- and di-anils derived from 4-aminodiphenyl, 2-amino-fluorene and -fluorenone, benzidine, and 2 : 7-diamino-fluorene and -fluorenone. The low mesomorphic thermal stabilities expected for the fluorenone acids and esters together with their high melting points explain the absence of mesophases in these compounds. The mesomorphic data indicate that the diphenyl ring system is planar in the mesomorphic states of such compounds.

7-Alkoxy-fluorene- and -fluorenone-2-carboxylic acids are not readily prepared, and their synthesis will be discussed before their mesomorphic behaviour. 2-Methoxyfluorene is known to give 7-acetyl-2-methoxyfluorene [3] (27%) which may be oxidised in two stages to give good yields of 7-methoxyfluorene-2-carboxylic acid and 7-methoxyfluorenone-2-carboxylic acid.[3] Because of the poor yield in the Friedel–Crafts reaction we started with 2-acetoxyfluorene which MacGregor, Neblett, and Cook [4] converted into 2-acetoxy-7-acetylfluorene in 85% yield, although our yields in a large number of runs were never higher than 58%. The ester was hydrolysed by alkali to 2-acetyl-7-hydroxyfluorene more satisfactorily than by the acid used by MacGregor *et al.*[4] The hydroxy-ketone was methylated and then oxidised to the known 7-methoxyfluorene-2-carboxylic acid, thereby verifying the orientation of the substituents in 2-acetoxy-7-acetylfluorene. The synthesis would have been considerably shortened had it not proved impossible to dealkylate the methoxy-acid or to oxidise 2-acetyl-7-hydroxyfluorene; the required 2-acetyl-7-alkoxyfluorenes had to be prepared separately, and each one oxidised to the 7-alkoxyfluorene-2-carboxylic acid. These sodium hypobromite oxidations must be carried out under fairly critical conditions, and quite small variations from the best reaction temperature may result in incomplete reaction or even oxidation of the methylene group. The alkoxyfluorene acids were then oxidised to the fluorenone acids by sodium dichromate. This procedure was adopted since 7-hydroxyfluorenone-2-carboxylic acid could not be obtained either by dealkylation of the methyl ether or by simultaneous oxidation of the acetyl and the methylene group in 2-acetyl-7-hydroxyfluorene. The complete synthesis is quite extended, and it did not seem justifiable to prepare the usual homologous series of thirteen alkoxy-acids when the average mesomorphic thermal stabilities of only four (heptyl–decyl) were to be used for comparison with other diphenyl, fluorene, and fluorenone compounds which have been studied. However, since the methoxyfluorene acid was known,[3] it seemed worth while to prepare the propyl and pentyl ethers in order to establish whether the nematic–isotropic transition point curve for acids with an odd number of carbon atoms in the alkyl chain was of the usual form.

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* Part VIII, Gray, Brynmor Jones, and Marson, *J.*, 1956, 393.

[1] Gray, Hartley, and Brynmor Jones, *J.*, 1955, 1412.

[2] Gray, Hartley, Ibbotson, and Brynmor Jones, *J.*, 1955, 4359.

[3] Gray, Hartley, and Ibbotson, *J.*, 1955, 2686.

[4] MacGregor, Neblett, and Cook, *J. Org. Chem.*, 1954, **19**, 626.

The acids and esters studied are contained in the following Tables, with their melting points and mesomorphic transition temperatures. Several of the 2-acetyl-7-alkoxyfluorenes exhibit smectic phases and are also recorded.

TABLE 1. *2-Acetyl-7-*n*-alkoxyfluorenes.*

Alkyl	Temp. of transition to : smectic	isotropic	Alkyl	Temp. of transition to : smectic	isotropic
Methyl	—	130·5°	Octyl	98°	108·5°
Propyl	—	153	Nonyl	100	110
Pentyl	—	117	Decyl	97·5	109
Heptyl	106°	108			

TABLE 2. *7-*n*-Alkoxyfluorene-2-carboxylic acids and* n*-propyl esters.*

Alkyl	Acids: Temp. of transition to smectic	nematic	isotropic	Esters: Temp. of transition to smectic	isotropic
Methyl	—	267·5°	294°	—	— *
Propyl	—	222	279	—	— *
Pentyl	—	197	266	—	— *
Heptyl	204·5°	216	255·5	68°	114°
Octyl	206·5	226·5	252·5	67	112
Nonyl	203·5	234	246	78	110
Decyl	200·5	236·5	241·5	68	108

* Not prepared.

TABLE 3. *7-*n*-Alkoxyfluorenone-2-carboxylic acids and* n*-propyl esters.*

Acids: Alkyl	M. p.	Alkyl	M. p.	Esters: Alkyl	M. p.	Alkyl	M. p.
Heptyl	277·5°	Nonyl	269·3°	Heptyl	84°	Nonyl	115°
Octyl	272·5	Decyl	265	Octyl	81	Decyl	96·5

Plots of the mesomorphic transition points against the number of carbon atoms in the alkyl chains for the above series are not given here since they reveal no unusual features. The nematic–isotropic transition points for the fluorene acids containing an odd number of carbon atoms in the alkyl chain lie on a smooth falling curve, similar to but steeper than that for the analogous 4′-*n*-alkoxydiphenyl-4-carboxylic acid.[1] The transition points for the even-chain members (octyl and decyl) are slightly above this curve as the usual alternation of mesomorphic–isotropic transition points in homologous series would lead one to expect. The smectic–nematic transition points for the heptyl–decyl fluorene acids lie on the customary rising curve. Only four smectic–isotropic transition points for the propyl 7-alkoxyfluorene-2-carboxylates were obtained, and between these there is a regular decrease of 2° for each unit increase in the alkyl chain length. The alternation is therefore reduced to such a degree in this series that the points lie on a falling straight line, which is again steeper than that for the analogous propyl esters of the diphenylcarboxylic acids. The four smectic–isotropic points for the 2-acetyl-7-alkoxyfluorenes on the other hand show appreciable alternation, but, of more interest than this, the two pairs of points obviously constitute sections of two rising smectic–isotropic transition-point curves. As already reported,[1] this effect has been observed in the propyl 4′-*n*-alkoxydiphenyl-4-carboxylates where the smectic–isotropic transition-point curves for the even and odd carbon chains rise in the initial stages of the homologous series, and is probably a function of the way in which the relative intermolecular terminal and lateral cohesions change along a homologous series.

The relative behaviours of these 7-alkoxy-fluorene- and -fluorenone-2-carboxylic acids and their propyl esters can be compared with one another and with those of the analogous

4′-alkoxydiphenyl-4-carboxylic acids and esters. These derivatives will henceforth be referred to simply as the diphenyl, fluorene, and fluorenone acids and esters. In the following comparisons of the relative mesomorphic behaviours of these compounds the average smectic–nematic, smectic–isotropic, and nematic–isotropic transition temperatures for the heptyl, octyl, nonyl, and decyl ethers have been used where appropriate in all cases.

Considering the diphenyl and fluorene esters first, there is a decrease in relative mesomorphic thermal stability of 9° from the fluorene to the diphenyl esters (see Table 4). This stability difference is very similar to that between the 2-*p*-alkoxybenzylideneaminofluorenes and the 4-*p*-alkoxybenzylideneaminodiphenyls,[2] where again the fluorene derivatives were the more stable.

The behaviour of the two sets of anils has already been discussed fully [2] and we need concern ourselves only with the relative properties of the esters and anils. To compare these, the smectic–nematic transition temperatures of the anils and the smectic–isotropic transition temperatures of the esters, which have no nematic properties, must be considered. The figures to be compared are the 10·5° and 9° decreases shown in Table 4. The effect of the diphenyl and fluorene ring systems on the thermal stabilities of the smectic phases of the anils and esters is therefore very similar, and indicates that these ring systems cause the same changes in molecular packing and intermolecular cohesion irrespective of whether the molecule is an ester or an anil.

TABLE 4.

Molecule type	Average transition temp. ($C_7 - C_{10}$)	Fluorene	Diphenyl	Decrease
Esters	Smectic–isotropic	111°	102°	9°
Monoanils	Smectic–nematic	166	155·5	10·5
	Nematic–isotropic	186·5	162	24·5

Despite the non-collinearity of the planar fluorene ring system [5] therefore, the fluorene esters and monoanils give more stable mesophases than are found in the analogous diphenyl derivatives. The reasons are doubtless the same in each case. If we make the reasonable assumption that the fluorene and diphenyl esters pack in approximately the same way in the smectic phase, we would expect the lateral cohesions to be greater in the fluorene esters, because of the permanent polarisation of the fluorene nucleus (0·65 D) and the greater polarisability of the fluorene compound. The latter effect will of course enhance the terminal cohesions too, but evidently not to such a degree that a nematic phase can exist in the fluorene esters. These considerations, already applied to the monoanils,[2] explain the greater smectic thermal stability in the fluorene derivatives.

TABLE 5.

Molecule type	Average transition temp. ($C_7 - C_{10}$)	Diphenyl	Fluorene	Decrease
Acids	smectic–nematic	255°	225°	30°
	nematic–isotropic	261·5	244·5	17
Dianils	smectic–nematic	313	296·5	16·5
	nematic–isotropic	345	321	24

In the light of the above information alone, it would seem reasonable to expect that the fluorene acids would give rise to more stable phases than would the diphenyl acids. However, the dimerisation of the acid molecules will mean that their molecular constitution is more similar to that of a dianil than to that of the esters and monoanils. Now, the behaviour of the 4 : 4′- and 2 : 7-di-(*p*-*n*-alkoxybenzylideneamino)-diphenyls and -fluorenes, *i.e.*, the dianils derived from benzidine and 2 : 7-diaminofluorene, is known,[2] and the diphenyl

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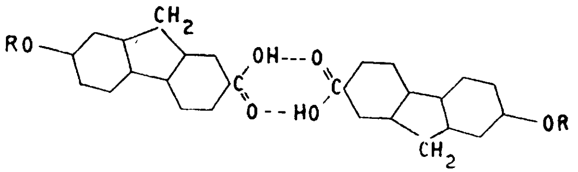
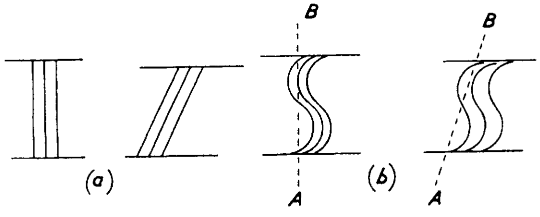
[5] Iball and Burns, *Nature*, 1954, **173**, 635.

derivatives exhibit more stable mesophases than the fluorene analogues. When the diphenyl acids were found to show the same effect relative to the fluorene acids, it was not therefore surprising to find this inversion of the order of decreasing mesomorphic thermal stability established for the esters. The results in Table 5 make clear the relative behaviours in the dianils and acids.

We will first consider the acids and the possible reasons for the greater thermal stability of both mesophase types in the diphenyl derivatives. In view of the inversion in the order of stabilities for the esters, the intermolecular cohesions must now be greater in the diphenyl acids, with the consequent inference that some effect must be counteracting the greater polarity and polarisability of the fluorene ring system. This effect may be due to the shape of the molecule, for whilst the dimerised diphenyl acids are rod-shaped and linear, the fluorene acid dimers, assumed to adopt the *trans*-configuration (of lowest potential energy), will be S-shaped because of the non-linearity of the fluorene ring system. This configuration is illustrated.

At first sight this would appear to have little bearing on the problem, since one would expect such molecules to be able to pack just as closely as linear molecules in the smectic mesophase. However, further consideration shows that this will be true only when the major axes (defined as the line AB) of the S-shaped molecules are at right angles to the planes of the smectic layers. If the molecules are at an angle to the layers—this has been shown to be the case in several compounds [6]—the average intermolecular separation of the S-shaped molecules will be greater than that for linear molecules, whose intermolecular separation is not affected by tilting. These considerations are made clear in the Figure.





(*a*) *Intermolecular separation of rod-shaped molecules unaffected by tilting.* (*b*) *Intermolecular separation of* S-*shaped molecules considerably increased by tilting at quite a small angle.*

Thus, if the fluorene acid molecules are tilted to the layers in the smectic mesophase, the intermolecular cohesions will be less and the smectic–nematic transition temperatures lower than for similarly tilted diphenyl acid molecules. However, unlike linear molecules, a greater separation of non-linear molecules may have to be achieved before the molecules are free to slide in the direction of their major axes at the smectic–nematic transition point. This effect would increase the smectic–nematic transition temperature of the fluorene acids. Consequently, the thermal stability of the smectic mesophase will be governed by (*a*) the thermal energy necessary to overcome the lateral intermolecular cohesive forces and (*b*) the thermal energy required to separate the molecules sufficiently for sliding to be possible. The two thermal energy requirements will differ for the fluorene and diphenyl acids, and it would appear that the sum of (*a*) and (*b*) for diphenyl exceeds that for fluorene. Only in these terms can the lower smectic–nematic transition temperatures of the fluorene acids be discussed. Considering the nematic phases now, the

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[6] K. Herrmann, *Trans. Faraday Soc.*, 1933, **29**, 972.

average intermolecular separation between the S-shaped fluorene acid molecules, in the parallel but randomly imbricated orientation of the nematic phase, should be greater than that between the linear diphenyl acid molecules. The residual lateral cohesions for the fluorene acids should therefore be smaller than for diphenyl, and if this separation effect is sufficient to counteract the higher terminal cohesions for the fluorene acids—because of their higher polarisability—then their lower nematic–isotropic transition temperatures are explained.

It appears then that the dimerisation of the acids magnifies the effect of the non-linearity of the fluorene ring system, whilst in the monomeric esters, the non-linearity cannot exert an effect which is sufficient to counteract the larger polarisation and polarisability of the fluorene ring system. Similar arguments have already been applied to comparisons of the diphenyl and fluorene mono- and di-anils.[2]

The dianils of both the diphenyl and the fluorene series exhibit nematic phases of higher average thermal stability than the corresponding acids, and it would seem that this stability difference is caused by the relative magnitudes of the intermolecular terminal cohesions. These attractive forces will depend on the polarisability along the molecular axis, and this should be greatest in the most conjugated molecule. Now the dianils should be more conjugated than the acid dimers, where the hydrogen-bonded carboxyl groups will not permit electronic shifts between the aromatic ring systems. On this basis, the nematic phases of the dianils should be the more thermally stable. In the smectic phases, the dipolar anil linkages should strengthen the intermolecular lateral cohesions and should lead to greater thermal stabilities for the smectic phases of the diphenyl and fluorene dianils compared with the analogous acid. When attempting to compare the smectic–nematic transition temperatures of different compounds, one must however consider the shapes of the molecules in relation to the intermolecular cohesions. In the diphenyl derivatives, the dimerised acid molecules are linear, whilst the dianils deviate from linearity. As discussed in general terms earlier in this paper, when comparing the diphenyl acids with the fluorene acids, the non-linear diphenyl dianils will not be packed as closely as the diphenyl acids if the molecular axes are inclined to the layers in the smectic phase, and this should lead to lower thermal stability of the phase. On the other hand a greater molecular separation may be required to allow the dianil molecules to slide into the imbricated nematic orientation, an effect which would give rise to a greater smectic thermal stability. These two opposing effects, together with the different intermolecular forces between the molecules of the diphenyl acids and dianils, must be the factors which determine the average smectic thermal stability increase of 58° on passing from the acids to the dianils of diphenyl. In the fluorene series, both the acids and the dianils are non-linear, but if equally close packing is assumed in each case, molecular models make it clear that the fluorene dianils must be separated much more than the acids before sliding of the molecules can occur. The greater thermal energy required because of this effect, together with the polarisation of the anil linkages should combine to separate the relative thermal stabilities of the smectic phases of the fluorene dianils and acids to an even greater extent than in diphenyl. The difference is now 71·5°.

It is noticeable from Table 5 that the fall in smectic thermal stability from the diphenyl to the fluorene compounds is, in the acids, almost double that in the dianils whilst in the case of the nematic thermal stability the larger decrease occurs between the dianils. It appears that it would be necessary to have much more exact information than an inspection of molecular models can give about the relative molecular separations occurring at the various smectic transitions before one could even attempt to assess these differences, and to try to do so in the absence of such data would be conjectural.

However, the above results on the acids and dianils, esters, and monoanils of diphenyl and fluorene are sufficiently comparable to enable one to predict the probable mesomorphic thermal stabilities for the fluorenone esters and acids. Considering the average smectic–nematic transition temperatures for the monoanils of diphenyl, fluorene, and fluorenone, and the average smectic–isotropic transition temperatures for the esters of diphenyl and fluorene, gives the following figures :

Monoanils	Fluorene		Diphenyl		Fluorenone
Smectic–nematic (C_7—C_{10})	166°	10·5°	155·5°	82·1°	73·4°
Esters	Fluorene		Diphenyl		Fluorenone
Smectic–isotropic (C_7—C_{10})	111	9	102	(72)	(30)

(The figures in parentheses are not experimentally determined points.)

If the esters follow the same trend as the monoanils, the average smectic–isotropic transition temperature for the fluorenone esters should be about 30°.

Analogous results for the nematic–isotropic transitions of the dianils and acids are :

Dianils	Diphenyl		Fluorene		Fluorenone
Nematic–isotropic (C_7—C_{10})	345°	24°	321°	24°	297°
Acids	Diphenyl		Fluorene		Fluorenone
Nematic–isotropic (C_7—C_{10})	261·5	17	244·5	(17)	(227·5)

The same decrease in nematic thermal stability being assumed from fluorene to fluorenone acid as is found between the analogous dianils, a nematic–isotropic transition temperature of 227·5° is to be expected for the fluorenone acids. However, the average m. p.s for these fluorenone esters and acids are 94° and 271·1° respectively, so that, if these compounds were to exhibit mesophases, the melts of the esters would require to supercool by an average of 64°, and the melts of the acids by 43·6°. If the smectic–nematic transition temperatures for the dianils and acids are considered, similar results are obviously obtained. The fluorenone esters and acids are therefore prevented from showing mesophases because of the high m. p.s of the solids. The reasons for these high m. p.s are obscure, but, since the m. p.s depend on the arrangement of the molecules in the crystal lattice, any attempt to explain them without the relevant physical data would be meaningless.

In previous Parts of this series,[1, 2] where analogous mesomorphic benzene and diphenyl derivatives have been compared, it was evident that the planarity of the diphenyl ring system in the mesophases had been assumed. An interplanar angle as high as 45° has been reported [7] for gaseous diphenyl, whilst crystalline diphenyl would appear to be planar.[8] An intermediate condition for the molecule would be expected in solution, and the unpublished calculations by Coulson and Longuet-Higgins quoted by Braude [9] indicate that free rotation about the 1–1′-bond in diphenyl is possible through an angle of up to or about 20°. The smectic and nematic mesomorphic states are however more closely allied to the solid state than to the solution or the gas phase, and so the assumption of diphenyl's planarity in the mesophases does not seem unreasonable. This appears to be supported by the relative mesomorphic behaviours of analogous diphenyl and fluorene derivatives, when it is borne in mind that the molecule of fluorene is planar in the solid, gaseous, and dissolved states as shown by *X*-ray,[10, 11] electron-diffraction,[12] and ultraviolet absorption spectra [9] respectively. Now the smectic phases of the fluorene monoanils and esters are more thermally stable than those of the analogous diphenyl monoanils and esters by 10·5° and 9° respectively. This difference is not large, but it could be contended that the diphenyl compounds yield the less stable mesophases because there is a molecular twist about the 1–1′-bond in the diphenyl nucleus. This would increase the thickness of the molecule and decrease the intermolecular cohesions by preventing the

[7] Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408.

[8] Dhar, *Indian J. Phys.*, 1932, **7**, 43; *Proc. Nat. Inst. Sci. India*, 1949, **15**, 11.

[9] Braude and Forbes, *J.*, 1955, 3777.

[10] Burns and Iball, *Nature*, 1954, **173**, 635; *Proc. Roy. Soc.*, 1954—1955, *A*, **227**, 220.

[11] Bortner and Brown, *Acta Cryst.*, 1954, **7**, 139.

[12] Brockway and Karle, *J. Amer. Chem. Soc.*, 1944, **66**, 1974.

closest packing of the molecules. However, the greater polarisation and polarisability of the fluorene derivatives would be expected to give rise to the greater intermolecular cohesions, and so the lower smectic thermal stability of the diphenyl compounds can be understood without proposing twisting in the diphenyl ring ststem. Further, in the dianils and acids this order of thermal stability is reversed, and the mesophases of the diphenyl compounds are the more thermally stable. The relative behaviours have already been discussed, but it is difficult to conceive that if the diphenyl ring system were not planar this order of stability would arise. In order to verify this statement, the exact effect of molecular twist on the mesomorphic behaviour of a diphenyl compound would have to be known. Work is now in progress which makes it clear that if the diphenyl ring system is forced out of the coplanar configuration, the mesomorphic thermal stability is greatly diminished. On this basis, the diphenyl ring system must be planar or have at the most a very small interplanar angle in the mesomorphic states of its derivatives.

EXPERIMENTAL

M. p.s are corrected for exposed stem.

Determination of Transition Temperatures.—The mesomorphic transition temperatures recorded in Tables 1—3 are without exception enantiotropic, and were determined in the usual way by using an electrically heated microscope block [13] in conjunction with a projection system.[14] The smectic phases of the esters showed fairly well-defined focal-conic groups, whereas in the acids these phases appeared as fine mosaics of very small focal-conic groups. The nematic phases of the acids were readily distinguished by their typical, threaded, homogeneous plane structures.

Preparation of Materials.—2-Hydroxyfluorene [3] was acetylated as described by MacGregor, Neblett, and Cook [4] and the crude 2-acetoxyfluorene (90%) crystallised from glacial acetic acid. The m. p. of 130° agreed with the recorded value.

2-*Acetoxy*-7-*acetylfluorene.*—The procedure used in the Friedel–Crafts reaction on 2-acetoxyfluorene was that described by MacGregor *et al.*[4] Although every care was taken, our yields in a number of preparations were very consistent and averaged 58% (m. p. 124—125°) after crystallisation from 75% acetic acid, compared with the 85% yield claimed by the above authors. The ketone is not easy to crystallise, but the crude 2-acetoxy-7-acetylfluorene, m. p. 115°, was suitable for hydrolysis in the next stage. MacGregor *et al.* report a lower m. p. of 104—106° for the crude product and the above m. p. of 124—125° for the crystallised material.

2-*Acetyl*-7-*hydroxyfluorene.*—Crude 2-acetoxy-7-acetylfluorene (5 g.) was refluxed for 3 hr. with potassium hydroxide (20 g.) in ethanol (75 ml.) and water (25 ml.), whereafter the reaction mixture was cooled and rendered acid with hydrochloric acid. The precipitated hydroxyketone was separated and crystallised twice from acetic acid to give colourless plates of 2-acetyl-7-hydroxyfluorene, m. p. 209° (Found: C, 80·4; H, 5·3. Calc. for $C_{15}H_{12}O_2$: C, 80·35; H, 5·35%). The average overall yield of pure 2-acetyl-7-hydroxyfluorene from 2-acetoxyfluorene was 35%. MacGregor *et al.*[4] effected this hydrolysis in unspecified yield with alcoholic hydrochloric acid and record the product's m. p. as 202°. Repetition of their hydrolysis gave a lower yield of less pure material (m. p. 202—209°) than is obtained by alkaline hydrolysis.

2-*Acetyl*-7-*alkoxyfluorenes.*—2-Acetyl-7-hydroxyfluorene (0·9 g.) was dissolved with stirring in a mixture of ethyl methyl ketone (20 ml.) and a 10% molar excess of the appropriate alkyl halide. A thin slurry of anhydrous potassium carbonate (2·4 g.) in ethyl methyl ketone (30 ml.) was added to the solution and the whole refluxed, with stirring, for 12 hr. with alkyl iodides and 20 hr. with alkyl bromides. During the reaction, the colour of the suspension changed gradually from yellow to light grey. The mixture was then cooled, the potassium salts were removed, and the filtrate was evaporated to crystallisation. The ethers were filtered off and crystallised three times from ethanol, straw-coloured crystals, whose m. p.s are recorded in Table 1, being obtained in yields averaging 66%. The analyses are summarised on p. 3235.

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[13] Gray, *Nature*, 1953, **172**, 1137.

[14] Gray and Ibbotson, *Nature*, 1955, **176**, 1160.

2-*Acetyl*-7-*alkoxyfluorenes.*

	Found (%)			Required (%)			Found (%)			Required (%)	
Alkyl	C	H	Formula	C	H	Alkyl	C	H	Formula	C	H
Methyl *	80·5	5·8	$C_{16}H_{14}O_2$	80·7	5·9	Octyl ...	82·3	8·5	$C_{23}H_{28}O_2$	82·2	8·3
Propyl ...	81·4	6·9	$C_{18}H_{18}O_2$	81·2	6·8	Nonyl ...	82·5	8·6	$C_{24}H_{30}O_2$	82·3	8·6
Pentyl ...	81·5	7·3	$C_{20}H_{22}O_2$	81·6	7·5	Decyl ...	82·3	9·0	$C_{25}H_{32}O_2$	82·4	8·8
Heptyl ...	82·1	8·2	$C_{22}H_{26}O_2$	82·0	8·1						

* Not new.[3]

7-*Alkoxyfluorene*-2-*carboxylic Acids.*—The 2-acetyl-7-alkoxyfluorenes (0·0036 mole) were dissolve in dioxan (20 ml.) with stirring at 40°, then cooled rapidly to 0° to give a fine suspension. A solution of sodium hypobromite, prepared by adding bromine (0·8 ml.) to an ice-cold solution of sodium hydroxide (2·25 g.) in water (11 ml.), was added to the suspension and the temperature raised gradually to 40°. When the solid had dissolved, the temperature was maintained at 40° for 15 min., before cooling again to 0°. Dilute aqueous sodium dithionite was added to remove excess of hypobromite, followed by concentrated hydrochloric acid to liberate the acids in almost quantitative yields. Three crystallisations from *n*-propyl alcohol were carried out to ensure accurate mesomorphic transition temperatures (Table 2), and these reduced the yields to about 55%.

7-*Alkoxyfluorene*-2-*carboxylic acids.*

	Found (%)			Required (%)			Found (%)			Required (%)	
Alkyl	C	H	Formula	C	H	Alkyl	C	H	Formula	C	H
Methyl *	75·1	4·9	$C_{15}H_{12}O_3$	75·0	5·0	Octyl ...	78·0	7·9	$C_{22}H_{26}O_3$	78·1	7·7
Propyl ...	76·3	6·2	$C_{17}H_{16}O_3$	76·1	6·0	Nonyl ...	78·6	8·2	$C_{23}H_{28}O_3$	78·4	7·95
Pentyl ...	77·0	6·7	$C_{19}H_{20}O_3$	77·0	6·75	Decyl ...	78·7	8·2	$C_{24}H_{30}O_3$	78·7	8·2
Heptyl ...	77·7	7·4	$C_{21}H_{24}O_3$	77·8	7·4						

* Not new.[3]

7-*Alkoxyfluorenone*-2-*carboxylic Acids.*—The 7-alkoxyfluorene-2-carboxylic acids (0·1 g.) were refluxed for 1·5 hr. with sodium dichromate (0·5 g.) in acetic acid (25 ml.). The orange crystals of the *fluorenone acids* obtained on cooling were collected and crystallised from acetic acid (twice) and xylene (twice). The yields after purification ranged from 25 to 50%. The m. p.s are recorded in Table 3.

7-*Alkoxyfluorenone*-2-*carboxylic acids.*

	Found (%)			Required (%)			Found (%)			Required (%)	
Alkyl	C	H	Formula	C	H	Alkyl	C	H	Formula	C	H
Heptyl ...	74·6	6·3	$C_{21}H_{22}O_4$	74·55	6·5	Nonyl ...	75·6	7·2	$C_{23}H_{26}O_4$	75·4	7·1
Octyl......	74·9	6·6	$C_{22}H_{24}O_4$	75·0	6·8	Decyl......	75·8	7·4	$C_{24}H_{28}O_4$	75·8	7·4

Propyl 7-*Alkoxy-fluorene- and -fluorenone-2-carboxylates.*—The esters were prepared and purified as described for the alkyl 4′-alkoxydiphenyl-4-carboxylates.[1] The physical constants are contained in Tables 2 and 3.

	Fluorene esters.					*Fluorenone esters.*				
	Found (%)			Required (%)		Found (%)			Required (%)	
Alkyl	C	H	Formula	C	H	C	H	Formula	C	H
Heptyl	78·6	8·0	$C_{24}H_{30}O_3$	78·7	8·2	76·0	7·5	$C_{24}H_{28}O_4$	75·8	7·4
Octyl	79·2	8·4	$C_{25}H_{32}O_3$	78·9	8·4	76·0	7·8	$C_{25}H_{30}O_4$	76·1	7·6
Nonyl	79·2	8·6	$C_{26}H_{34}O_3$	79·2	8·6	76·4	7·8	$C_{26}H_{32}O_4$	76·5	7·8
Decyl	79·6	8·8	$C_{27}H_{36}O_3$	79·4	8·8	76·5	8·0	$C_{27}H_{34}O_4$	76·8	8·1

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