Mesomorphism and Chemical Constitution. Part VI. Certain Mono- and Di-anils of the Benzene, Diphenyl, Fluorene, and Fluorenone Series.*

By G. W. GRAY, J. B. HARTLEY, A. IBBOTSON, and BRYNMOR JONES.

[Reprint Order No. 6521.]

Although the anils derived from aniline and *p*-*n*-alkoxybenzaldehydes are not mesomorphic, the corresponding anils from 4-aminodiphenyl exhibit phases of appreciable thermal stability, and the mesophases of the dianils of benzidine are much more stable than those of *p*-phenylenediamine. These observations confirm the earlier view that diphenyl derivatives display a greater tendency than benzene systems to produce mesophases of high thermal stability. The monoanils from 2-amino-fluorene and -fluorenone, and the dianils from 2 : 7-diamino-fluorene and -fluorenone are also mesomorphic, and an attempt has been made to relate their mesomorphic behaviour to recent interpretations of the structure of fluorene and fluorenone.

THE effects of structure on the mesomorphic behaviour of certain substituted and unsubstituted alkoxyarenecarboxylic acids have been discussed in preceding Parts of this series. By using the mesomorphic transition temperatures as an indication of the relative thermal stabilities of the phases, it has been possible to establish the effect of different aromatic ring systems, both substituted and unsubstituted, on the mesomorphic stability, and to show that the thermal stabilities of analogous derivatives based on diphenyl are greater than those derived from naphthalene which, in turn, are greater than those based on benzene. In an attempt to extend this series, it was decided to investigate the 7-alkoxy-fluorene- and -fluorenone-2-carboxylic acids. That these tricyclic systems would yield mesomorphic derivatives was by no means certain, for while the fluorene molecule, and probably that of fluorenone, would appear to be planar, *X*-ray studies suggest that they are distorted (Iball and Burns, *Nature*, 1954, **173**, 635). If this is so, then a 2 : 7-disubstituted fluorene would not be strictly linear. Unfortunately the synthesis of these acids is not straightforward and, in case they should fail to exhibit mesomorphism, the more readily accessible anils

---

* Part V, *J.*, 1955, 1412.

from 2-amino-fluorene and -fluorenone with *p*-alkoxybenzaldehydes were first examined. The pronounced mesomorphism of these Schiff's bases made it seem highly likely that the fluorene- and fluorenone-carboxylic acids would exhibit mesomorphism, and the synthesis of the acids and examination of their mesomorphic properties are now in progress. The behaviour of the anils themselves however is of interest, and they are here compared with corresponding anils derived from aniline and 4-aminodiphenyl.

A homologous series of anils was prepared by condensation of the methyl to decyl, dodecyl, hexadecyl, and octadecyl ethers of *p*-hydroxybenzaldehyde with the amine. Among the monoanils, the *p*-alkoxybenzylideneanilines show no mesomorphism, and here a representative few (containing the alkyl groups methyl, heptyl, dodecyl, hexadecyl, and octadecyl) were prepared to establish the complete absence of anisotropy. Their m. p.s are included in the Experimental section.

All thirteen anils in each of the series of 4-*p*-alkoxybenzylideneaminodiphenyls and 2-*p*-alkoxybenzylideneamino-fluorenes and -fluorenones are mesomorphic, and their m. p.s and mesomorphic transition temperatures are summarised in Tables 1, 2, and 3 respectively. In the first two of these three series, the plots of the mesomorphic transition temperatures against the number of carbon atoms in the *n*-alkyl chain show the usual regularities found in other homologous series. The nematic and smectic–isotropic transition points lie on two falling curves, the lower referring to ethers with an odd and the upper to those with an even number of carbon atoms in the alkyl chain. The alternation of these transition points between odd and even members is appreciable in both series. It is, of course, absent in the smectic–nematic transition points, which lie on smooth rising curves, and these become coincident with the upper transition-point curves for the even members.

TABLE 1. 4-p-n-*Alkoxybenzylideneaminodiphenyls.*

	Temp. of transition to				Temp. of transition to		
Alkyl	smectic	nematic	isotropic	Alkyl	smectic	nematic	isotropic
Methyl	—	161·5°	173·5°	Octyl	142·5°	155·5°	164°
Ethyl	—	146·5	190	Nonyl	140·5	157	160·5
Propyl	—	154·5	170	Decyl	140	157·5	159·5
Butyl	—	147·5	176	Dodecyl	137·5	—	155·5
Pentyl	137°	137·5	167	Hexadecyl	121	—	149
Hexyl	132	146	168·5	Octadecyl	124	—	146
Heptyl	141·5	151·5	163·5				

TABLE 2. 2-p-n-*Alkoxybenzylideneaminofluorenes.*

	Temp. of transition to				Temp. of transition to		
Alkyl	smectic	nematic	isotropic	Alkyl	smectic	nematic	isotropic
Methyl	—	169·5°	211·5°	Octyl	117·5°	165·5°	189·5°
Ethyl	—	154	221·5	Nonyl	116·5	169	184
Propyl	—	156	204·5	Decyl	115	170·5	181
Butyl	—	140	208·5	Dodecyl	112·5	171	174
Pentyl	132°	137	197	Hexadecyl	113	—	164·5
Hexyl	125	149·5	198·5	Octadecyl	118	—	160·5
Heptyl	121·5	159	191				

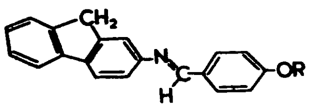
TABLE 3. 2-p-n-*Alkoxybenzylideneaminofluorenones.*

	Temp. of transition to				Temp. of transition to		
Alkyl	smectic	nematic	isotropic	Alkyl	smectic	nematic	isotropic
Methyl	—	(141°)	157°	Octyl	(70°)	86°	142°
Ethyl	—	141·5	155	Nonyl	(80)	88·5	138·5
Propyl	—	130·5	132·5	Decyl	88·5	89	139·5
Butyl	—	110·5	146·5	Dodecyl	92	103·5	136
Pentyl	—	115·5	138	Hexadecyl	95·5	121·5	130·5
Hexyl	—	119·5	145	Octadecyl	101·8	123·5	129·5
Heptyl	(54°)	90	139·5				

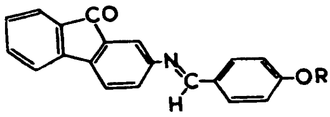
The last of the three series, the 2-*p*-alkoxybenzylideneaminofluorenones, appears to behave abnormally when a similar plot is made of their mesomorphic transition temperatures against the *n*-alkyl chain length. The smectic–nematic points constitute the normal rising curve, which, although it is steep, fails to become coincident with the upper curve for the transition points. In other words, nematic properties persist even in the hexadecyl and the octadecyl ether. Further, the nematic–isotropic transition points do not conform to the usual pattern of two smoothly falling curves. Possible reasons for this behaviour are discussed later in this section, where the plot of these transition temperatures is represented in the Figure.

In the 2-*p*-alkoxybenzylideneaminofluorenones, monotropic properties are found in the nematic phase of the methyl ether, and in the smectic phases of the heptyl, octyl, and nonyl ethers. These monotropic transitions are recorded in parentheses.

It must be borne in mind that, as a result of the stereochemistry of the –CH=N– link, the anils are not strictly linear, and a comparison of their relative behaviours is consequently even less straightforward than that of various linear alkoxyarenecarboxylic acids. Therefore the suggested explanations of the relative stabilities of the mesophases in the anils must be tentative. Further, since free rotation cannot be considered with certainty to occur in a mesophase, it is necessary to assume that, both as solid and as mesomorphic melts, the molecules of the monoanils of fluorene (I) and fluorenone (II) adopt a *trans*-configuration, which is probably their lowest potential-energy state, and that fluorenone is distorted to the degree suggested by Iball and Burns (*loc. cit.*) for fluorene.



(I)



(II)

The absence of mesomorphism in the *p*-alkoxybenzylideneanilines, and the occurrence of considerably stable mesophases in the 4-*p*-alkoxybenzylideneaminodiphenyls again emphasise the greater mesomorphic stability of a diphenyl structure. To test this view further, and to obtain figures comparable with those for the *p*-alkoxybenzoic acids and the 4′-alkoxydiphenyl-4-carboxylic acids (Gray, Hartley, and Brynmor Jones, *J.*, 1955, 1412), the dianils derived from *p*-phenylenediamine and from 4 : 4′-diaminodiphenyl were examined. The results (m. p.s and mesomorphic transition temperatures) are summarised in Tables 4 and 5.

TABLE 4. NN′-*Di*-(p-n-*alkoxybenzylidene*)-p-*phenylenediamines.*

	Temp. of transition to				Temp. of transition to		
Alkyl	smectic	nematic	isotropic	Alkyl	smectic	nematic	isotropic
Methyl	—	214·5°	>330°	Octyl	160°	209°	238°
Ethyl	—	202·5	>330	Nonyl	150·8	211·5	228
Propyl	—	193	313	Decyl	145·5	212	222
Butyl	—	186·5	297·5	Dodecyl	137·5	208	209
Pentyl	(171·5°)	175	271	Hexadecyl	127·5	—	191
Hexyl	169·5	189	259·5	Octadecyl	135·5	—	187
Heptyl	164·5	202·5	245				

TABLE 5. 4 : 4′-*Di*-(p-n-*alkoxybenzylideneamino*)*diphenyls.*

	Temp. of transition to				Temp. of transition to		
Alkyl	smectic	nematic	isotropic	Alkyl	smectic	nematic	isotropic
Methyl	—	266°	>390°	Octyl	202·5°	314°	353°
Ethyl	—	239	>390	Nonyl	204·5	314	338
Propyl	—	255·5	>390	Decyl	202·5	311·5	324
Butyl	264°	280·5	>390	Dodecyl	187	301	302·5
Pentyl	244	301	393·5	Hexadecyl	177·5	—	280·5
Hexyl	221	308	384·8	Octadecyl	175·5	—	271·5
Heptyl	214	312·5	365				

In the phenylenediamine series, the very high thermal stability of the phases made it impossible to determine the nematic–isotropic transition temperatures for the methyl and ethyl ethers since in the nematic phases they sublimed and decomposed rapidly at about 330°.

The nematic–isotropic transition temperatures of the first three members of the diaminodiphenyl series, which are purely nematic, and of the butyl ether, which exhibits an additional smectic phase, could not be determined because of the high thermal stability of the nematic phases and their subsequent decomposition on further heating.

In order to compare the dianils of the diphenyl series with those of benzene, the average smectic–nematic and nematic–isotropic transition temperatures for the heptyl—decyl ethers (inclusive) have been calculated in each case. These values give an indication of the relative stabilities of the smectic and the nematic phase in the two series.

Average transition temp. (C_7—C_{10})	Dianils of benzene	Dianils of diphenyl	Increase
Smectic–nematic	208·8°	313°	104·2°
Nematic–isotropic	233·3	345	111·7

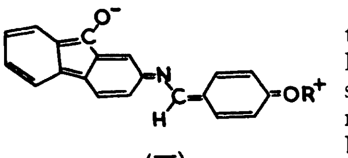
The incorporation of the second benzene ring in the diphenyl dianils increases the relative stability of the nematic phase by 111·7°, and of the smectic phase by 104·2°. The stability increases are appreciable in both cases, but the increase is greater in the nematic phase. At first this seems surprising, since intermolecular cohesions arising from the polarisability of the second ring in diphenyl would be expected to increase the lateral and planar cohesions to a greater extent than the terminal cohesions—a result which would lead to a greater increase in stability of the smectic phase. This has already been observed for the *p*-alkoxybenzoic acids and the 4′-alkoxydiphenyl-4-carboxylic acids (cf. Part V, *loc. cit.*), where the average transition temperatures for the heptyl—decyl ethers indicate stability increases of 143·5° and 116·9°, for the smectic and the nematic phase respectively. These increases are a result of a change from two to four benzene rings in the " dimers " of the benzoic and diphenic acids. The increases are therefore larger than those involved in passing from a benzene dianil (3 benzene rings) to a diphenyl dianil (4 benzene rings).

On this basis the relative stability of the nematic phases in the diphenyl dianils is larger than would be expected. The reason for this may be that the 1 : 1′-bond in diphenyl has enough double-bond character to make possible a fully conjugated system in a diphenyl dianil. In the 4′-alkoxydiphenyl-4-carboxylic acids the hydrogen bonds will not transmit the effects of conjugation in the two monomer units. It would seem, therefore, that the polarisability of a diphenyl dianil in the direction of its long axis could be greater than expected—a result which would be reflected in an enhancement of nematic stability. This could account for the differences in the behaviour of benzoic and diphenic acids on the one hand and of anils on the other. Apart from these considerations, the behaviour of these dianils emphasises the high mesomorphic stability of the phases produced by derivatives of diphenyl which are at least approximately linear in character. For a comparison of the monoanils of the fluorene (Table 2) and the fluorenone series (Table 3) with those of the diphenyl series an indication of the relative thermal stabilities in the three series is again obtained by averaging separately the smectic–nematic and nematic–isotropic transition temperatures for four ethers (heptyl—decyl) in each case. These averages, with the appropriate decreases in the average transition temperatures, are annexed.

Average transition temp. (C_7—C_{10})	Monoanils from				
	fluorene		diphenyl		fluorenone
Smectic–nematic	166°	10·6°	155·4°	82·1°	73·3°
Nematic–isotropic	186·4	24·5	161·9	22	139·9

These average transition temperatures indicate the order of decreasing thermal stability, with respect to both phase types, to be fluorene, diphenyl, fluorenone. Thus, despite the distortion of the fluorene molecule from linearity (Iball and Burns, *loc. cit.*), the monoanils of fluorene exhibit the most stable mesophases. Scale drawings of 2-*p*-alkoxybenzylideneaminofluorenes show that the molecules are broader than the analogous 4-*p*-alkoxybenzylideneaminodiphenyls by 1·23—1·24 Å. Such an effect would be expected to decrease the thermal stability (Gray and Brynmor Jones, *J.*, 1954, 2556; 1955, 236), and it is obvious that some other influence must be operating to counteract the effect of an increase in breadth, so that the overall result is an increase in intermolecular cohesion. A fluorene monoanil has a higher calculated polarisability than a diphenyl monoanil, and the exaltation of the molecular refraction (2·56 c.c.) is greater for fluorene than for diphenyl (1·86 c.c.). This means that as a result of conjugation a fluorene monoanil will have an even greater polarisability than calculated. The increase in dispersion forces which will accompany the higher molecular polarisability must be sufficiently great to counteract the increase in molecular separation in the fluorene monoanils, and to result in more stable mesophases. It is of interest that the increase in average transition temperature from diphenyl to fluorene anils is greater for the nematic phase (24·5°) than for the smectic phase (10·6°). In the fluorene monoanil, the greater conjugation, which is likely to extend from one end of the molecule to the other, will probably increase the intermolecular terminal cohesions more than it will the lateral cohesions, and so may be responsible for the greater increase in the nematic stability. A similar argument has been used to explain the higher stability of the nematic phases in the dianils of benzidine than in those of *p*-phenylenediamine.

The most noticeable effect in a comparison of the monoanils from diphenyl and fluorenone is the marked reduction in smectic stability (82·1°) of the fluorenone derivatives. This reduction may be accounted for by the considerably increased breadth (1·59—1·6 Å) of the fluorenone molecule. Acting to counterbalance this effect, however, is the dipole moment (2·75 μ) of the carbonyl group. Consideration of the conjugation in a fluorenone monoanil would suggest that the contribution from a structure involving $>\overset{+}{C}-\overset{-}{O}$ will be greatly reduced through inclusion of structures such as (III), in which the positive charge is no longer localised on the carbonyl-carbon atom.



(III)

The conjugation will have two complementary effects, that of decreasing the influence of the dipole moment on lateral cohesions, since the overall dipole in a canonical structure such as (III) is no longer directed across the molecule, and of increasing the terminal cohesions, again because of the direction of the dipole. In these terms it is possible to offer a qualitative explanation of the large reduction in stability of the smectic phase and of the much smaller reduction in stability of the nematic phase on passing from a diphenyl to a fluorenone monoanil.

TABLE 6. 2 : 7-*Di*-(p-n-*alkoxybenzylideneamino*)*fluorenes.*

	Temp. of transition to				Temp. of transition to		
Alkyl	smectic	nematic	isotropic	Alkyl	smectic	nematic	isotropic
Methyl	—	263°	> 380°	Octyl	166°	298°	325·7°
Ethyl	—	213	> 380	Nonyl	147	296·5	315·8
Propyl	213°	214·5	373	Decyl	144	294·3	306
Butyl	182	256·5	366·5	Dodecyl	136	286·5	288·5
Pentyl	179	285	353·7	Hexadecyl	123	—	264
Hexyl	176	295·5	345·8	Octadecyl	130	—	255·3
Heptyl	164	298·5	336·5				

TABLE 7. 2 : 7-*Di*-(p-n-*alkoxybenzylideneamino*)*fluorenones.*

	Temp. of transition to				Temp. of transition to		
Alkyl	smectic	nematic	isotropic	Alkyl	smectic	nematic	isotropic
Methyl	—	250°	> 350°	Octyl	150°	253·5°	302°
Ethyl	—	187	> 350	Nonyl	141·5	261	291·8
Propyl	—	200	> 350	Decyl	136·5	263	282
Butyl	—	179·5	> 350	Dodecyl	130	261	266
Pentyl	175·5°	189	333·5	Hexadecyl	119·5	—	244·5
Hexyl	166	217·5	328	Octadecyl	121·5	—	240
Heptyl	157·5	237	311·5				

In an attempt to verify this order of decreasing thermal stability for derivatives of fluorene, diphenyl, and fluorenone, the dianils from 2 : 7-diamino-fluorene and -fluorenone were examined and compared with the analogous diphenyl dianils (Table 5). The results (m. p.s and mesomorphic transition temperatures) are summarised in Tables 6 and 7.

Decomposition and sublimation of the phases of the first two members in Table 6 and of the first four members in Table 7 prevented the measurement of the nematic–isotropic transition temperatures. The four series of dianils (cf. Tables 4—7) exhibit the normal behaviour of diphenyl and fluorene anils when their smectic–nematic and mesomorphic–isotropic transition temperatures are plotted against the number of carbon atoms in the *n*-alkyl chain.

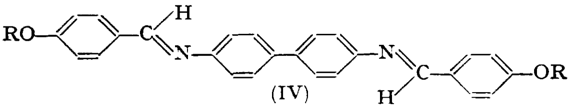
In order to compare the diphenyl, fluorene, and fluorenone dianils, the smectic–nematic and nematic–isotropic transition temperatures of the heptyl—decyl ethers have been averaged, and these averages give an indication of the relative stabilities of the smectic and the nematic phases in the three series. The summarised results are annexed, the stability decreases also being indicated.

Average transition temp. (C_7—C_{10})	Dianils from				
	diphenyl		fluorene		flluorenone
Smectic–nematic	313°	16·2°	296·8°	43·2°	253·6°
Nematic–isotropic	345	24°	321	24·2°	296·8

These values indicate a partial inversion in the order of decreasing mesomorphic thermal stability found for the monoanils. The order now becomes diphenyl, fluorene, fluorenone.

Unless free rotation about bonds is assumed, the dianils from benzidine, 2 : 7-diaminofluorene, and 2 : 7-diaminofluorenone will probably adopt a *trans*-configuration—the probable shape of a diphenyl dianil is shown in (IV).

The molecule is essentially linear, although the major axis of the molecule, through the 4 : 4′-positions, lies parallel to, but not coincident with, the axes of the *p*-alkoxybenzylidene groups. The distortion in fluorene and fluorenone will alter this shape, so that the dianils will be planar but saucer-shaped, and it may well be that this deviation from linearity prevents the close packing in the mesophase which is possible in the diphenyl dianils. Any attempt to assess these differences in packing by use of models would be highly hypothetical. A more open packing would prevent the greater polarisability and conjugation of fluorene from producing the more stable mesophases. That packing of the molecules is probably important in the fluorene dianils is shown by the greater reduction in nematic stability (24°) than in smectic stability (16·2°) on passing from a diphenyl to a fluorene anil. This may be explained in terms of the ability of saucer-shaped molecules to pack more closely in a smectic phase than in a nematic phase, where the molecules must be sufficiently separated to slide over one another in a direction parallel to the inter-ring bond in the fluorene nucleus.



(IV)

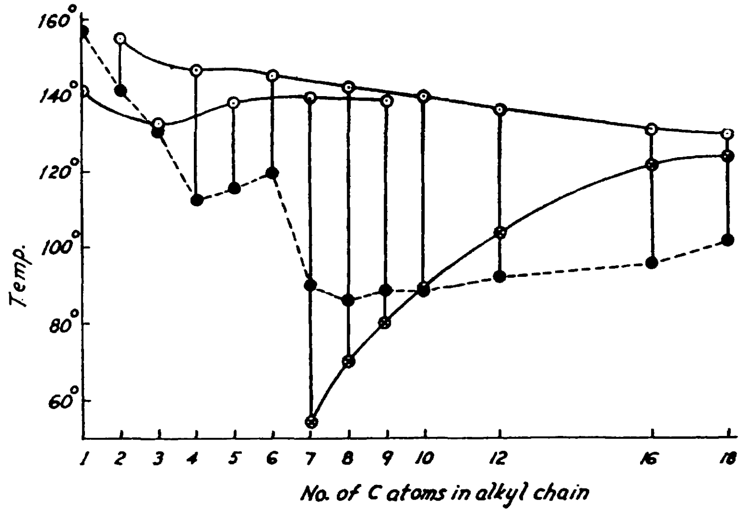
Comparison of the fluorene dianils with those from fluorenone illustrates a further thermal stability decrease in both phase types, the smectic stability decrease being the more marked. The identical packing of the molecules in the smectic phases will involve a greater separation in the fluorenone dianils as a result of the increase in breadth caused by the carbonyl group. This will not only reduce the smectic stability, but will also involve a smaller increase in separation of the molecules on passing from a fluorenone smectic phase to the nematic phase. These effects explain the smaller nematic stability decrease from a fluorene to a fluorenone dianil. As with the monoanils the decrease in stability on passing from a diphenyl to a fluorenone dianil is greater for the smectic phase (59·4°) than for the nematic phase (48·2°). The difference between the two stability changes is, however, much less. Conjugation in the fluorenone dianil can yield two canonical structures in which the carbonyl-oxygen atom is negatively charged, but in which the positive charge will be localised on opposite ends of the molecule. Such canonical structures will contribute equally to a hybrid in which the dipole will act across the molecule. The latter will reduce the extent of the smectic stability decrease as obtained for the monoanils, while at the same time decreasing the stability of the nematic phase of the fluorenone dianils.

The qualitative considerations, arising from the behaviour of the anils, cannot yet be discussed in more quantitative terms.

Finally, there is the anomalous behaviour of the mesomorphic transition temperatures when they are plotted against the number of carbon atoms in the *n*-alkyl chain of the fluorenone monoanils. The Figure illustrates the effects and shows the departure from the usual smooth, falling curves on which nematic–isotropic transition points lie, and the persistence of nematic phases at the end of the series so that the smectic–nematic curve no longer becomes coincident with the upper transition point curve.

The disappearance of nematic behaviour in the higher homologues of a series has been interpreted (Gray, Hartley, and Brynmor Jones, *J.*, 1955, 1412) in terms of the gradual increase in lateral cohesions and in smectic stability with the gradual decrease in terminal cohesions and nematic stability as the *n*-alkyl chain length grows. The result will be a stage at which the smectic phase passes direct to the isotropic liquid, because of reduction in the cohesion between the terminal groups of individual smectic layers, and before any sliding of the molecules in one layer can take place to give a nematic phase. It has already been noted that the lateral cohesions in the fluorenone monoanils are very weak, as illustrated by the large stability decrease from a diphenyl monoanil. The terminal cohesions will therefore be relatively much stronger than the lateral cohesions (cf. the large nematic phase lengths in the fluorenone monoanils). Consequently, the stage at which terminal cohesion weakness or nematic instability causes the smectic phase to pass direct to the isotropic liquid may well be delayed to longer chain lengths, with the result that nematic properties may persist in the dodecyl, hexadecyl, and octadecyl ethers.

2-p-n-*Alkoxybenzylideneaminofluorenones.*



Temp. of transition to (○) *isotropic,* (●) *mesomorphic or isotropic, and* (⊗) *smectic phase.*

It is more difficult to explain the curious shape of the first part of the nematic–isotropic curves, but the relative differences between the terminal and lateral cohesions may also cause this effect. At the beginning of the series, where the terminal cohesions are at their strongest, and the lateral cohesions are presumably relatively weak, the trend of the curves from methyl to propyl, and from ethyl to butyl may be determined solely by the former of these effects. As the chain length increases, the lateral cohesions increase, and will supplement the terminal cohesions. This may conceivably explain the rise in the curve from propyl to pentyl to heptyl, and the levelling off from butyl to hexyl. After the hexyl and heptyl ethers, the two curves fall normally, presumably because the increasing lateral cohesions can no longer counterbalance the decreasing terminal cohesions. The difference between this series and other series examined therefore appears to arise from the small relative contribution of lateral cohesions to the stability of the nematic phases of the first four members.

When this graph was first produced, the presence of impurities in the fluorenone monoanils was suspected, but the behaviour of several samples prepared and purified by different methods confirmed the results and eliminated the possibility of contamination.

EXPERIMENTAL

M.p.s are corrected.

Determination of Transition Temperatures.—These temperatures (solid–smectic and nematic, smectic–nematic, and smectic and nematic–isotropic) were determined in an electrically heated microscope block (Gray, *Nature*, 1953, **172**, 1137). All transitions between mesophases and those from the isotropic liquid to the mesophase were reversible at the same temperature. In general, the nematic phases appeared from the isotropic liquid in spherical droplets which coalesced to give homogeneous plane structures containing varying numbers of threads. In the anils which exhibit no nematic properties, the appearance of the smectic phase from the isotropic liquid was apparent by the formation of well-defined bâtonnets. All the smectic phases consisted of focal-conic groups, which were frequently large and very well defined. In most cases the usual accuracy of measurement (±0·25°) of the transition temperatures in the microscope heating block can be claimed. The only exceptions were the nematic–isotropic transition temperatures of the dianils from 4 : 4′-diaminodiphenyl and of 2 : 7-diaminofluorene. These transition temperatures (Tables 5 and 6) are high, and the nematic melts are inclined to decompose in the vicinity of the transition point. It was therefore important to expose the slide for as short a time as possible to high temperatures, and the following procedure was adopted to fulfil these requirements. The solid was heated on the slide until the nematic or smectic phase was produced; then the cover slip was pressed down to give a uniform section. In this way an unnecessary heating to the isotropic liquid was avoided. Rough values for the nematic–isotropic transition temperatures having been previously obtained by using an electric m. p. apparatus, the heating block was raised to within 5° of this temperature. The cold slide was inserted and the block heated rapidly in order to obtain the approximate value of the nematic–isotropic transition temperature. A fresh slide was mounted, and, with the temperature of the block at 1—2° below the expected transition temperature, inserted in the block. The cold slide lowered the temperature of the heating instrument by some 8°. With a gradual rate of heating, the block soon regained its original temperature, and finally the transition temperature was reached. In this way, the slide is exposed to high temperatures for as short a time as possible. The reversal temperature to the nematic phase was also measured, and the observations were repeated on a fresh slide, until measurements agreeing within 0·5° were obtained. Transition temperatures measured in this way are probably accurate to within ±1·0°.

Preparation of Materials.—Of the amines required for the preparation of the anils, purified samples of *p*-phenylenediamine, 4-aminodiphenyl, and 4 : 4′-diaminodiphenyl were available commercially, and modified methods of preparing 2-aminofluorene and 2-aminofluorenone have recently been described (Gray, Hartley, and Ibbotson, *J.*, 1955, 2686). 2 : 7-Diaminofluorene and 2 : 7-diaminofluorenone were prepared according to the methods of Morgan and Thomason (*J.*, 1926, 2691) and Barker and Barker (*J.*, 1954, 870) respectively. The preparation of the *p*-*n*-alkoxybenzaldehydes has already been described (Gray and Brynmor Jones, *J.*, 1954, 1467).

The anils of the above amines were prepared by dissolving the mono- or di-amine (0·2 g.) in absolute ethyl alcohol (25 ml.), and adding a 10% molar excess of *p*-alkoxybenzaldehyde, with a few drops of glacial acetic acid as catalyst. In general, the reaction was complete after 15 minutes' warming on the water-bath, but, for the dianils from 2 : 7-diaminofluorenone, it was necessary to increase the amount of alcohol to 75 ml. and to heat the reaction mixture for 1 hr., to overcome the low solubility of the diamine. In all cases, the reaction mixtures were cooled, and the products collected, washed with ethyl alcohol, and crystallised from ethyl alcohol and benzene until the m. p.s were constant. When the solubility in alcohol was very low, the anils were digested with boiling alcohol and the suspensions filtered before the products were crystallised to constant m. p. from benzene.

As indicated in the discussion, the 2-*p*-alkoxybenzylideneaminofluorenones exhibit a peculiar behaviour of the nematic–isotropic transition point curves. To ascertain whether the anils were pure, methods of preparation and purification, other than those described in the general method above, were attempted. Condensations were carried out in twice the volume of absolute ethyl alcohol, in glacial acetic acid, in benzene, and in 2-ethoxyethanol. In the last of these, condensation occurred, but the product was difficult to purify, whilst in benzene no reaction took place. The products obtained from the first three of these solvents were purified, but showed no change in the original m. p.s or mesomorphic transition temperatures. Rigid purification of the *p*-alkoxybenzaldehydes was likewise ineffective in altering the constants. Other methods of purification were also investigated, but chromatography on activated alumina, with carbon tetrachloride as solvent, appeared to decompose the anils. Vacuum-sublimation and repeated crystallisation from alcohol, benzene, and light petroleum, did not alter the constants, which were therefore finally accepted as the correct values.

The analytical figures for all the *anils* are summarised in the following Tables.

	Found (%)				Required (%)		
Alkyl	C	H	N	Formula	C	H	N
			4-p-n-*Alkoxybenzylideneaminodiphenyls.*				
Me	83·6	6·1	4·7	$C_{20}H_{17}ON$	83·6	6·0	4·9
Et	83·6	6·7	4·6	$C_{21}H_{19}ON$	83·7	6·4	4·6
Pr^{n}	83·8	6·7	4·6	$C_{22}H_{21}ON$	83·8	6·7	4·6
Bu^{n}	83·7	7·0	4·1	$C_{23}H_{23}ON$	83·9	7·0	4·2
C_5H_{11}	83·9	7·3	4·3	$C_{24}H_{25}ON$	84·0	7·4	4·1
C_6H_{13}	83·7	7·4	3·7	$C_{25}H_{27}ON$	84·0	7·6	3·9
C_7H_{15}	83·8	7·6	3·7	$C_{26}H_{29}ON$	84·1	7·9	3·8
C_8H_{17}	84·0	8·0	3·4	$C_{27}H_{31}ON$	84·2	8·1	3·6
C_9H_{19}	84·2	8·2	3·3	$C_{28}H_{33}ON$	84·2	8·3	3·5
$C_{10}H_{21}$	84·0	8·5	3·5	$C_{29}H_{35}ON$	84·3	8·5	3·4
$C_{12}H_{25}$	84·1	8·9	3·1	$C_{31}H_{39}ON$	84·4	8·9	3·2
$C_{16}H_{33}$	84·3	9·6	2·6	$C_{35}H_{47}ON$	84·5	9·5	2·8
$C_{18}H_{37}$	84·7	9·7	2·5	$C_{37}H_{51}ON$	84·6	9·7	2·6
			2-p-n-*Alkoxybenzylideneaminofluorenes.*				
Me	84·2	5·7	4·5	$C_{21}H_{17}ON$	84·2	5·7	4·7
Et	84·3	5·9	4·6	$C_{22}H_{19}ON$	84·3	6·1	4·5
Pr^{n}	84·3	6·5	4·3	$C_{23}H_{21}ON$	84·4	6·4	4·3
Bu^{n}	84·2	6·8	4·2	$C_{24}H_{23}ON$	84·4	6·7	4·1
C_5H_{11}	84·4	6·9	4·0	$C_{25}H_{25}ON$	84·5	7·0	3·9
C_6H_{13}	84·6	7·3	3·8	$C_{26}H_{27}ON$	84·5	7·3	3·8
C_7H_{15}	84·7	7·5	3·8	$C_{27}H_{29}ON$	84·6	7·6	3·7
C_8H_{17}	84·5	7·9	3·7	$C_{28}H_{31}ON$	84·6	7·8	3·5
C_9H_{19}	84·6	8·1	3·5	$C_{29}H_{33}ON$	84·7	8·0	3·4
$C_{10}H_{21}$	84·7	8·2	3·4	$C_{30}H_{35}ON$	84·7	8·2	3·3
$C_{12}H_{25}$	84·8	8·6	3·2	$C_{32}H_{39}ON$	84·8	8·6	3·1
$C_{16}H_{33}$	84·7	9·2	3·0	$C_{36}H_{47}ON$	84·9	9·2	2·8
$C_{18}H_{37}$	85·0	9·4	2·5	$C_{38}H_{51}ON$	84·9	9·5	2·6
			2-p-n-*Alkoxybenzylideneaminofluorenones.*				
Me	80·2	4·9	4·6	$C_{21}H_{15}O_2N$	80·5	4·8	4·5
Et	80·8	5·1	4·2	$C_{22}H_{17}O_2N$	80·7	5·2	4·3
Pr^{n}	81·1	5·7	4·1	$C_{23}H_{19}O_2N$	80·9	5·6	4·1
Bu^{n}	81·2	5·7	4·1	$C_{24}H_{21}O_2N$	81·1	6·0	3·9
C_5H_{11}	81·2	6·1	3·9	$C_{25}H_{23}O_2N$	81·3	6·3	3·8
C_6H_{13}	81·4	6·4	3·6	$C_{26}H_{25}O_2N$	81·4	6·6	3·6
C_7H_{15}	81·7	6·7	3·7	$C_{27}H_{27}O_2N$	81·6	6·8	3·5
C_8H_{17}	81·8	7·2	3·5	$C_{28}H_{29}O_2N$	81·7	7·1	3·4
C_9H_{19}	81·6	7·3	3·4	$C_{29}H_{31}O_2N$	81·8	7·3	3·3
$C_{10}H_{21}$	82·0	7·4	3·1	$C_{30}H_{33}O_2N$	81·9	7·6	3·2
$C_{12}H_{25}$	82·4	7·8	2·9	$C_{32}H_{37}O_2N$	82·2	8·0	3·0
$C_{16}H_{33}$	82·7	8·7	2·6	$C_{36}H_{45}O_2N$	82·5	8·7	2·7
$C_{18}H_{37}$	82·8	8·8	2·5	$C_{38}H_{49}O_2N$	82·7	8·9	2·5
			4 : 4′-*Di*-(p-n-*alkoxybenzylideneamino*)*diphenyls.*				
Me	80·2	5·9	6·5	$C_{28}H_{24}O_2N_2$	80·0	5·7	6·7
Et	80·5	6·2	6·3	$C_{30}H_{28}O_2N_2$	80·4	6·3	6·3
Pr^{n}	80·6	6·6	5·8	$C_{32}H_{32}O_2N_2$	80·7	6·7	5·9
Bu^{n}	80·8	7·0	5·6	$C_{34}H_{36}O_2N_2$	81·0	7·1	5·6
C_5H_{11}	81·2	7·4	5·3	$C_{36}H_{40}O_2N_2$	81·2	7·5	5·3
C_6H_{13}	81·4	7·6	5·4	$C_{38}H_{44}O_2N_2$	81·4	7·9	5·0
C_7H_{15}	81·4	8·2	5·0	$C_{40}H_{48}O_2N_2$	81·6	8·2	4·8
C_8H_{17}	81·6	8·4	4·8	$C_{42}H_{52}O_2N_2$	81·8	8·4	4·6
C_9H_{19}	81·6	8·6	4·3	$C_{44}H_{56}O_2N_2$	82·0	8·7	4·4
$C_{10}H_{21}$	82·0	9·0	4·2	$C_{46}H_{60}O_2N_2$	82·1	8·9	4·2
$C_{12}H_{25}$	82·5	9·6	3·7	$C_{50}H_{68}O_2N_2$	82·4	9·3	3·8
$C_{16}H_{33}$	83·0	9·8	3·4	$C_{58}H_{84}O_2N_2$	82·7	10·0	3·3
$C_{18}H_{37}$	83·0	10·2	3·0	$C_{62}H_{92}O_2N_2$	83·0	10·3	3·1

Alkyl	Found (%)			Formula	Required (%)		
	C	H	N		C	H	N
2 : 7-*Di*-(p-n-*alkoxybenzylideneamino*)*fluorenes.*							
Me	80·4	5·4	6·7	$C_{29}H_{24}O_2N_2$	80·6	5·6	6·5
Et	80·8	6·1	6·2	$C_{31}H_{28}O_2N_2$	80·8	6·1	6·1
Pr^n	81·2	6·4	5·8	$C_{33}H_{32}O_2N_2$	81·1	6·6	5·7
Bu^n	81·6	6·8	5·3	$C_{35}H_{36}O_2N_2$	81·4	7·0	5·4
C_5H_{11}	81·4	7·3	5·3	$C_{37}H_{40}O_2N_2$	81·6	7·3	5·2
C_6H_{13}	81·8	7·9	4·8	$C_{39}H_{44}O_2N_2$	81·8	7·7	4·9
C_7H_{15}	82·3	7·8	4·7	$C_{41}H_{48}O_2N_2$	82·0	8·0	4·7
C_8H_{17}	82·2	8·2	4·4	$C_{43}H_{52}O_2N_2$	82·2	8·3	4·5
C_9H_{19}	82·3	8·6	4·2	$C_{45}H_{56}O_2N_2$	83·2	8·5	4·3
$C_{10}H_{21}$	82·4	8·7	4·1	$C_{47}H_{60}O_2N_2$	82·5	8·8	4·1
$C_{12}H_{25}$	82·4	9·1	3·6	$C_{51}H_{68}O_2N_2$	82·7	9·2	3·8
$C_{16}H_{33}$	82·8	9·8	3·3	$C_{59}H_{84}O_2N_2$	83·1	9·8	3·3
$C_{18}H_{37}$	83·5	9·9	3·0	$C_{63}H_{92}O_2N_2$	83·3	10·1	3·1
2 : 7-*Di*-(p-n-*alkoxybenzylideneamino*)*fluorenones.*							
Me	77·8	4·9	6·5	$C_{29}H_{22}O_3N_2$	78·0	4·9	6·3
Et	78·5	5·6	5·7	$C_{31}H_{26}O_3N_2$	78·5	5·5	5·9
Pr^n	78·8	5·8	5·6	$C_{33}H_{30}O_3N_2$	78·9	6·0	5·6
Bu^n	79·0	6·5	5·4	$C_{35}H_{34}O_3N_2$	79·2	6·4	5·3
C_5H_{11}	79·3	6·7	4·8	$C_{37}H_{38}O_3N_2$	79·6	6·8	5·0
C_6H_{13}	79·6	7·1	4·7	$C_{39}H_{42}O_3N_2$	79·9	7·2	4·8
C_7H_{15}	79·8	7·5	4·7	$C_{41}H_{46}O_3N_2$	80·1	7·5	4·6
C_8H_{17}	80·6	7·9	4·2	$C_{43}H_{50}O_3N_2$	80·4	7·8	4·4
C_9H_{19}	80·4	7·8	4·0	$C_{45}H_{54}O_3N_2$	80·6	8·0	4·2
$C_{10}H_{21}$	80·7	8·4	4·1	$C_{47}H_{58}O_3N_2$	80·8	8·3	4·0
$C_{12}H_{25}$	80·7	8·7	3·8	$C_{51}H_{66}O_3N_2$	81·2	8·8	3·7
$C_{16}H_{33}$	81·3	9·5	3·0	$C_{59}H_{82}O_3N_2$	81·7	9·5	3·2
$C_{18}H_{37}$	82·1	9·7	2·7	$C_{63}H_{90}O_3N_2$	82·0	9·8	3·0
p-n-*Alkoxybenzylideneanilines* (*m. p. in parentheses*).							
Me (56°)	79·5	6·3	6·5	$C_{14}H_{13}ON$	79·6	6·2	6·6
C_7H_{15} (58)	81·2	8·6	4·8	$C_{21}H_{27}ON$	81·4	8·5	4·8
$C_{12}H_{25}$ (73)	82·1	9·6	3·7	$C_{25}H_{35}ON$	82·2	9·6	3·8
$C_{16}H_{33}$ (76·5)	82·6	10·2	3·2	$C_{29}H_{43}ON$	82·7	10·2	3·3
$C_{18}H_{37}$ (84)	82·7	10·4	3·0	$C_{31}H_{47}ON$	82·9	10·5	3·1
NN′-*Di*-(p-n-*alkoxybenzylidene*)-p-*phenylenediamines.*							
Me	76·5	5·9	7·9	$C_{22}H_{20}O_2N_2$	76·7	5·8	8·1
Et	77·1	6·4	7·5	$C_{24}H_{24}O_2N_2$	77·4	6·5	7·5
Pr^n	78·1	7·2	6·9	$C_{26}H_{28}O_2N_2$	78·0	7·0	7·0
Bu^n	78·8	7·4	6·8	$C_{28}H_{32}O_2N_2$	78·5	7·5	6·5
C_5H_{11}	79·1	8·0	5·8	$C_{30}H_{36}O_2N_2$	78·9	7·9	6·1
C_6H_{13}	79·2	8·5	6·0	$C_{32}H_{40}O_2N_2$	79·3	8·3	5·8
C_7H_{15}	79·8	8·4	5·2	$C_{34}H_{44}O_2N_2$	79·7	8·6	5·5
C_8H_{17}	80·2	8·9	5·0	$C_{36}H_{48}O_2N_2$	80·0	8·9	5·2
C_9H_{19}	80·1	9·3	5·0	$C_{38}H_{52}O_2N_2$	80·3	9·2	4·9
$C_{10}H_{21}$	80·8	9·6	4·9	$C_{40}H_{56}O_2N_2$	80·5	9·4	4·7
$C_{12}H_{25}$	81·1	9·8	4·2	$C_{44}H_{64}O_2N_2$	81·0	9·8	4·3
$C_{16}H_{33}$	81·9	10·4	3·7	$C_{52}H_{80}O_2N_2$	81·7	10·5	3·7
$C_{18}H_{37}$	82·2	10·7	3·2	$C_{56}H_{88}O_2N_2$	82·0	10·7	3·4

The authors are indebted to the Distillers Co., Ltd., and to Imperial Chemical Industries Limited, for financial assistance. Two of them (J. B. H. and A. I.) are indebted to Dewsbury Education Committee and to the University of Hull, respectively, for grants.

THE UNIVERSITY, HULL.

[*Received, June* 16*th*, 1955.]