71. *Mesomorphism and Chemical Constitution. Part VIII.* The Effect of 3′-Substituents on the Mesomorphism of the 4′-*n*-Alkoxydiphenyl-4-carboxylic Acids and their Alkyl Esters.*

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The relative thermal stabilities of the mesophases of the 4′-*n*-alkoxydiphenyl-4-carboxylic acids and their alkyl esters are decreased by chloro-, bromo-, and nitro-substituents in the 3′-position. The results are in general agreement with the effects produced by such substituents in the 3-positions of the *p*-alkoxybenzoic acids and *trans*-*p*-alkoxycinnamic acids, and in the 5-position of the 6-alkoxy-2-naphthoic acids, but these additional data emphasise the fact that there is no simple relation between a substituent's size and dipole moment and its effect on the thermal stability of mesophases. The 4′-alkoxy-3′-nitrodiphenyl-4-carboxylic acids are predominantly smectic in behaviour, and since individual members may show two or three smectic phases, they afford interesting examples of polymesomorphism. The purely smectic esters of the nitro-acids are unusual in that their smectic–isotropic transition points give almost continuously rising curves when they are plotted against the number of carbon atoms in the alkyl chain.

THE effect of introducing simple substituents into the 3-position of the *p*-alkoxybenzoic [1] and *trans*-*p*-alkoxycinnamic acids [2] and the 5-position of the 6-alkoxy-2-naphthoic acids [3] has already been established. Recently the 4′-alkoxydiphenyl-4-carboxylic acids have been studied [4] and shown to exhibit mesophases of high thermal stability, and, in order to complete the data, the 3′-chloro-, 3′-bromo-, and 3′-nitro-derivatives of these acids have now been prepared and their mesomorphic characteristics determined. The relative thermal stabilities of the mesophases are still quite high, and in view of the interesting results which have already been obtained on the mesomorphic alkyl 4′-alkoxydiphenyl-4-carboxylates,[4] the esters of the chloro- and nitro-substituted acids have been included in this study. The bromo-esters were not examined when it was found that only the dodecyl, hexadecyl, and octadecyl ethers of the propyl 4′-alkoxy-3′-chlorodiphenyl-4-carboxylates exhibited transient monotropic smectic mesophases whose transition temperatures could not be obtained. The m. p.s and mesomorphic transition temperatures of these substituted acids and esters are contained in Tables 1—5.

TABLE 1. *4′-Alkoxy-3′-chlorodiphenyl-4-carboxylic acids.*

	Temp. of transition to				Temp. of transition to		
Alkyl	smectic	nematic	isotropic	Alkyl	smectic	nematic	isotropic
Methyl	—	—	284°	Octyl	146°	225°	233°
Ethyl	—	243·5°	260	Nonyl	130·5	226	229
Propyl	—	208	248·5	Decyl	126	225·5	226·5
Butyl	187·5°	190	249·5	Dodecyl	120·5	—	221·5
Pentyl	171	207·5	241·5	Hexadecyl	107·5	—	211
Hexyl	170	218	240·5	Octadecyl	108·5	—	206·5
Heptyl	148·5	223	235				

There are no unusual features about the mesomorphic properties of the 4′-alkoxy-3′-chloro- and -3′-bromodiphenyl-4-carboxylic acids, and if the mesomorphic transition temperatures in Tables 1 and 3 are plotted against the number of carbon atoms in the alkyl chain the customary regularities are obtained. That is, the mesomorphic–isotropic

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* Part VII, Gray, Brynmor Jones, and Marson, *J.*, 1956, 1417.

[1] Gray and Brynmor Jones, *J.*, 1954, 2556.

[2] Gray, Brynmor Jones, and Marson, *J.*, 1956, 1417.

[3] Gray and Brynmor Jones, *J.*, 1955, 236.

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

TABLE 2. *Alkyl 4′-alkoxy-3′-chlorodiphenyl-4-carboxylates.*

Ethyl esters		Propyl esters		
Alkyl	M. p.	Alkyl	M. p.	
Methyl	110·5°	Methyl	71°	
Octyl	56	Octyl	51	
Hexadecyl	52	Dodecyl	43	Monotropic smectic phases observed
Octadecyl	63	Hexadecyl	51	
		Octadecyl	60·5	

TABLE 3. *4′-Alkoxy-3′-bromodiphenyl-4-carboxylic acids.*

	Temp. of transition to				Temp. of transition to		
Alkyl	smectic	nematic	isotropic	Alkyl	smectic	nematic	isotropic
Methyl	—	—	281°	Octyl	160°	214°	224°
Ethyl	—	—	254	Nonyl	145	215·5	220
Propyl	—	219·5°	239	Decyl	142	215·5	216·5
Butyl	—	202	241	Dodecyl	129·5	—	212
Pentyl	192·5°	196·5	232·5	Hexadecyl	124·5	—	202
Hexyl	183	206	232	Octadecyl	126	—	198
Heptyl	166	211	226·5				

TABLE 4. *4′-Alkoxy-3′-nitrodiphenyl-4-carboxylic acids.*

	Temperature of transition to				
Alkyl	smectic I	smectic II	smectic III	nematic	isotropic
Methyl	—	—	—	—	309·5°
Ethyl	—	—	—	—	279
Propyl	—	—	—	210·5°	224
Butyl	—	—	181°	198	223
Pentyl	—	—	157	208	219
Hexyl	—	136°	158	213·5	218
Heptyl	—	142	170·5	—	215
Octyl	—	173·5	179·5	—	214
Nonyl	—	174·5	186	—	211·5
Decyl	—	141·5	190	—	210
Dodecyl	(103°)	103	194·5	—	206·5
Hexadecyl	116·5	161	193·5	—	198·5
Octadecyl	123·5	161	186·5	—	195

The transition in parentheses is monotropic.

TABLE 5. *Propyl 4′-alkoxy-3′-nitrodiphenyl-4-carboxylates.*

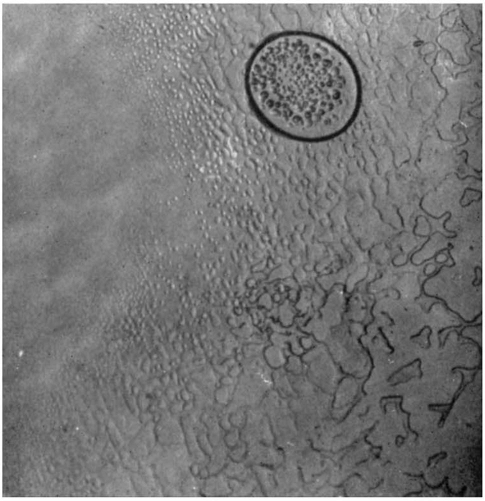
	Temp. of transition to			Temp. of transition to	
Alkyl	smectic	isotropic	Alkyl	smectic	isotropic
Methyl	—	78·5°	Octyl	(47°)	57°
Ethyl	—	77·5	Nonyl	(48)	56
Propyl	(<23°)	64	Decyl	(50·5)	54
Butyl	(34)	80·5	Dodecyl	50	53
Pentyl	(37·5)	57·5	Hexadecyl	51	56
Hexyl	(42·5)	62·5	Octadecyl	(55·5)	67
Heptyl	(44)	58·5			

Monotropic transitions are in parentheses.

transition points lie on two smoothly falling curves, the upper curve passing through the points for ethers with an even number, and the lower through those with an odd number of carbon atoms in the alkyl chain. The smectic–nematic transitions form a curve which rises steeply at first and then levels off and becomes coincident with the upper transition-point curve between the points for the decyl and dodecyl ethers, where nematic properties cease to appear.

The 4′-alkoxy-3′-nitrodiphenyl-4-carboxylic acids on the other hand give quite remarkable examples of polymesomorphism. The melting points of the methyl and the ethyl ether are high, and no mesophases are observed, but in the lower-melting propyl

Plate 1.

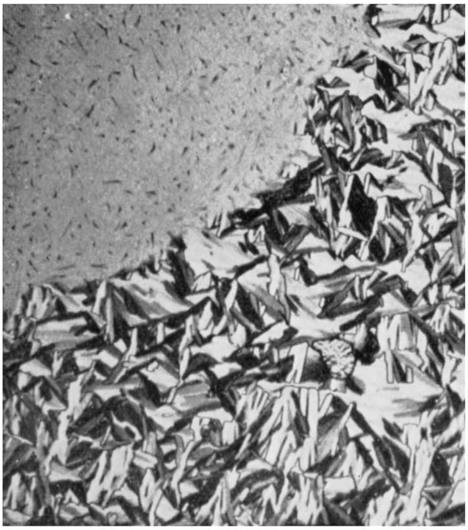


Isotropic–smectic III *transition* (× 8).

Plate 2.

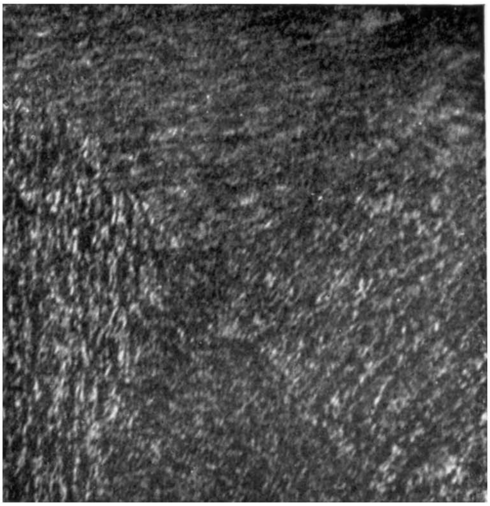
Smectic III–*smectic* II *transition* (× 40).

Plate 3.



Smectic III–*smectic* II *transition* (× 8).

Plate 4.



Smectic II–*smectic* I *transition* (× 8)((*crossed nicols*).

3′-*Nitro*-4′-*octadecyloxydiphenyl*-4-*carboxylic acid.*

In Plates **1**, **2**, *and* **3** *the nicols have been moved slightly away from the crossed position to one which gave more illumination and contrast to the photographs. The fairly large, circular region in Plate* **1** *is an air bubble.*

ether a characteristic, enantiotropic nematic phase is readily visible. The continued fall in melting point of the butyl and pentyl ether allows them to show a smectic and a nematic phase, the latter phase, like that of the propyl ether, having a transient threaded appearance before becoming homœotropic and scintillating when a cover-slip displacement is made. The hexyl ether, which melts still lower, exhibits two smectic phases as well as a nematic phase, and the changes observed on heating the crystals are solid–smectic II–smectic III–nematic–isotropic. The heptyl–decyl ethers also exhibit both smectic phases, but not the nematic phase, which is therefore last found in the hexyl ether of this series. The last three members of the series show yet another smectic phase—three in all. For the hexadecyl and the octadecyl ether the changes occurring on heating the crystals are solid–smectic I–smectic II–smectic III–isotropic, but in the dodecyl ether smectic phase I is not enantiotropic and is observed only when cooling from smectic II. The smectic II–smectic I transition occurs in fact at the same temperature as the melting point of the solid. The three smectic phase types are readily distinguished from one another by the different characteristic appearances which they adopt when mounted between a glass slide and cover-slip and observed between crossed nicols. Smectic III has a marked tendency to homœotropy and in only one or two cases are transient focal-conic groups observed. The change from the homœotropic nematic phase or the isotropic liquid to the homœotropic condition of smectic III is not therefore the most obvious of transitions, but it can be seen as the passage of fine lines which mark discontinuities in the melt. Plate 1 shows the border of the transition from isotropic to smectic III for the octadecyl ether where the isotropic liquid is on the left of the photograph. Smectic II adopts a typical focal-conic pattern, and it is interesting that the homœotropic smectic III–smectic II transition is marked by a border of well-defined bâtonnets which are shown in Plate 2. Plate 3 is a photograph of the transition at lower magnification. The bâtonnets are still visible in the top left-hand corner, but in the remainder of the field these have coalesced to give the large focal-conic groups of smectic phase II. Smectic I appears as a dense mosaic of minute focal-conic groups (Plate 4) readily distinguished from smectic II. However, if smectic I is heated, smectic II does not appear in such well-defined focal-conic groups, and the change is more difficult to see. The four photographs refer to the octadecyl ether and mark each of its transitions, *i.e.*, isotropic (Plate 1)–smectic III (Plates 2 and 3)–smectic II–smectic I (Plate 4). These transitions are easily seen only if the microscope heating-block [5] is used. In a melting-point capillary tube the smectic–nematic and the mesomorphic–isotropic changes are readily visible, but, as all three smectic phases are viscous and adhere to the capillary walls, the smectic–smectic transitions are seen only as

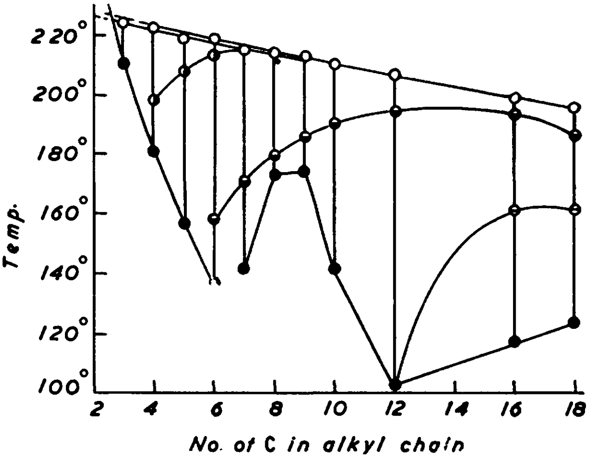


FIG. 1.

● Solid-mesomorphic.
○ Nematic or smectic III-isotropic.
◑ Smectic III-nematic.
◒ Smectic II-smectic III.
⊖ Smectic I-smectic II.

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

indefinite changes in opacity. The photographs do however make it clear that definite smectic–smectic changes occur. Added proof of this is given by the perfect reproducibility and reversibility of all the transitions and by the curves which may be drawn through transition points of a given type when these are plotted against the number of carbon atoms in the alkyl chain. This has been done in Fig. 1, where the usual alternation of the nematic- and smectic III–isotropic transitions is obvious. These points lie on two fairly flat, falling curves, the upper and the lower curve being respectively for ethers with even and odd numbers of carbon atoms in the alkyl chain. The smectic III–nematic transitions form a steeply rising curve which is drawn to coincide with the upper transition point curve after the point at which nematic properties last appear. The smectic II–smectic III transition point curve is again smooth and rises to the hexadecyl ether. The curve falls to the octadecyl ether, and to verify that this is correct this ether was very rigorously purified, but the smectic II–III transition temperature did not alter. The thermal stability of smectic I decreases rapidly as the alkyl chain becomes shorter, as is shown by the steep rise in the smectic I–II curve from the dodecyl to the hexadecyl ether before it levels off sharply to the octadecyl ether.

These nitro-derivatives therefore provide very fine examples of polymesomorphism, and although no reason for this behaviour is obvious, it is interesting to remember that the 6-alkoxy-5-nitro-2-naphthoic acids are similar in constitution and also give rise to this phenomenon.

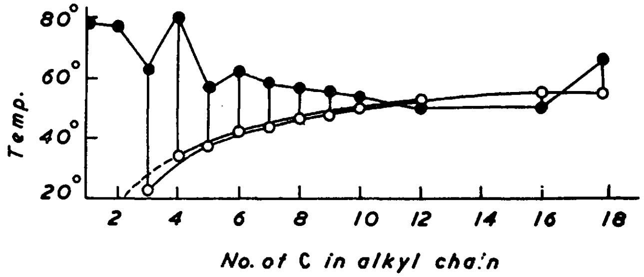

FIG. 2.

● Solid–mesomorphic or isotropic.
○ Smectic–isotropic.

As mentioned above, the esters derived from the 3′-chloro-acids do not yield phases on which transition-point determinations can be made, but this is not so for the propyl 4′-alkoxy-3′-nitrodiphenyl-4-carboxylates. These nitro-esters are purely smectic in behaviour, and, although in most cases the mesophases are monotropic, smectic–isotropic transition points are obtainable (Table 5) for ten of the esters because of the marked supercooling of the isotropic liquid. The appearance of the smectic phase from the isotropic liquid is marked in all cases by large bâtonnets which coalesce to give comparatively small focal-conic groups. The interest in these esters lies in the curves (Fig. 2) which are obtained when the smectic–isotropic transition points are plotted against the number of carbon atoms in the alkyl chain. As the transitions involve the isotropic liquid, two curves are obtained with the usual alternation. Both curves rise steadily, and the upper curve, for ethers with an even number of carbons, reaches a maximum only at the hexadecyl ether, and the fall to the octadecyl ether is only 0·5°. Increases in smectic–isotropic transition temperatures with increasing alkyl chain length have already been recorded for the propyl 4′-alkoxydiphenyl-4-carboxylates,[4] but only at the beginning of the homologous series. The purely smectic behaviour of these unsubstituted esters was attributed to the relatively large lateral cohesive forces between molecules compared with the terminal cohesions. Since the lateral cohesions will increase and the terminal cohesions decrease with increasing alkyl chain length, it is possible to imagine a maximum in the smectic–isotropic transition point curve, which will begin to fall only when the increasing lateral cohesions can no longer counterbalance the falling terminal cohesions. Now, in the nitro-esters the lateral cohesions will be much higher than in the unsubstituted esters because of the large $C-NO_2$

dipole. For this reason alone the purely smectic nature of the esters and the continued rise in the smectic–isotropic curve to such a late stage in the homologous series as the hexadecyl ether are understandable.

Finally, a comparison of the relative thermal stabilities of the mesophases in various series of substituted and unsubstituted alkoxyarenecarboxylic acids may be made. In Table 6 and 7, average nematic–isotropic and smectic–nematic transition temperatures of substituted and unsubstituted diphenyl acids are compared.

TABLE 6.

3'-Substituent in the 4'-alkoxydiphenyl-4-carboxylic acid ...	H	Cl	Br	NO_2
Average nematic–isotropic transition temp. (C_3–C_6)	279·8°	245°	236·1°	221°
Decrease in transition temp. from unsubstituted acid	—	34·8°	43·7°	58·8°

TABLE 7.

3'-Substituent in the 4'-alkoxydiphenyl-4-carboxylic acid	H	Cl	Br	NO_2
Smectic–nematic transition temp. (C_6 only)	243°	218°	206°	213·5°
Decrease in transition temp. from unsubstituted acid	—	25°	37°	29·5°

As usual, the chlorine and bromine atoms decrease the relative thermal stabilities of both the nematic and the smectic phases, the larger bromine atom having the greater effect, and, as already discussed,[3] the substituents affect the stability of the smectic phase less than that of the nematic phase. This is doubtless due to the substituent's dipole moment, which will enhance the smectic stability more than that of the nematic phase, and so will counteract the increase in breadth to some extent. This is most noticeable with the nitro-group which decreases the nematic stability by 58·8° and the smectic stability by only 29·5°. In fact, there is an increase of 7·5° from the smectic–nematic transition point of the bromo- to the nitro-acid in Table 7. This effect must be attributed to the $C-NO_2$ dipole which is much higher than the approximately equal C–Cl and C–Br dipoles.

These results are in general agreement with those obtained for other similar substituted and unsubstituted systems. However, when the effects of any one substituent on different alkoxyarenecarboxylic acids are compared there are noticeable differences. The effects of a chlorine atom on the relative mesomorphic thermal stabilities of the *p*-alkoxybenzoic, *trans*-*p*-alkoxycinnamic, and 4'-alkoxydiphenyl-4-carboxylic acids are shown in Table 8.

TABLE 8.

Acid type	Benzoic		Cinnamic		Diphenyl	
3- or 3'-Substituent	H	Cl	H	Cl	H	Cl
Average nematic–isotropic transition temp. (C_8–C_{10})	144°	91·5°	171·5°	138·3°	260°	229·5°
Decrease from unsubstituted acid	52·5°		33·2°		30·5°	

The corresponding decreases for the average smectic–nematic transition temperature (C_9 and C_{10}) are 34·7°, 15·3°, and 30·7°.

The chlorine atom therefore decreases the relative mesomorphic thermal stability of all three acid types, but the order of the effect is far from uniform. This state of affairs is also found with the bromo- and nitro-substituents, and quantitative attempts have been made to assess the importance of the differences. For example, the smaller effect which the chlorine atom has on the cinnamic acids compared with the benzoic acids has already been discussed [2] in terms of the greater breadth of the cinnamic acid molecule. However, the chlorine's effect is still smaller in the case of the nematic phases of the diphenyl acids where no such breadth effect can be considered. It can only be concluded that no simple relation exists between a substituent's size and dipole moment and its effect on the relative smectic or nematic thermal stability. That the breadth and dipole moment are important is shown by the qualitative agreement among results, but any attempt to seek a quantitative relation between molecular structure and mesomorphic transition temperatures must take into account other properties, such as molecular polarisability, and some considerable progress is being made in this direction.

EXPERIMENTAL

M. p.s are corrected for exposed stem.

Determination of Transition Temperatures.—The mesomorphic and polymorphic transition temperatures were determined in an electrically heated microscope block,[5] and enantiotropic changes were measured in the usual way. All values, except certain of the polymesomorphic smectic–smectic transitions of the 4′-alkoxy-3′-nitrodiphenyl-4-carboxylic acids and the changes from the solid to the mesophase, were checked by obtaining the temperature at which the transition occurs both when heating and cooling the specimen. Between crossed nicols, the changes observed in the 4′-alkoxy-3′-chloro- and -3′-bromo-diphenyl-4-carboxylic acids were from the solid to the fine mosaic of smectic focal-conic groups, from the solid or smectic phase to the threaded nematic phase, and from the solid or the mesophase to the isotropic liquid. The changes shown by the polymesomorphic 4′-alkoxy-3′-nitrodiphenyl-4-carboxylic acids and their esters have been described above.

In several of these substituted diphenyl acids the transition temperatures are high and the samples under observation sublime rapidly. This was counteracted by first finding a rough value for each transition at a rapid rate of heating. The temperature of the heating block was then stabilised within 2° of this value, and a freshly prepared slide of the sample was inserted, the temperature was raised slowly, and an accurate transition-point value determined.

The monotropic transitions of the propyl 4′-alkoxy-3′-nitrodiphenyl-4-carboxylates were determined by allowing the isotropic liquid to cool slowly in the heating block until the appearance of the bâtonnets which characterise the smectic phase. In most cases it was possible to raise the temperature, when the specimens were in their monotropic states, without the occurrence of crystallisation and thus to obtain the transition temperatures in reverse. Excellent agreement was found with the values obtained on slow cooling. In the case of the butyl ether crystallisation always occurred on slowly cooling the isotropic liquid. The slide was therefore heated to give the isotropic liquid and inserted in the block at a temperature some 5° above the suspected transition temperature, and the measurement carried out in the usual way, with slow cooling. The transition point for the propyl ether could not be obtained.

Polymorphism occurs in the 4′-alkoxy-3′-chloro- and -3′-bromo-diphenyl-4-carboxylic acids, and the enantiotropic solid–solid transition temperatures are summarised below, where solid I is the stable modification at room temperature.

3′-Chloro-	
Alkyl	Solid I–solid II
Nonyl	103·5°
Decyl	monotropic
Dodecyl	111·5
Hexadecyl	101

3′-Bromo-	
Alkyl	Solid I–solid II
Nonyl	116·5°
Decyl	141
Dodecyl	96
Hexadecyl	96·5
Octadecyl	monotropic

Preparation of Materials.—The preparation of 4′-methoxydiphenyl-4-carboxylic acid has already been described.[4]

3′-Chloro-4′-methoxydiphenyl-4-carboxylic Acid.—4′-Methoxydiphenyl-4-carboxylic acid (22·8 g., 0·1 mole) and dichloramine-T (12 g., 0·05 mole) were dissolved separately in glacial acetic acid (1500 and 250 ml. respectively). The dichloramine-T solution, together with concentrated hydrochloric acid (0·2 ml.), was added to the first solution at 90°, and the mixture heated at 100° for 4 hr. Cooling yielded the colourless chloro-acid, which was filtered off, washed with glacial acetic acid and water, and crystallised from ethanol and then glacial acetic acid. The yield of colourless crystals, m. p. 284°, was 52%.

3′-Chloro-4′-hydroxydiphenyl-4-carboxylic Acid.—The methoxy-acid (13·1 g., 0·05 mole) was dissolved in glacial acetic acid (1200 ml.), and 48% hydrobromic acid (300 ml.) was added slowly to the refluxing solution. After 7 hours' boiling, water (1200 ml.) was added to the boiling solution until the precipitate only just redissolved. The solution was cooled and the colourless crystals collected by filtration. The *hydroxy-acid*, m. p. 246—251° (Found: C, 63·0; H, 13·9; Cl, 14·4. $C_{13}H_9O_3Cl$ requires C, 62·8; H, 13·6; Cl, 14·3%), was washed with water and dried to give an 80% yield. Some slight inprovement in m. p. to 247·5—251° was obtained on crystallisation from xylene, but further crystallisation and chromatographic methods effected no further change. The product was however quite satisfactory for the preparation of the alkyl ethers.

4′-Alkoxy-3′-chlorodiphenyl-4-carboxylic Acids.—The hydroxy-acid (3·0 g., 1 mol.), potassium hydroxide (1·4 g., 2 mols.), 90% ethanol (100 ml.), and the *n*-alkyl halide (1·2 mols.) were refluxed for 10 hr. when using an alkyl iodide and for 12—14 hr. in the case of an alkyl bromide. Owing to the loss of halide in the ethylation, the amount of ethyl iodide used was 2·5 mols. Any ester formed during alkylation was hydrolysed by adding a solution of potassium hydroxide (1·5 g.) in 50% ethanol (100 ml.) and refluxing for a further 1·5 hr. The hot solution was then diluted with water (150 ml.) and acidified with concentrated hydrochloric acid, and the precipitate collected. The *products* were first crystallised from glacial acetic acid, the yields being 80—90%, and then from ethanol and from benzene until no alteration in their physical constants (Table 1) was observed.

4′-Alkoxy-3′-chlorodiphenyl-4-carboxylic acids.

	Found (%)				Required (%)		
Alkyl	C	H	Cl	Formula	C	H	Cl
Methyl	64·2	4·6	13·4	$C_{14}H_{11}O_3Cl$	64·0	4·2	13·5
Ethyl	65·4	4·6	12·7	$C_{15}H_{13}O_3Cl$	65·1	4·7	12·8
Propyl	66·1	5·1	12·2	$C_{16}H_{15}O_3Cl$	66·1	5·2	12·2
Butyl	67·0	5·4	11·7	$C_{17}H_{17}O_3Cl$	67·0	5·6	11·7
Pentyl	67·8	5·9	10·9	$C_{18}H_{19}O_3Cl$	67·8	6·0	11·1
Hexyl	68·6	6·2	10·7	$C_{19}H_{21}O_3Cl$	68·6	6·3	10·7
Heptyl	68·9	6·7	10·1	$C_{20}H_{23}O_3Cl$	69·3	6·6	10·2
Octyl	70·0	7·2	9·6	$C_{21}H_{25}O_3Cl$	69·9	6·9	9·8
Nonyl	70·7	7·3	9·3	$C_{22}H_{27}O_3Cl$	70·5	7·2	9·5
Decyl	71·3	7·8	8·9	$C_{23}H_{29}O_3Cl$	71·0	7·5	9·1
Dodecyl	72·4	8·2	8·4	$C_{25}H_{33}O_3Cl$	72·0	7·9	8·5
Hexadecyl	73·8	8·9	7·2	$C_{29}H_{41}O_3Cl$	73·7	8·7	7·5
Octadecyl	74·4	9·1	6·8	$C_{31}H_{45}O_3Cl$	74·3	9·1	7·1

3′-Bromo-4′-methoxydiphenyl-4-carboxylic Acid.—4′-Methoxydiphenyl-4-carboxylic acid (22·8 g., 0·1 mole) and sodium acetate (16·4 g., 0·2 mole) were dissolved in glacial acetic acid (1 l.). Bromine (24 g., 0·15 mole) in glacial acetic acid (200 ml.) was added to the solution at 100° during 4 hr., then the solution was refluxed for 30 min. to complete the reaction, and allowed to cool overnight. An almost quantitative yield of the nearly pure bromo-acid was obtained, and two crystallisations from glacial acetic acid yielded the pure acid in colourless needles (25·4 g., 83%), m. p. 281° (for analysis see Table).

3′-Bromo-4′-hydroxydiphenyl-4-carboxylic Acid.—The methoxy-acid (15·3 g.) was dissolved in glacial acetic acid (1 l.), and 48% hydrobromic acid (150 ml.) added slowly to the refluxing solution. After 12 hr., the hot solution was diluted with water (3 l.), and allowed to cool overnight. The colourless solid, when filtered off, thoroughly washed with water, and dried, gave a yield of 97% of *acid*, m. p. 234° (Found : C, 53·1; H, 3·3; Br, 27·4. $C_{13}H_9O_3Br$ requires C, 53·2; H, 3·1; Br, 27·3%). Crystallisation from glacial acetic acid, ethanol, benzene, and *cyclo*hexane–dioxan failed to alter the m. p.

4′-Alkoxy-3′-bromodiphenyl-4-carboxylic Acids.—3′-Bromo-4′-hydroxydiphenyl-4-carboxylic acid was alkylated and the *ethers* purified as described for the analogous chloro-compounds (see Table).

4′-Alkoxy-3′-bromodiphenyl-4-carboxylic acids.

	Found (%)				Required (%)		
Alkyl	C	H	Br	Formula	C	H	Br
Methyl	54·9	3·9	25·9	$C_{14}H_{11}O_3Br$	54·7	3·6	26·1
Ethyl	56·2	4·2	24·8	$C_{15}H_{13}O_3Br$	56·1	4·0	25·0
Propyl	57·6	4·5	23·7	$C_{16}H_{15}O_3Br$	57·3	4·5	23·9
Butyl	58·6	5·1	23·0	$C_{17}H_{17}O_3Br$	58·5	4·9	22·9
Pentyl	59·8	5·5	22·0	$C_{18}H_{19}O_3Br$	59·5	5·2	22·0
Hexyl	60·7	5·7	21·4	$C_{19}H_{21}O_3Br$	60·5	5·6	21·2
Heptyl	61·7	6·1	20·3	$C_{20}H_{23}O_3Br$	61·4	5·9	20·5
Octyl	62·4	6·3	19·7	$C_{21}H_{25}O_3Br$	62·2	6·2	19·8
Nonyl	62·9	6·6	19·1	$C_{22}H_{27}O_3Br$	63·0	6·4	19·1
Decyl	63·7	6·8	18·2	$C_{23}H_{29}O_3Br$	63·7	6·7	18·5
Dodecyl	65·2	7·4	17·2	$C_{25}H_{33}O_3Br$	65·1	7·2	17·4
Hexadecyl	67·5	8·1	15·7	$C_{29}H_{41}O_3Br$	67·3	7·9	15·5
Octadecyl	68·3	8·5	14·9	$C_{31}H_{45}O_3Br$	68·3	8·2	14·7

4′-Alkoxy-3′-nitrodiphenyl-4-carboxylic Acids.—The pure 4′-alkoxydiphenyl-4-carboxylic acids (3 g.) were dissolved in the minimum volume of glacial acetic acid at 95°, except in the case of the methyl ether whose nitro-derivative is so insoluble that twice this volume of solvent was used. A mixture of fuming nitric acid (9 ml.) and glacial acetic acid (9 ml.) was then added slowly, after which the mixture was maintained at 90—95° for 1 hr. and finally refluxed for 10 min. before being allowed to cool and crystallise. The pale yellow crystalline 3′-*nitro-derivatives* (see Table) were separated and crystallised from glacial acetic acid to give an average 85% yield. One or two further crystallisations from ethanol gave constant m. p.s.

4′-Alkoxy-3′-nitrodiphenyl-4-carboxylic acids.

	Found (%)				Requires (%)		
Alkyl	C	H	N	Formula	C	H	N
Methyl	61·4	3·9	5·1	$C_{14}H_{11}O_5N$	61·5	4·1	5·1
Ethyl	62·7	4·4	4·8	$C_{15}H_{13}O_5N$	62·7	4·6	4·9
Propyl	64·1	5·3	4·5	$C_{16}H_{15}O_5N$	63·8	5.0	4·7
Butyl	64·4	5·4	4·1	$C_{17}H_{17}O_5N$	64·8	5·4	4·4
Pentyl	65·8	6·1	4·1	$C_{18}H_{19}O_5N$	65·6	5·8	4·3
Hexyl	66·5	6·0	3·9	$C_{19}H_{21}O_5N$	66·5	6·2	4·1
Heptyl	67·3	6·4	3·9	$C_{20}H_{23}O_5N$	67·2	6·5	3·9
Octyl	68·2	6·8	3·9	$C_{21}H_{25}O_5N$	67·9	6·8	3·8
Nonyl	68·8	7·2	3·7	$C_{22}H_{27}O_5N$	68·5	7·1	3·6
Decyl	68·8	7·3	3·6	$C_{23}H_{29}O_5N$	69·1	7·3	3·5
Dodecyl	70·0	7·9	3·2	$C_{25}H_{33}O_5N$	70·2	7·8	3·3
Hexadecyl	72·2	8·6	2·8	$C_{29}H_{41}O_5N$	72·0	8·5	2·9
Octadecyl	72·5	8·7	2·9	$C_{31}H_{45}O_5N$	72·8	8·9	2·7

Alkyl 4′-Alkoxy-3′-nitro- and -3′-chlorodiphenyl-4-carboxylates.—The ethyl and *n*-propyl esters (Tables 2 and 5) were prepared in the usual way from the acid, the appropriate alcohol, and concentrated sulphuric acid. The clear solutions obtained after esterification were poured into an excess of sodium hydrogen carbonate. The solid was collected, washed with water,

Ethyl 4′-alkoxy-3′-chlorodiphenyl-4-carboxylates.

	Found (%)			Required (%)	
Alkyl	C	H	Formula	C	H
Methyl	66·3	5·3	$C_{16}H_{15}O_3Cl$	66·1	5·2
Octyl	71·0	7·7	$C_{23}H_{29}O_3Cl$	71·0	7·5
Hexadecyl	74·4	9·1	$C_{31}H_{45}O_3Cl$	74·3	9·1
Octadecyl	75·1	9·3	$C_{33}H_{49}O_3Cl$	74·9	9·3

Propyl 4′-alkoxy-3′-chlorodiphenyl-4-carboxylates.

	Found (%)			Required (%)	
Alkyl	C	H	Formula	C	H
Methyl	66·8	5·7	$C_{17}H_{17}O_3Cl$	67·0	5·6
Octyl	71·7	7·4	$C_{24}H_{31}O_3Cl$	71·6	7·7
Dodecyl	73·3	8·2	$C_{28}H_{39}O_3Cl$	73·3	8·5
Hexadecyl	74·4	9·1	$C_{32}H_{47}O_3Cl$	74·6	9·1
Octadecyl	75·2	9·4	$C_{34}H_{51}O_3Cl$	75·2	9·4

Propyl 4′-alkoxy-3′-nitrodiphenyl-4-carboxylates.

	Found (%)			Required (%)	
Alkyl	C	H	Formula	C	H
Methyl	64·8	5·2	$C_{17}H_{17}O_5N$	64·8	5·4
Ethyl	65·6	5·8	$C_{18}H_{19}O_5N$	65·6	5·8
Propyl	66·5	6·3	$C_{19}H_{21}O_5N$	66·5	6·2
Butyl	67·3	6·6	$C_{20}H_{23}O_5N$	67·2	6·5
Pentyl	67·8	6·8	$C_{21}H_{25}O_5N$	67·9	6·8
Hexyl	68·5	7·1	$C_{22}H_{27}O_5N$	68·5	7·1
Heptyl	69·2	7·4	$C_{23}H_{29}O_5N$	69·1	7·3
Octyl	69·9	7·2	$C_{24}H_{31}O_5N$	69·7	7·5
Nonyl	70·1	7·8	$C_{25}H_{33}O_5N$	70·2	7·8
Decyl	70·8	7·8	$C_{26}H_{35}O_5N$	70·8	7·95
Dodecyl	71·6	8·3	$C_{28}H_{39}O_5N$	71·6	8·3
Hexadecyl	73·1	9·0	$C_{32}H_{47}O_5N$	73·1	8·95
Octadecyl	73·8	9·2	$C_{34}H_{51}O_5N$	73·8	9·2

and pressed dry. The crude esters were digested with boiling ethyl alcohol, then filtered hot to remove the unchanged acid, and the ester crystallised from the filtrate, after concentration if necessary. The esters were then crystallised from light petroleum (b. p. 40—60°), the solution being filtered if necessary from any remaining carboxylic acid which is insoluble. Crystallisation was continued until the m. p.s were constant, but since the highly pure acids were used for esterification the *esters* were usually pure after the first crystallisation. The physical constants for the esters are recorded in Tables 2 and 5.

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