Mesomorphism and Chemical Constitution. Part V. The Mesomorphic Properties of the 4′-n-Alkoxydiphenyl-4-carboxylic Acids and their Simple Alkyl Esters.*

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[Reprint Order No. 5878.]

Thirteen 4′-*n*-alkoxydiphenyl-4-carboxylic acids have been prepared and their mesomorphic behaviour is compared with that of the 4-*n*-alkoxybenzoic acids. They exhibit mesophases of much greater relative thermal stability than the simpler benzoic acids; this is attributed to the enhanced intermolecular cohesion arising from the second aromatic ring and to the greater molecular length of the diphenyl compounds. The high relative thermal stability of the mesophases is emphasised by the mesomorphic behaviour of the methyl, ethyl, and *n*-propyl alkoxydiphenylcarboxylates, and the absence of anisotropic melts in the analogous alkoxybenzoates.

In order to establish whether certain diphenyl compounds can exhibit mesomorphism, some thirteen 4′-*n*-alkoxydiphenyl-4-carboxylates have been prepared. All have anisotropic melts, and the relative thermal stabilities of their mesophases are much higher than those of other mesomorphic compounds examined hitherto. The melting points and mesomorphic transition temperatures are summarised in Table 1, and in Fig. 1 the latter are plotted against the number of carbon atoms in the alkyl chain.

Although all thirteen ethers are mesomorphic, the first four alone possess purely nematic properties, but in the pentyl ether an additional, short, enantiotropic smectic phase appears. Thereafter, there is a gradual increase in smectic phase length and in the smectic–nematic transition temperature, which reaches its maximum at 256·5° in the nonyl and decyl ethers. At the same time there is a gradual decrease in nematic phase length, until, in the dodecyl, hexadecyl, and octadecyl ethers, purely smectic properties are encountered. It is clear from Fig. 1 that the mesomorphic–isotropic transition temperatures exhibit the usual alternations associated with homologous series of mesomorphic ethers containing alkyl chains made up of odd and even numbers of carbon atoms.

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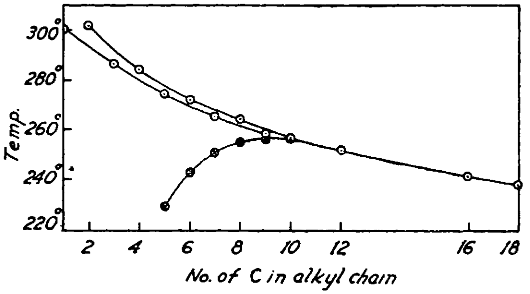
* Part IV, *J.*, 1955, 236.

Hence, these transition points lie on two falling curves, the upper one determined by those ethers containing an even number, and the lower by those with an odd number of carbons in the alkyl chain. As a result of this alternation, the highest mesomorphic–isotropic transition temperature is 301·5°—found for the nematic–isotropic change in the ethyl ether. The smectic–nematic transition points also lie on a smooth curve (Fig. 1), which, after an initial rise, levels off for the nonyl and decyl ethers. The curve is then drawn to coincide with the mesomorphic–isotropic transition point curve for members containing an even number of carbons in the alkyl group, since the decyl ether is the last to exhibit a nematic phase. In their general characteristics, the 4′-alkoxydiphenyl-4-carboxylic acids constitute a typical homologous series of mesomorphic compounds, similar to other series of alkoxyarenecarboxylic acids which have been examined previously (Gray and Brynmor Jones, *J.*, 1953, 4179; 1954, 683, 1467). With all these carboxylic acids (and these include the *p*-alkoxybenzoic acids, the *trans-p*-alkoxycinnamic acids, and the 6-alkoxy-2-naphthoic acids), the esters showed no mesomorphism. This probably arises from their inability to form a dimerised molecule, which is most probably the effective unit in the mesophases of the acids—and the cohesive forces which exist between the shorter, monomeric ester molecules are insufficient to allow of the existence of a mesophase. In view of the high relative thermal stability of the diphenylcarboxylic acids, it seemed possible that their alkyl esters, the alkyl 4′-alkoxydiphenyl-4-carboxylates, would be mesomorphic, since both their length and the intermolecular cohesion will be greater than those of the alkyl 4-alkoxybenzoates or the alkyl 6-alkoxy-2-naphthoates. The methyl, ethyl, and *n*-propyl esters of all thirteen 4′-alkoxydiphenyl-4-carboxylic acids were therefore prepared and examined, and in many cases mesomorphic phases were found. The m. p.s and smectic–isotropic transition temperatures (*T*) for these esters are summarised in Table 2, and in Fig. 2 (*a*)—(*c*) these are plotted against the number of carbon atoms in the alkoxy-group.

TABLE 1. 4′-n-*Alkoxydiphenyl-4-carboxylic acids*, 4′-RO·C_6H_4·C_6H_4·CO_2H-4 (I).

R in (I)	Temp. of transition to smectic	Temp. of transition to nematic	Temp. of transition to isotropic	Phase length of smectic	Phase length of nematic
Me	—	258°	300°	—	42°
Et	—	256·5	301·5	—	45
Pr	—	260	287	—	27
Bu	—	234	284·5	—	50·5
C_5H_{11}	227·5°	229·5	275	2°	45·5
C_6H_{13}	213	243	272·5	30	29·5
C_7H_{15}	194·5	251	265·5	56·5	14·5
C_8H_{17}	183°	255°	264·5°	72°	9·5°
C_9H_{19}	176	256·5	258·5	80·5	2
$C_{10}H_{21}$	172·5	256·5	257	84	0·5
$C_{12}H_{25}$	165	—	252	87	—
$C_{16}H_{33}$	151	—	241·5	90·5	—
$C_{18}H_{37}$	150	—	238	88	—

FIG. 1.



It is significant that the esters exhibit only smectic phases, and that in the three series of methyl, ethyl, and propyl esters the first members to be mesomorphic are the hexyl, pentyl, and ethyl ethers, respectively. The smectic–isotropic transition temperatures for the methyl esters fall as the alkyl chain length is increased, and, although only two of the ethers containing an odd number of carbon atoms are mesomorphic, the usual alternation of the transition points is evident. The transition temperatures for the even carbon chain ethers (hexyl–octadecyl) lie on a smooth, falling, curve, whilst those for the heptyl and nonyl ethers lie slightly below and on this curve, respectively, and constitute what is no doubt the end of a lower curve, whose exact position would be determined by the methyl, propyl, and pentyl ethers had they too been mesomorphic. In Fig. 2(*a*), these curves are extrapolated towards the shorter carbon chain lengths to show that the intercepts lie well below the m. p.s, and that phases are not observed in the methyl–pentyl ethers.

The hexadecyl and octadecyl methyl esters exhibit monotropic mesomorphism when the isotropic liquid is cooled—the isotropic–smectic reversal temperature was readily obtained for the hexadecyl ether, but, with the octadecyl ether, unless the isotropic liquid was chilled rapidly, crystallisation occurred before the phase appeared. Although no accurate reversal point for this monotropic phase could therefore be obtained, extrapolation of the smectic–isotropic transition point curve for even carbon chain ethers indicates that the value should be about 112·5° [Fig. 2(*a*)].

FIG. 2 (*a*).

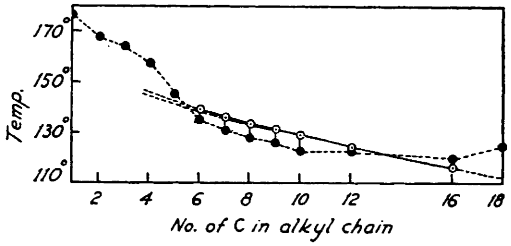


FIG. 2 (*b*).

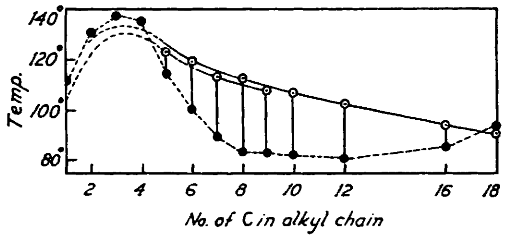


FIG. 2 (*c*).

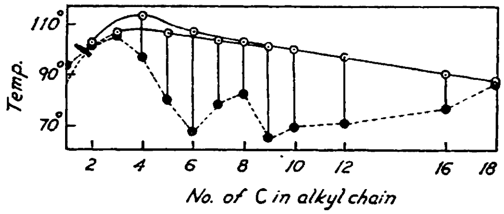


TABLE 2. *Alkyl 4′-alkoxydiphenyl-4-carboxylates,* 4′-RO·C_6H_4·C_6H_4·CO_2R'-4 (II).

R in	R = Me		R′ = Et		R′ = Prⁿ		R in	R′ = Me		R′ = Et		R′ = Prⁿ	
(II)	M. p.	*T*	M. p.	*T*	M. p.	*T*	(II)	M. p.	*T*	M. p.	*T*	M. p.	*T*
Me	176·5°	—	112°	—	94°	—	C_8H_{17}	127·5°	133·5°	83·5°	112°	82·5°	103°
Et	167·5	—	131	—	102	103°	C_9H_{19}	126	131	83	108	64·5	101
Pr	164	—	137·5	—	105	107	$C_{10}H_{21}$	122·5	128·5	82	107	69·5	100
Bu	157	—	135	—	97	113·5	$C_{12}H_{25}$	122·5	124	80·5	102·5	71	97
C_5H_{11}	145	—	114·5	123·5°	80	106·5	$C_{16}H_{33}$	119·5	(116) *	85·5	94	76·5	90·5
C_6H_{13}	134·5	139°	100·5	119·5	67·5	107	$C_{18}H_{37}$	125	(<121·5) *	93·5	(90·5) *	86·5	87·5
C_7H_{15}	130·5	135·5	89·5	113·5	78	103·5							

* Monotropic transition temperatures are in parentheses.

In the ethyl esters, the alternation in the smectic–isotropic transition points is more noticeable, and two distinct curves are produced for the members of the series containing odd and even numbers of carbon atoms. Here, only the octadecyl ether exhibits a monotropic phase, whose isotropic–smectic reversal was readily determined by cooling the melt slowly. The distribution of the m. p.s of the first four non-mesomorphic ethyl esters is interesting, since they rise to a maximum at propyl and then fall to butyl. Therefore, if the smectic–isotropic transition-point curves [Fig. 2(*b*)] for the ethyl esters are extrapolated backwards in such a way that they conform to the shape of a normal nematic–isotropic transition point curve (Fig. 1), the methyl and ethyl ethers, and probably the propyl and butyl ethers too, should exhibit enantiotropic smectic phases. Since these are not in fact observed, it must be inferred that these m. p.s are higher than the maximum temperatures at which mesophases could exist in these ethers; *i.e.*, their " mesophases," if they could be detected, would be monotropic. They fail to appear because the isotropic liquids do not supercool sufficiently before crystallisation occurs. The inference is that these " monotropic points " (isotropic–smectic) lie below the m. p.s in each case, so that the complete smectic–isotropic transition point curve can be envisaged only by extrapolation (broken curves) as shown in Fig. 2(*b*). The precise shapes of these portions of the curve are of course conjectural but, both for the odd and even members, some such curve, which rises to a maximum and then falls through the experimentally determined enantiotropic points, is indicated. It is legitimate to draw these broken curves quite close to the actual m. p.s, because the isotropic melts of the ethyl–butyl ethers crystallise within 0·5° of their m. p.s, and that of the methyl ether at 108°, only 4° below the m. p.

It may be that the same state of affairs obtains in the methyl esters, but here, because of the steady fall in m. p. from the methyl ether to the first mesomorphic member, there is no evidence to suggest that this is the case. However, the propyl esters provide evidence that a smectic–isotropic transition point curve can rise to a maximum and then fall. This is apparent from Fig. 2(*c*), where a steep rise in smectic–isotropic transition temperature is indicated on passing from the ethyl to the butyl ether, and this in turn is followed by a gradual decrease along the remainder of the ethers which have even numbers of carbons in the alkoxy-group. Further, the smectic–isotropic transition point (107°) for the propyl ether is only slightly higher than that of the pentyl ether (106·5°), and it would appear that these two points define the optimum portion of a similar curve which lies below the first, and falls through the points for the heptyl and nonyl ethers. This curve has again been extrapolated (broken curve) to fall below the m. p. of 94° of the non-mesomorphic methyl ether. Such smectic–isotropic curves are of course similar in shape to the curve which may be drawn through the smectic–nematic and smectic–isotropic points in a homologous series which exhibits both phase types.

In the case of an alkoxyarenecarboxylic acid which can exhibit both a smectic and a nematic phase, it is evident that, as the temperature of its smectic phase is raised, a stage is reached when the thermal energy is sufficient to overcome the lateral cohesive forces which keep the molecules parallel to one another. The molecules therefore are free to slide in the direction of their long axes and so produce an imbricated nematic melt. The molecular orientation in the nematic phase will therefore be maintained by the residual lateral cohesions and by the terminal cohesive forces between molecules arranged end-to-end. In the 4′-alkoxydiphenyl-4-carboxylic acids, and in other homologous series which have been examined, the smectic–nematic transition points lie on a curve which rises steeply at first and then levels off as the alkyl chain is lengthened. This effect must be related to an increase of the same order in the lateral cohesive forces. On the other hand, the falling curve on which the nematic–isotropic transitions lie may be accounted for if the overall cohesion arising from the terminal and residual lateral cohesions decreases as the alkyl chain is extended. The alternations in the mesomorphic–isotropic transition temperatures may result from differences in packing and cohesion between the terminal methyl groups of alkyl chains containing odd and even numbers of carbon atoms. Such an explanation was originally suggested by Malkin (*Trans. Faraday Soc.*, 1933, **29**, 977) to account for the alternation of m. p.s in homologous series. Since the cohesive forces which determine the nematic–isotropic change decrease as the chain length grows, whilst the lateral cohesions determining the smectic–nematic change increase and then level off, a stage will be reached when the terminal cohesions, which must be the decreasing component of the overall cohesions in the nematic phase, become so weak that they may well determine the mesomorphic–isotropic change before sliding takes place. When this occurs, no nematic phase should appear, and the smectic phase must be imagined as passing direct to the isotropic liquid as a result of breakdown of the cohesion between the orientated layers of the phase. In this way, the occurrence of purely smectic properties in the longer-chain members of a series can be understood, and also the fact that the nematic and smectic–isotropic transitions fall on one curve for the even carbon chain ethers. At the other end of the series, the shorter molecules are usually purely nematic, presumably because their lateral cohesions are so low that, when the solid melts, the molecules also slide along their long axes without producing a smectic phase. On the basis of these arguments, it seems probable that a compound will exhibit purely smectic properties when the lateral cohesive forces are relatively much greater than the terminal cohesions. Such a condition does obtain in the alkyl 4′-alkoxydiphenyl-4-carboxylates (II). Here, the resultant dipole of the ethoxycarbonyl group, which acts across the molecule, will make a considerable contribution to the lateral cohesions between molecules in a smectic layer packing—in which the molecules lie parallel to one another, with their ends in line. In a dimerised carboxylic acid there is, of course, no such effect to increase the lateral cohesions. The dipole which acts across a molecule's long axis has already been shown to increase the stability of a smectic phase to a much greater extent than a nematic phase (Part IV, *loc. cit.*).

For example, the increase in relative thermal stability of the nematic phase in passing from 6-octyloxy-2-naphthoic acid to its 5-chloro-derivative, in which the dipole again acts across the molecule's long axis, is only 7·5°, whereas the relative stability of the smectic phase increases by 20°. (As explained in Part IV, *loc. cit.*, it is realised throughout this paper that mesomorphic temperatures are only an *indication* of relative thermal stability and are not a *measure* of stability.) Both these effects are presumably brought about by the C–Cl dipole moment. The 5-bromo- and 5-iodo-6-alkoxy-2-naphthoic acids illustrate the same effect, while the 5-nitro-compounds, containing the larger C–NO_2 dipole, exhibit only smectic properties. The alkyl esters appear therefore to have the same characteristics as those compounds which are either purely smectic or exhibit smectic phases of relatively high thermal stability.

In the light of the preceding discussion, we now review the shape of the smectic–isotropic transition point curve in the propyl esters. In the esters which contain a short alkoxy-group, the transition temperature from the smectic phase to the isotropic liquid is probably determined by the loosening of the lateral cohesive forces. Since no nematic phase is exhibited, it seems likely that the terminal cohesions are not sufficiently strong to maintain the order in a nematic phase, and these cohesions presumably are weakened at the same time as the lateral cohesions. The lateral attractive forces between molecules increase as the alkyl-chain length grows, with the result that the smectic–isotropic transition temperatures like the smectic–nematic changes would be expected to rise, *e.g.*, from ethoxy- to butyloxy- in the propyl esters. However, the increase in lateral cohesions is accompanied by a decrease in the already relatively small terminal attractions. At a certain alkyl-chain length (pentyl in this series) the weakness of these terminal cohesions may begin to determine when the phase becomes isotropic by permitting the individual layers in the smectic packing to move apart and, ultimately, to result in a condition of isotropy. At the pentyl ether, the smectic–isotropic transition temperatures should begin to decrease. The relative strengths of the lateral and terminal cohesions will determine the precise position in a series at which the maximum smectic–isotropic transition temperature is found, or, indeed, whether such a maximum will appear at all. That terminal cohesions do play a part in determining these transitions is shown by the alternation of smectic–isotropic transition temperatures between members containing odd and even numbers of carbon atoms in the alkoxy-group. The smectic–nematic transition points do not alternate, since this change is determined by a sliding of the molecules when the lateral cohesions become sufficiently reduced by the thermal energy supplied.

A homologous series of alkyl esters of one particular 4-*n*-alkoxydiphenyl-4-carboxylic acid would constitute another potential series of mesomorphic esters. Since increments in the length of the ester alkyl group would produce the same effects as lengthening the alkoxy-group, it is likely that the behaviour of such a series would be similar to that of the present methyl, ethyl, or propyl esters. A complete series of this kind has not been prepared, but if the m. p.s and smectic–isotropic transition points for the methyl, ethyl, and propyl esters of each individual alkoxy-compound are plotted in turn against the number of carbon atoms in the ester chains, the relative behaviour of the first three members of the various series can be established. The changes from methyl to ethyl to propyl ester indicate that the graphs would be similar to those obtained for the complete series of methyl esters [Fig. 2(*a*)], and would give no further evidence for the smectic–isotropic transition-point curve of the type found for the propyl esters [Fig. 2(*c*)]. In any one set of three homologous, mesomorphic esters, the decrease in smectic–isotropic transition temperature is greater from methyl to ethyl than from ethyl to propyl. In a complete series of homologous alkyl esters, an alternation of this type would mean that the smectic–isotropic transitions for the odd carbon chain esters (methyl, propyl, etc.) would lie on one curve, and those for the even chain esters on a lower curve. The opposite effect of odd–even alternation is always observed in homologous series of alkoxy-compounds, where the ethers containing an even number of carbon atoms in the alkyl chain give transition points which constitute the upper of the two curves (cf. Fig. 1). This difference is readily explained, because a methoxy-group, with its one carbon atom, may be considered equivalent to an ethyl group containing two carbon atoms, since the oxygen atom affects the length of the chain, and the orientation of the terminal methyl group, almost exactly as a carbon atom would do. Hence, an alkyl ester with an even number of carbon atoms gives the same orientation of its terminal methyl group as an alkyl ether with an odd number of carbon atoms in the alkyl chain. This effect has already been observed by Weygand and Gabler (*Z. physikal. Chem.*, 1940, **46**, *B*, 270) in the *p*-*n*-alkylbenzoic acids, which are purely nematic in character. The nematic–isotropic transition points for these acids alternate appreciably and, in contrast to the *p*-*n*-alkoxybenzoic acids (Gray and Brynmor Jones, *J.*, 1953, 4179), are considerably higher for the odd members (pentyl–nonyl) than for the even carbon chain compounds (butyl–decyl).

As already mentioned, the 4′-alkoxydiphenyl-4-carboxylic acids exhibit a relative mesomorphic stability which is much greater than in any series so far encountered. The extent of this effect is made clear by comparison with the *p*-alkoxybenzoic acids. Table 3 summarises the average mesomorphic–isotropic transition temperature for propyl–octadecyl (A), the average smectic–nematic transition temperature for heptyl–decyl (B), and the average smectic–nematic and smectic–isotropic transition temperature for heptyl–octadecyl (C) of the *p*-alkoxybenzoic and 4′-alkoxydiphenyl-4-carboxylic acids.

TABLE 3.

Average transition type	*p*-$RO\cdot C_6H_4\cdot CO_2H$	4′-$RO\cdot C_6H_4\cdot C_6H_4\cdot CO_2H$-4	Increase in relative thermal stability
A	145·1°	263·3°	118·2°
B	111·25	254·75	143·5
C	119·6	250·1	130·5

The molecule of the monomer of the diphenyl acid is longer because of the second aromatic ring, which, as a result of its polarisability, increases the intermolecular cohesive forces. The mesophases of the diphenyl acids would be expected therefore to exhibit a greater relative thermal stability. Moreover, the second aromatic ring probably increases the lateral cohesions to a greater extent than the terminal cohesions. Compared with the benzoic acids, the smectic phases of the diphenyl acids should show a greater increased relative stability than the nematic phases. This effect is, in fact, found. Comparison of the heptyl–decyl ethers in each case shows that the average relative stability of the smectic phases in the diphenyl acids is greater by 143·5°, whilst the relative nematic stability is higher by only 116·9°.

When these relative stability effects are taken into account it is not surprising that the alkyl *p*-alkoxybenzoates are not mesomorphic, for their relative mesomorphic stabilities would be much lower than those of the alkyl 4′-alkoxydiphenyl-4-carboxylates. The average smectic–isotropic transition temperatures for all enantiotropic mesomorphic members in the methyl, ethyl, and propyl esters of the diphenyl acids are 131·9°, 110°, and 101·6° respectively. Therefore, if the same degree of decrease in relative stability, found in passing from the diphenyl acids to the benzoic acids occurs in the esters, the " mesomorphic–isotropic transitions " of the alkyl *p*-alkoxybenzoates would take place at temperatures below 0°, and certainly at temperatures substantially less than the m. p.s of the esters.

EXPERIMENTAL

M. p.s are corrected.

The mesomorphic and polymorphic transitions were determined in an electrically heated block (Gray, *Nature*, 1953, **172**, 1137). The enantiotropic mesomorphic changes were measured in the usual way: all values except those from the solid to the mesophase were checked both by heating and by cooling the specimen. In the case of the diphenyl acids, the changes observed in polarised light were from the solid to the fine mosaic of smectic focal-conics, from the solid or smectic phase to the mobile, threaded nematic phase, and from the solid or mesophase to the extinct isotropic liquid. In many cases the temperatures of transition are high, and frequently the sample under observation underwent rapid sublimation. This was reduced by using a freshly mounted sample for the determination of each transition, and by raising the temperature of the block to within 10° of the expected transition before inserting the slide, the approximate transition point having previously been determined in a m. p. capillary. The alkyl esters exhibit no nematic phase, but their smectic phases appear in clearly defined focal-conic groups which are frequently maintained when the solid is obtained by cooling from the mesophase. This pseudomesomorphic condition frequently makes it difficult to observe the change of the solid to the smectic phase, but the disappearance of cleavage lines in the solid can, with care, be used as a reliable indication of the occurrence of the transition. The reversal from the isotropic liquid to the mesophase is characterised by the appearance of typical bâtonnets which coalesce to the focal-conic pattern. Several of the esters exhibit monotropic smectic properties, and these transitions were determined by carefully observing the isotropic liquid as it cooled slowly until the bâtonnets appeared. It was sometimes possible to raise the temperature, while the specimens were in these monotropic states, without inducing crystallisation, and thus to obtain the transition temperature in reverse. Good agreement was found with the values obtained on cooling. In the case of methyl 4'-octadecyloxydiphenyl-4-carboxylate, the low rate of cooling (about 1° per min.), which was necessary for accurate measurement of the transitions, was too slow, and crystallisation occurred. Here, the value for the isotropic–smectic reversal temperature was obtained only by extrapolation of the curve constructed from experimentally determined values for the other members of the series.

Polymorphic Transition Temperatures.—See following Table. Here solid I is the stable solid at room temperature. No polymorphism was observed in the 4'-alkoxydiphenyl-4-carboxylic acids.

Solid I–*solid* II *transition temperatures in* RO·C_6H_4·C_6H_4·CO_2R'.*

R	R' = Me	R' = Et	R' = Pr	R	R' = Me	R' = Et	R' = Pr
Me	—	—	*	C_7H_{15}	120·5°	52°	—
Et	—	*	*	C_8H_{17}	120·5	58	—
Pr	—	98°	71°	C_9H_{19}	122·5	53	—
Bu	138°	*	56	$C_{10}H_{21}$	121	59	67°
C_5H_{11}	122·5	41	68·5	$C_{12}H_{25}$	*	75	*
C_6H_{13}	123	50	59				

* The esters so denoted exhibit a monotropic form.

Preparation of Materials.—*4-Methoxydiphenyl.* 4-Hydroxydiphenyl (85 g., 1 mol.), dissolved in hot 1·5N-sodium hydroxide (1·5 l.), was treated with methyl sulphate (2 mols.) so that the temperature did not exceed 60°. The temperature was then raised to 70° for 30 min. The product crystallised from ethanol as colourless plates, m. p. 80·5° (90—95%).

4-Acetyl-4'-methoxydiphenyl. Crystallised 4-methoxydiphenyl (11·5 g., 1 mol.) was dissolved in dry, redistilled carbon disulphide (75 ml.), contained in a three-necked flask, equipped with stirrer, dropping-funnel, and condenser. The solution was cooled to 0—2°, and sieved, anhydrous aluminium chloride (9·5 g., 1·12 mol.) was added quickly, with stirring. Acetyl chloride (5·8 ml., 1 mol.) was then added during 5—10 min., and the temperature raised gradually to 35°. The mixture was kept at 35° until the reaction seemed to be over, whereupon the whole was refluxed for 45 min. Ice-cold, concentrated hydrochloric acid (60 ml.) was then added to the cooled mixture to decompose the yellow-green complex. The condenser was removed, and steam passed under the surface of the solution to remove the solvent and complete the decomposition of the complex. Stirring was continued as the mixture was cooled quickly, in order to obtain the brownish-pink solid in a finely divided state. The solid was separated, dried, and triturated twice by stirring for 15 min. with ether (40 ml.). The insoluble 4'-acetyl derivative was thus separated from the isomeric 3-ketone, which is soluble in ether. The 4-acetyl-4'-methoxydiphenyl crystallised from *iso*propyl alcohol as colourless flakes, m. p. 156·5°. Johnson, Gutsche, and Offenhauer (*J. Amer. Chem. Soc.*, 1946, **68**, 1649) gave m. p. 153—154°. The yield varied between 25 and 60%. However, when the aluminium chloride was dried for several hours at 100—120°, and the amounts of acetyl chloride and aluminium chloride were increased to 1·1 and 1·17 mol., respectively, the yields were 60—77% in three consecutive preparations.

4'-Methoxydiphenyl-4-carboxylic acid. The foregoing compound was oxidised by aqueous sodium hypobromite, as described by Johnson, Gutsche, and Offenhauer (*loc. cit.*), although a more dilute solution of the ketone in dioxan was used (18 g. in 285 ml.). The crude product

(95% yield), crystallised from ethyl alcohol and acetic acid, had m. p. 258° (75—85%). Johnson *et al.* give m. p. 248—249°.

4′-Hydroxydiphenyl-4-carboxylic acid. The methyl ether (25 g.), acetic acid (1 l.), and 48% hydrobromic acid (200 ml.) were refluxed for 12—14 hr., then poured into water (2·5 l.) and cooled, and the precipitate was separated. The dried material, m. p. 288—291° (90—95%), was not quite pure, but the m. p. could not be improved by repeated crystallisation or by chromatography. The product was, however, satisfactory for the preparation of the alkyl ethers. A pure sample of the hydroxy-compound (Found: C, 72·7; H, 4·66. Calc. for $C_{13}H_{10}O_3$: C, 72·9; H, 4·67%), m. p. 294·5°, was obtained by hydrolysing the purified *acetyl* derivative (Found: C, 70·2; H, 4·7. $C_{15}H_{12}O_4$ requires C, 70·3; H, 4·7%), m. p. 260—262° (decomp.), obtained from the crude hydroxy-compound by acetylation and crystallisation once from glacial acetic acid, once from xylene, and twice from ethyl acetate. The acetyl derivative is mesomorphic. Fieser and Bradscher (*J. Amer. Chem. Soc.*, **1936**, **58**, 1738) claim that the hydroxy-compound can be purified by crystallisation from dioxan–*cyclo*hexane, and give m. p. 293—294°, but, although this procedure was tried, no improvement in the m. p. of the crude product was observed.

*4′-*n*-Alkoxydiphenyl-4-carboxylic acids.* The hydroxy-acid (0·01 mole) and potassium hydroxide (0·02 mole) were dissolved in hot alcohol (300 ml.) and water (30 ml.). The *n*-alkyl halide (1·2 moles) was then added, and the mixture refluxed for 12 hr. Any ester formed during alkylation was hydrolysed by adding a 10% solution of potassium hydroxide (0·02 mol.) in 70% ethanol and refluxing for a further 2 hr. The *alkoxy-acids* (see Table) crystallised from glacial acetic acid, and at this stage the yields were 85—90%. The products were then crystallised from ethyl alcohol and glacial acetic acid alternately until no alteration in their physical constants (Table 1) was observed.

4′-n-*Alkoxydiphenyl-4-carboxylic acids.*

	Found (%)			Required (%)			Found (%)			Required (%)	
Alkyl	C	H	Formula	C	H	Alkyl	C	H	Formula	C	H
* Methyl ...	73·7	5·3	$C_{14}H_{12}O_3$	73·7	5·3	Octyl	77·3	7·9	$C_{21}H_{26}O_3$	77·2	8·0
Ethyl	74·5	5·6	$C_{15}H_{14}O_3$	74·4	5·8	Nonyl	77·5	8·2	$C_{22}H_{28}O_3$	77·6	8·3
Propyl ...	74·8	6·1	$C_{16}H_{16}O_3$	74·9	6·3	Decyl	76·7	8·3	$C_{23}H_{30}O_3$	77·9	8·5
Butyl	75·3	6·5	$C_{17}H_{18}O_3$	75·5	6·7	Dodecyl ...	78·5	8·9	$C_{25}H_{34}O_3$	78·5	9·0
Pentyl ...	76·0	7·1	$C_{18}H_{20}O_3$	76·0	7·1	Hexadecyl	79·5	9·6	$C_{29}H_{42}O_3$	79·4	9·65
Hexyl ...	76·5	7·5	$C_{19}H_{22}O_3$	76·5	7·4	Octadecyl ...	79·6	9·9	$C_{31}H_{46}O_3$	79·8	9·9
Heptyl ...	76·8	7·7	$C_{20}H_{24}O_3$	76·9	7·7						

* Not new.

Alkyl 4′-alkoxydiphenyl-4-carboxylates. The *methyl, ethyl,* and n-*propyl* esters (see following Table) were prepared in the usual way from the appropriate alcohol and concentrated sulphuric

	Found (%)			Required (%)			Found (%)			Required (%)	
Alkyl	C	H	Formula	C	H	Alkyl	C	H	Formula	C	H
Methyl 4′-alkoxydiphenyl-4-carboxylates.											
Me	74·4	5·9	$C_{15}H_{14}O_3$	74·4	5·8	C_8H_{17} ...	77·6	8·2	$C_{22}H_{28}O_3$	77·6	8·3
Et	75·0	6·3	$C_{16}H_{16}O_3$	74·9	6·3	C_9H_{19} ...	78·1	8·5	$C_{23}H_{30}O_3$	77·9	8·5
Pr	75·7	6·8	$C_{17}H_{18}O_3$	75·5	6·7	$C_{10}H_{21}$ ...	78·4	8·7	$C_{24}H_{32}O_3$	78·3	8·7
Bu	76·0	7·0	$C_{18}H_{20}O_3$	76·0	7·1	$C_{12}H_{25}$ ...	78·8	9·0	$C_{26}H_{36}O_3$	78·8	9·1
C_5H_{11} ...	76·6	7·3	$C_{19}H_{22}O_3$	76·5	7·4	$C_{16}H_{33}$ ...	79·8	9·8	$C_{30}H_{44}O_3$	79·65	9·7
C_6H_{13} ...	76·9	7·8	$C_{20}H_{24}O_3$	76·9	7·7	$C_{18}H_{37}$ ...	80·1	10·0	$C_{32}H_{48}O_3$	80·0	10·0
C_7H_{15} ...	77·3	8·0	$C_{21}H_{26}O_3$	77·2	8·0						
Ethyl 4′-alkoxydiphenyl-4-carboxylates.											
Me	75·0	6·2	$C_{16}H_{16}O_3$	74·9	6·3	C_8H_{17} ...	78·1	8·4	$C_{23}H_{30}O_3$	77·9	8·5
Et	75·4	6·8	$C_{17}H_{18}O_3$	75·5	6·7	C_9H_{19} ...	78·3	8·7	$C_{24}H_{32}O_3$	78·3	8·7
Pr	76·1	6·9	$C_{18}H_{20}O_3$	76·0	7·1	$C_{10}H_{21}$ ...	78·4	8·9	$C_{25}H_{34}O_3$	78·5	8·9
Bu	76·6	7·6	$C_{19}H_{22}O_3$	76·5	7·4	$C_{12}H_{25}$ ...	79·1	9·3	$C_{27}H_{38}O_3$	79·0	9·3
C_5H_{11} ...	76·9	7·8	$C_{20}H_{24}O_3$	76·9	7·7	$C_{16}H_{33}$ ...	79·9	9·9	$C_{31}H_{46}O_3$	79·8	9·9
C_6H_{13} ...	77·2	8·0	$C_{21}H_{26}O_3$	77·2	8·0	$C_{18}H_{37}$ ...	80·2	10·2	$C_{33}H_{50}O_3$	80·2	10·1
C_7H_{15} ...	77·7	8·2	$C_{22}H_{28}O_3$	77·6	8·3						
n-*Propyl 4′-alkoxydiphenyl-4-carboxylates.*											
Me	75·6	6·8	$C_{17}H_{18}O_3$	75·5	6·7	C_8H_{17} ...	78·3	8·7	$C_{24}H_{32}O_3$	78·3	8·7
Et	75·9	7·1	$C_{18}H_{20}O_3$	76·0	7·1	C_9H_{19} ...	78·5	8·9	$C_{25}H_{34}O_3$	78·5	9·0
Pr	76·5	7·5	$C_{19}H_{22}O_3$	76·5	7·4	$C_{10}H_{21}$ ...	78·8	9·2	$C_{26}H_{36}O_3$	78·8	9·1
Bu	76·9	7·6	$C_{20}H_{24}O_3$	76·9	7·7	$C_{12}H_{25}$ ...	79·3	9·4	$C_{28}H_{40}O_3$	79·2	9·4
C_5H_{11} ...	77·3	8·1	$C_{21}H_{26}O_3$	77·2	8·0	$C_{16}H_{33}$ ...	80·1	9·9	$C_{32}H_{48}O_3$	80·0	10·0
C_6H_{13} ...	77·5	8·3	$C_{22}H_{28}O_3$	77·6	8·3	$C_{18}H_{37}$ ...	80·3	10·2	$C_{34}H_{52}O_3$	80·3	10·3
C_7H_{15} ...	77·9	8·4	$C_{23}H_{30}O_3$	77·9	8·5						

acid. In all cases, after esterification, the mixture was a colourless solution, which was poured into an excess of aqueous sodium hydrogen carbonate. The solid was collected, washed with water, and pressed dry. The crude esters were digested with boiling ethyl alcohol, filtered hot to remove unchanged acid, and the ester crystallised from the filtrate. The solubility in ethyl alcohol is variable—in general it increases from methyl to ethyl to propyl ester—and frequently the alcoholic filtrate had to be concentrated before crystals appeared. The esters were then crystallised from light petroleum (b. p. 40—60° or 60—80° according to solubility), 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 Table 2.

The authors are indebted to the Distillers Co., Ltd., and to Imperial Chemical Industries Limited, for financial assistance, and one of them (J. B. H.) is also indebted to Dewsbury Education Committee for a Grant which enabled him to participate in this work.

THE UNIVERSITY, HULL. [*Received, November* 15*th*, 1954.]