

Mesomorphism and Chemical Constitution. Part IV. The Effect of Substitution on the Mesomorphism of the 6-n-Alkoxy-2-naphthoic Acids.*

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Certain 6-*n*-alkoxy-5-halogeno- and -5-nitro-2-naphthoic acids have been prepared and their mesomorphic properties determined. The most stable mesophases are found in the 5-chloro-series and, as the size of the halogen substituent increases, the stability of the mesophases decreases. Despite the large dipole of the nitro-group, the 5-nitro-derivatives have the lowest mesomorphic thermal stability of the 5-substituted compounds which have been examined. These results are discussed with particular reference to the behaviour of the substituted series in relation to the parent 6-*n*-alkoxy-2-naphthoic acids.

IN Part III * the effect of halogen substitution on the mesomorphism of the 4-alkoxybenzoic acids was examined and in particular the mesomorphic behaviour of the 4-alkoxy-3-fluoro- and -3-chloro-benzoic acids was compared with that of the unsubstituted 4-alkoxybenzoic acids. When comparing the mesomorphic behaviour of two compounds, the temperature of transition of the mesophase to the isotropic liquid may be used as an indication of the relative stability of the two mesophases, although, for any one compound, the mesomorphic-isotropic transition temperature cannot be taken as a measure of the absolute stability of the mesophase. The true stability of a compound's mesophase would be obtained only by thermodynamic reasoning. In the above case the relative mesomorphic stability was found to decrease with increasing size of the halogen substituent. The study of the effect of substitution on mesomorphic stability has now been extended to the 6-*n*-alkoxy-5-chloro-, -bromo-, -iodo-, and -nitro-2-naphthoic acids, whose mesomorphic stabilities have been compared with those of the unsubstituted 6-alkoxy-2-naphthoic acids (Gray and Brynmor Jones, *J.*, 1954, 683). A qualitative comparison of the effect of substitution on the benzoic and naphthoic acids shows a pronounced difference. For instance, all the 6-alkoxy-5-halogeno-2-naphthoic acids possess considerable mesomorphic stability, whereas in the benzoic acids only 4-alkoxy-3-chloro- and -3-fluoro-benzoic acids exhibit mesomorphism, and the 3-bromo-acids are non-mesomorphic. Such behaviour reflects in part the greater thermal stability of the mesophases of the naphthoic acids (Gray and Brynmor Jones, *loc. cit.*).

The transition temperatures (solid-smectic and nematic, smectic-nematic and isotropic, and nematic-isotropic) of the series of naphthoic acids are tabulated below (the monotropic

* Part III, *J.*, 1954, 2556.

transitions and phase lengths are in parentheses). The smooth-curve relationships which have been found to be a feature of homologous series of mesomorphic compounds are again observed (Figs. 1—4) when the transition temperatures (the upper transition points and the smectic-nematic transitions) are plotted against the number of carbon atoms in the alkyl chain. In the nitro-series, because mesomorphic behaviour does not appear until the nonyl ether, only a selected few of the lower ethers were prepared. In the Table of results for the nitro-compounds no phase lengths have been included, since all the effects are monotropic.

Alkyl group	Temp. of transition to			Phase length of			
	smectic	nematic	isotropic	smectic	nematic		
<i>6-Alkoxy-5-chloro-2-naphthoic acids</i>							
Methyl	—	—	320.5°	—	—		
Ethyl	—	—	269	—	—		
Propyl	—	(217°)	220.5	—	(3.5°)		
Butyl	—	209.5	216.5	—	7		
Pentyl	—	189	208	—	19		
Hexyl	(160.5°)	163.5	207	(3°)	43.5		
Heptyl	165.5	176.5	201	11	24.5		
Octyl	169	183	199	14	16		
Nonyl	169	185.5	194.5	16.5	9		
Decyl	167	186.5	192.5	19.5	6		
Dodecyl	152	185.5	187.5	33.5	2		
Hexadecyl	142.5	—	178.5	36	—		
Octadecyl	138.5	—	174.5	36	—		
<i>6-Alkoxy-5-bromo-2-naphthoic acids</i>							
Methyl	—	—	303° (d)	—	—		
Ethyl	—	—	281 (d)	—	—		
Propyl	—	(<220.5°)	224	—	(>3.5°)		
Butyl	—	(213)	214.5	—	(1.5)		
Pentyl	—	196.5	207	—	10.5		
Hexyl	—	178	203.5	—	25.5		
Heptyl	158°	162	199	4°	37		
Octyl	164	174.5	196	10.5	21.5		
Nonyl	168	180	192.5	12	12.5		
Decyl	167	182.5	189.5	15.5	7		
Dodecyl	151.5	182	183.5	30.5	1.5		
Hexadecyl	138.5	—	173.5	35	—		
Octadecyl	136.5	—	169.5	33	—		
<i>6-Alkoxy-5-iodo-2-naphthoic acids</i>							
Methyl	—	—	296.5° (d)	—	—		
Ethyl	—	—	286.5	—	—		
Propyl	—	—	230	—	—		
Butyl	—	(<208.5°)	219	—	(>10.5°)		
Pentyl	—	(198)	204	—	(6)		
Hexyl	—	191	195	—	4		
Heptyl	—	176	189	—	13		
Octyl	(<144°)	161.5	185.5	(>17.5)	24		
Nonyl	(157.5)	163	182	(5.5)	19		
Decyl	(164.5)	165	178.5	(0.5)	13.5		
Dodecyl	146.5	169	172	22.5	3		
Hexadecyl	133.5	—	165	31.5	—		
Octadecyl	127	—	163	36	—		
<i>6-Alkoxy-5-nitro-2-naphthoic acids</i>							
Alkyl group	Temp. of transition to			Alkyl group	Temp. of transition to		
	smectic I	smectic II	isotropic		smectic I	smectic II	isotropic
Methyl	—	—	302°	Decyl	—	(166.5°)	175°
Pentyl	—	—	211	Dodecyl ...	(<162°)	(167)	173.5
Octyl	—	—	187	Hexadecyl	(<157)	(161)	163.5
Nonyl	—	(<159°)	173.5	Octadecyl...	(<154)	(157.5)	162

In the 6-alkoxy-5-chloro-2-naphthoic acids (Fig. 1), the first phase (monotropic nematic) is shown by the propyl ether, and smectic properties are first introduced with a monotropic phase in the hexyl ether. In the 5-bromo-series also (Fig. 2) nematic properties

first appear at the propyl ether and the phase is monotropic, but, in this case, the isotropic liquid crystallised when it cooled slowly, and no accurate value could be obtained for the reversal to the mesophase. This phase is therefore seen only on cooling the isotropic liquid rapidly. The butyl ether too is monotropic in its nematic behaviour. Smectic properties now appear one unit later, at the heptyl ether. The onset of nematic properties in the 5-iodo-series (Fig. 3) occurs in the butyl ether and smectic properties do not appear until the octyl ether which, like the nonyl and the decyl ether, exhibits a monotropic phase. Such differences in the three series have only a qualitative significance, since the point at which a series first exhibits mesomorphism is dependent upon the relative values of the *m. p.* and the mesomorphic transition, and on the ability of the isotropic liquid to exist in a supercooled condition. The three 5-halogeno-series are, however, similar in that their hexadecyl and octadecyl ethers are purely smectic, and that their nematic- and smectic-isotropic transitions lie on smooth curves. In each series, the points for those ethers with an even number of carbon atoms in the alkyl chain lie on the upper curve, and those with an odd number on the lower curve. The smectic-nematic transitions also lie on smooth curves, which become coincident with the curve through the upper transition points for even-carbon-chain ethers. The only smectic-nematic transition which could not be determined was that for 5-iodo-6-*n*-octyloxy-2-naphthoic acid. Normally the nematic melt crystallises but, when the cooling was very rapid, the monotropic smectic phase was observed. In general character the three series are similar to the 6-alkoxy-2-naphthoic acids (Gray and Brynmor Jones, *loc. cit.*). Here again, the lower ethers are purely nematic, the nematic properties decrease and the smectic properties increase as the chain length grows, the hexadecyl and octadecyl ethers are purely smectic, and the smectic-nematic, and smectic- and nematic-isotropic transitions fall on curves.

The 6-alkoxy-5-nitro-2-naphthoic acids (Fig. 4) show a completely different behaviour. No mesophases are observed until the nonyl ether, which exhibits a monotropic phase, and this only when the isotropic liquid is rapidly chilled. In consequence, the transition temperature could not be obtained, nor could the texture of the phase be determined because of the rapid appearance of the crystals. It was, however, observed that the phase appears from the isotropic liquid in elongated particles, which are probably bâtonnets. The decyl ether behaves similarly, but here the temperature of reversal to the monotropic phase was easily determined, and the anisotropic particles coalesced and became homœotropic with positive uniaxial properties. The true nature of these elongated particles is very difficult to establish because of their transient existence before becoming homœotropic. The transition temperature of reversal to this monotropic, homœotropic phase, which is probably smectic, the possible existence of bâtonnets, and the positive uniaxial character of the phase were also established for the dodecyl, hexadecyl, and octadecyl ethers. However, these three ethers exhibit an additional phase which, when observed with the unaided eye, passes across the homœotropic phase (smectic II) as a well-defined wave front, succeeded rapidly by crystals. Since the first phase to appear from the isotropic liquid appears to be smectic (smectic II), the second phase occurring at a lower temperature must also be smectic (smectic I), and not nematic, because in all known cases in which smectic and nematic properties occur in the same compound, the nematic phase exists at the higher temperature. Further, the phases (smectic I) are anisotropic and, by rapid chilling, their appearances were easily examined under a microscope. They were found to consist of minute focal-conic groups, but in no case was it possible to determine the smectic II-smectic I transition temperature. These ethers therefore seem to provide further examples of polymesomorphism (Vorländer, *Trans. Faraday Soc.*, 1933, 29, 913; Bernal and Crowfoot, *ibid.*, p. 1032), which requires the existence in one compound of two phases of the same type but of different characteristic texture or appearance. This does not imply two individual structural types of the same phase, but rather that two different orientations of the same layer structure to the glass surface can give rise to two different appearances of the phase. Apart from this, there is further evidence for regarding phase II as smectic—the trend of the smectic-isotropic transition points when these are plotted against the number of carbon atoms in the alkyl chain (Fig. 4). These points lie on a curve which rises to a maximum and then falls to the hexadecyl and octadecyl ethers, and is quite unlike the

FIG. 1. 6-Alkoxy-5-chloro-2-naphthoic acids.

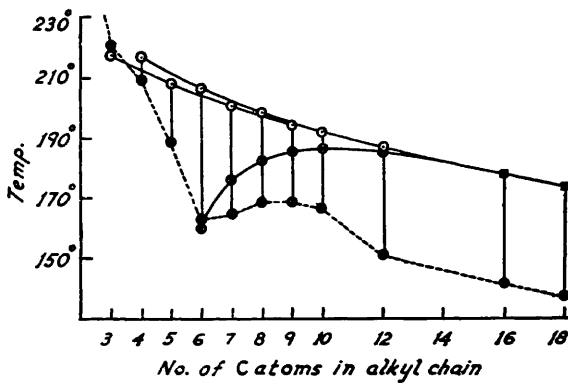
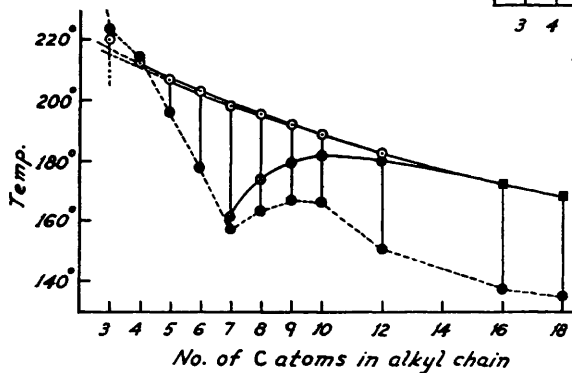


FIG. 2. 6-Alkoxy-5-bromo-2-naphthoic acids.

FIG. 3. 6-Alkoxy-5-iodo-2-naphthoic acids.

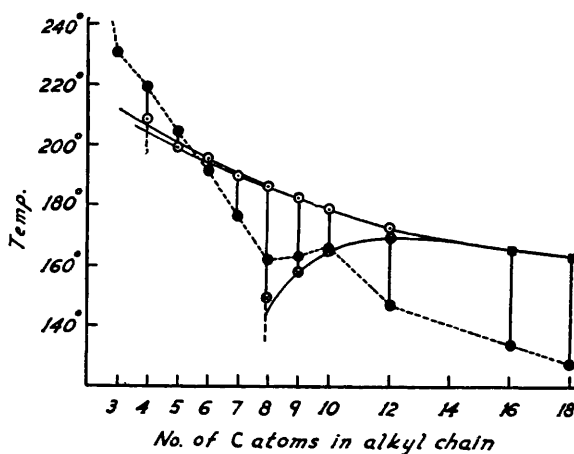
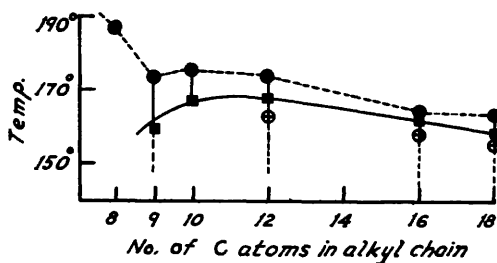


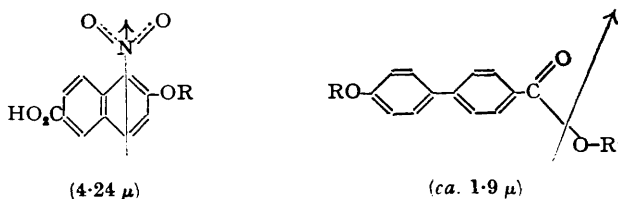
FIG. 4. 6-Alkoxy-5-nitro-2-naphthoic acids.



- Solid-mesophase or isotropic liquid.
- ⊗ Smectic-nematic.
- Nematic-isotropic.
- Smectic-isotropic.
- ⊕ Smectic I-smectic II.

nematic-isotropic transition point curves which invariably fall along their entire length. Moreover, the curve for the nitro-compounds is very similar to that for the purely smectic alkyl esters of 4-*n*-alkoxy-4'-carboxydiphenyls (Gray, Hartley, and Brynmor Jones, unpublished work), whose smectic-isotropic transitions follow a curve which rises and then falls. This is, of course, the normal curve for smectic-nematic and smectic-isotropic transition points in a homologous series, and it shows that the relative stability of a smectic phase to the isotropic liquid in a purely smectic series is the same as the relative stability of a smectic phase to the nematic phase and to the isotropic liquid in a series exhibiting both phase types. In Fig. 4 the curve through the smectic II-isotropic transitions is drawn to pass above the optimum point for the nonyl ether. This is because there is known to be an odd-even alternation for smectic-isotropic transitions in the esters of 4-*n*-alkoxy-4'-carboxydiphenyls, and consequently the curve through the nitro-decyl, -dodecyl, -hexadecyl, and -octadecyl ethers should pass above the point for the nonyl ether. No comment can be made about the smectic II-smectic I transitions which could not be determined.

The absence of nematic properties in these compounds can be related to the high dipole moment of the nitro-group (4.24μ), which operates at about 60° to the molecule's long axis, which, in the dimer, will be parallel to the 3 : 4-bond. Now, mesomorphic esters, *e.g.*, 4-*n*-alkoxy-4'-carboxydiphenyl alkyl esters, are always purely smectic and they, too, have a dipole acting across the molecule at about 70° to the long axis :



Thus, the nitro-compounds have the same characteristics as other typically smectic compounds, and the dipole will tend to align the molecules in parallel layers so that the dipoles reinforce one another.

A brief preliminary account of the effect of substitution on the mesomorphism of the 6-alkoxy-2-naphthoic acids has already been given (Gray and Brynmor Jones, *Nature*, 1952, **170**, 451). At that time it was thought that the mesophases in the 5-nitro-compounds consisted of a smectic and a nematic phase, and that the phases were short but enantiotropic. A detailed microscopic examination and rigid purification of the materials have shown this to be wrong, and the compounds are now known to show monotropic phases. Moreover, the use of the microscope heating block (Gray, *Nature*, 1953, **172**, 1137) has resulted in more accurate determination of the transition points, with the result that there are slight differences between the phase lengths now recorded and those originally reported.

Because of their similarity, it is possible to compare the three series of 5-halogenoacids with the unsubstituted 6-alkoxy-2-naphthoic acids. In all four series, the meso-

TABLE I

5-Substituent	H	Cl	Br	I
Average transition of mesophase to isotropic liquid (C_5-C_{18})	181.9°	193.6°	190.4°	180.9°
Change in transition temperature from unsubstituted	—	+11.7°	+8.5°	-1°
Increase in breadth from unsubstituted (Å)	—	0	0.22	0.6
Change in dipole moment from unsubstituted (μ)	—	1.73	1.71	1.48

morphic-isotropic transitions can be determined accurately for the pentyl to octadecyl ethers, and from these an average mesomorphic-isotropic transition temperature has been obtained for each series. The results show that there is an increase in average stability of the mesophase from the unsubstituted to the 5-chloro- and 5-bromo-acids, and a slight decrease from unsubstituted to the 5-iodo-acid. These results are summarised in Table 1.

As the size of the halogen substituent increases, there is a gradual decrease in mesomorphic stability in the 5-halogeno-series—which is in agreement with the behaviour of the 4-alkoxy-3-fluoro- and -3-chloro-benzoic acids (Gray and Brynmor Jones, *J.*, 1954, 2556). However, in the 4-alkoxybenzoic acids there is also a substantial decrease in stability on substitution in the 3-position, whereas the unsubstituted naphthoic acids are less stable in their phases than the 5-chloro- and 5-bromo-derivatives, and only a little more stable than the 5-iodo-acids. These differences arise from the smaller increase in breadth which any one substituent produces in the 5-position in a naphthoic acid compared with in the 3-position in a benzoic acid. In the naphthoic acids the substituent is in part accommodated in the space between the 5-carbon atom and the line determining the perimeter of the molecule, as shown in the inset. This space is large enough to accommodate a chlorine atom, so that the calculated breadths (d) for the unsubstituted and the 6-alkoxy-5-chloro-2-naphthoic acids are the same, whereas a 4-alkoxy-3-chlorobenzoic acid is broader by 0.75 Å than a 4-alkoxybenzoic acid. Since the changes in breadth are less in the naphthoic acids, the mesomorphic stability would not be expected to decrease to the same extent as in the benzoic acids. The greater stability of the 5-chloronaphthoic acids must therefore arise from the introduction of the C-Cl dipole, which, in these compounds, is not counteracted by a breadth increase as in the 4-alkoxy-3-chlorobenzoic acids. The increase in intermolecular cohesion which accompanies this dipole (1.73 μ) is equal to 11.7° (Table 1). From unsubstituted to 5-bromo-acid, the relative mesomorphic stability increase is less (8.5°), and this may be attributed to the slightly smaller C-Br dipole moment and to the increase in breadth of 0.22 Å occasioned by the larger bromine atom—both of these effects will reduce the intermolecular cohesion and the thermal stability of the bromo-acids. The 5-iodo-acids show a relative stability *decrease* of 1.0° compared with the unsubstituted naphthoic acids, and, again, this may be related to the smaller C-I dipole and to the fact that the large iodine atom increases the molecular breadth by 0.6 Å. However, it cannot yet be stated with any certainty whether or not the effect of a substituent on a compound's mesomorphic behaviour is directly related to its size and to the dipole it produces.

The average smectic-nematic transition temperatures for the nonyl, decyl, and dodecyl ethers of the four series have also been considered, and the results are summarised in Table 2.

TABLE 2.

5-Substituent	H	Cl	Br	I
Average smectic-nematic transition temp. (C_9 - C_{12}) ...	148.5°	185.8°	181.5°	163.7°

Here again there is a decrease in the thermal stability as the size of the substituent increases, but, in all cases, the stability is greater than in the unsubstituted acid. The dipole moment would seem here to have a greater effect in determining the temperature at which the smectic phase becomes nematic, than it has on the transition of the nematic to the isotropic liquid. The effect of a dipole acting across a molecule in increasing the thermal stability of the smectic phase has already been discussed under the 5-nitro-compounds.

In order to compare the behaviour of the 5-nitro-derivatives with the other series, the average smectic-nematic and smectic-isotropic transition temperatures for the decyl to octadecyl ethers of the 5-halogeno- and the unsubstituted acids must be related to the average smectic II-isotropic transition temperature for the same range of 5-nitro-compounds. These figures are summarised in Table 3.

TABLE 3.

5-Substituent	H	Cl	Br	I	NO ₂
Average smectic-nematic or smectic-isotropic transition temp. (C_{10} - C_{18})	156.25°	181.25°	176.9°	165.4°	163°

The behaviour of the chloro-, bromo-, and iodo-acids relative to the unsubstituted naphthoic acids is similar to that shown in Table 2, but an indication of the difficulty in

relating the size and dipole of a substituent to its effect on mesomorphic behaviour is given by the low average transition temperature of the 5-nitro-series. The C-NO₂ dipole (4.24 μ) might have been expected to increase the relative thermal stability to a considerable extent, particularly as the increase in breadth due to the nitro-group is only 0.48 Å, considerably less than that arising from an iodine atom. If a substituent's dipole is indeed directly related to the substituent's effect on mesomorphic stability, some other factor must be reducing the intermolecular cohesion which should arise from the nitro-group's dipole moment. Molecular models indicate that the nitro-group, as a result of rotation about the C-N bond, is forced out of the plane of the naphthalene ring through the steric effect of the hydrogen atom on the 8-carbon atom. The result is a thickening of the molecule which would reduce the intermolecular cohesion between the planes of neighbouring molecules. It is difficult to estimate the extent of this effect, or to decide whether it is sufficient to account for the low average thermal stability of the nitro-compounds. A study of the behaviour of an analogous type of molecule, a mesomorphic, nitro-substituted, alkoxy-arene-carboxylic acid, in which the nitro-group can remain planar, would be of interest, and this is now being made.

EXPERIMENTAL

(M. p.s are corrected for exposed stem.)

Determination of Transition Temperatures.—These temperatures (solid–solid, solid–smectic and nematic, smectic–nematic, and smectic and nematic–isotropic) were determined in an electrically heated microscope block (Gray, *Nature*, *loc. cit.*). The procedure adopted for the observation of the monotropic changes was the same as described for the 4-alkoxy-3-halogenobenzoic acids (Gray and Brynmor Jones, *J.*, 1954, 2556). All transitions between mesophases, and those from the isotropic liquid to the mesophase, were reversible at the same temperature. The nematic phases of the 5-halogeno-derivatives appeared from the isotropic liquid as spherical droplets which coalesced to give, in general, homogeneous plane structures containing varying numbers of threads. In the hexadecyl and octadecyl ethers, the formation of the smectic phase from the isotropic liquid became apparent by the appearance of bâtonnets which, in all cases, yielded fine mosaics comprised of tiny focal-conic groups. In the nitro-series, smectic phase I was also of this type, but smectic II was almost totally homœotropic, except for minute patches of focal-conic groups formed by the coalescing bâtonnets. These, although very transient, were much larger than those observed in the purely smectic 5-halogeno-derivatives.

Polymorphism became increasingly marked as the size of the halogen substituent increased. It was also pronounced in the 5-nitro-series. The data for the enantiotropic polymorphic transitions are summarised below, where solid I is the stable solid at room temperature.

Alkyl	Solid I–solid II transition temp.	Alkyl	Solid I–solid II transition temp.
<i>6-n-Alkoxy-5-chloro-2-naphthoic acids</i>		<i>6-n-Alkoxy-5-bromo-2-naphthoic acids</i>	
Pentyl	162°	Pentyl	163°
Hexyl	134	Hexyl	163
The butyl, octyl, and nonyl ethers exhibit a monotropic solid.		Heptyl	144.5
<i>6-n-Alkoxy-5-iodo-2-naphthoic acids</i>		Octyl	122
Propyl	213°	The butyl ether exhibits a monotropic solid.	
Butyl	203	<i>6-n-Alkoxy-5-nitro-2-naphthoic acids</i>	
Pentyl	176.5	Octyl	153.5°
Hexyl	162	Nonyl	112
Heptyl	149.5	Decyl	133
Octyl	138	Dodecyl	131
Nonyl	125	Hexadecyl	107
Decyl	119	Octadecyl	75.5
Dodecyl	113	The pentyl ether exhibits a monotropic solid.	
Hexadecyl	103		
Octadecyl	118		

Preparation of Materials.—The 6-alkoxy-5-chloro-2-naphthoic acids were prepared by alkylation of 5-chloro-6-hydroxy-2-naphthoic acid prepared from 6-methoxy-2-naphthoic acid (Gray and Brynmor Jones, *J.*, 1954, 678). Alkylation of 5-bromo-6-hydroxy-2-naphthoic acid

invariably left some unalkylated material, and, since this is difficult to remove, all the 6-alkoxy-5-bromo-, -5-iodo-, and -5-nitro-2-naphthoic acids were prepared by bromination, iodination, and nitration of the pure 6-alkoxy-2-naphthoic acids (*idem, loc. cit.*).

5-Chloro-6-methoxy-2-naphthoic Acid.—6-Methoxy-2-naphthoic acid (5.05 g., 1 mol.) and dichloramine-T (3 g., 0.5 mol.) were dissolved separately in glacial acetic acid (150 ml. and 20 ml., respectively) at 40°. The solutions were mixed, a few drops of concentrated hydrochloric acid were added, and the mixture was heated for 1 hr. on the water-bath. Cooling yielded the colourless *chloro-acid* (4.75 g., 82%), and the toluene-*p*-sulphonamide remained in solution. The acid was filtered off, washed with glacial acetic acid, and crystallised from the same solvent. The yield of colourless needles was 80%, m. p. 320.5° (Found: C, 60.7; H, 3.9; Cl, 15.2. C₁₃H₉O₃Cl requires C, 60.9; H, 3.8; Cl, 15.0%).

5-Chloro-6-hydroxy-2-naphthoic Acid.—The methyl ether (23.7 g.) was suspended in a solution of 48% hydrobromic acid (250 ml.) in glacial acetic acid (250 ml.). The mixture, after being refluxed until a solution was obtained (14–16 hr.), was poured into water (1 l.), and the pale pink precipitate (20 g.; m. p. 270–275°) was filtered off, washed with water, and dried. Soxhlet extraction with ether removed some insoluble, high-melting material, and the ether solution yielded 5-chloro-6-hydroxy-2-naphthoic acid (18.5 g., 83%), m. p. 271° (decomp.). Crystallisation from a small volume of absolute methyl alcohol, followed by sublimation at 160–180°/1–2 mm., yielded colourless needles, 17.6 g. (79%), m. p. 279° (decomp.) (Found: C, 59.1; H, 3.3; Cl, 16.0. C₁₁H₇O₃Cl requires C, 59.4; H, 3.15; Cl, 15.9%).

6-Alkoxy-5-chloro-2-naphthoic Acids.—5-Chloro-6-hydroxy-2-naphthoic acid (2.23 g., 1 mol.), potassium hydroxide (1.1 g., 2 mols.), water (5 ml.), ethyl alcohol (40 ml.), and the *n*-alkyl halide (1.2 mols.) were refluxed for 8 hr. (alkyl iodides) or 16 hr. (alkyl bromides). Aqueous potassium hydroxide (10 ml., 10%) was added, and the refluxing continued for 2 hr. to hydrolyse any ester. The acids were obtained as pure, colourless products after two crystallisations from glacial acetic acid and one from 95% ethyl alcohol, and, in the case of the hexyl–decyl, dodecyl, hexadecyl, and octadecyl ethers, one sublimation at 1–2 mm. The yields after the first crystallisation were 80–90%.

6-n-Alkoxy-5-chloro-2-naphthoic acids.

Alkyl	Found (%)			Formula	Required (%)		
	C	H	Cl		C	H	Cl
Ethyl.....	62.3	4.4	14.3	C ₁₃ H ₁₁ O ₃ Cl	62.3	4.4	14.2
Propyl.....	63.5	5.0	13.5	C ₁₄ H ₁₃ O ₃ Cl	63.5	4.9	13.4
Butyl.....	64.8	5.5	12.8	C ₁₅ H ₁₅ O ₃ Cl	64.6	5.4	12.75
Pentyl.....	65.8	5.8	12.1	C ₁₆ H ₁₇ O ₃ Cl	65.6	5.8	12.1
Hexyl.....	66.6	6.2	11.4	C ₁₇ H ₁₉ O ₃ Cl	66.6	6.2	11.6
Heptyl.....	67.4	6.6	11.1	C ₁₈ H ₂₁ O ₃ Cl	67.4	6.55	11.1
Octyl.....	68.6	6.9	10.6	C ₁₉ H ₂₃ O ₃ Cl	68.2	6.9	10.6
Nonyl.....	68.9	7.2	10.1	C ₂₀ H ₂₅ O ₃ Cl	68.9	7.2	10.2
Decyl.....	69.5	7.5	9.8	C ₂₁ H ₂₇ O ₃ Cl	69.5	7.45	9.8
Dodecyl.....	70.7	8.0	9.1	C ₂₃ H ₃₁ O ₃ Cl	70.7	7.9	9.1
Hexadecyl.....	72.4	8.9	7.7	C ₂₇ H ₃₉ O ₃ Cl	72.6	8.7	7.95
Octadecyl.....	73.4	9.1	7.4	C ₂₉ H ₄₃ O ₃ Cl	73.3	9.1	7.5

6-n-Alkoxy-5-bromo-2-naphthoic acids.

Alkyl	Found (%)			Formula	Required (%)		
	C	H	Br		C	H	Br
Methyl.....	51.1	3.1	28.5	C ₁₂ H ₉ O ₃ Br	51.25	3.2	28.5
Ethyl.....	52.8	3.8	26.9	C ₁₃ H ₁₁ O ₃ Br	52.9	3.7	27.1
Propyl.....	54.2	4.1	25.9	C ₁₄ H ₁₃ O ₃ Br	54.4	4.2	25.9
Butyl.....	55.5	4.6	24.8	C ₁₅ H ₁₅ O ₃ Br	55.7	4.6	24.8
Pentyl.....	57.2	4.9	23.6	C ₁₆ H ₁₇ O ₃ Br	57.0	5.0	23.7
Hexyl.....	58.1	5.3	22.7	C ₁₇ H ₁₉ O ₃ Br	58.1	5.4	22.8
Heptyl.....	59.3	5.8	21.7	C ₁₈ H ₂₁ O ₃ Br	59.2	5.75	21.9
Octyl.....	60.3	6.0	20.9	C ₁₉ H ₂₃ O ₃ Br	60.2	6.1	21.1
Nonyl.....	61.0	6.3	20.5	C ₂₀ H ₂₅ O ₃ Br	61.1	6.4	20.4
Decyl.....	61.9	6.6	19.4	C ₂₁ H ₂₇ O ₃ Br	61.9	6.6	19.7
Dodecyl.....	63.4	7.0	18.4	C ₂₃ H ₃₁ O ₃ Br	63.4	7.1	18.4
Hexadecyl.....	66.1	7.9	16.2	C ₂₇ H ₃₉ O ₃ Br	66.0	7.9	16.3
Octadecyl.....	67.1	8.3	15.4	C ₂₉ H ₄₃ O ₃ Br	67.0	8.3	15.4

6-Alkoxy-5-bromo-2-naphthoic Acids.—The 6-alkoxy-2-naphthoic acid (1 mol.), dissolved in the minimum volume of glacial acetic acid at 80°, was treated with bromine (1 mol.) in twice its volume of glacial acetic acid. The mixture was stirred at 80° for 20 min., although part of the product had separated from solution almost as soon as all the bromine had been added. When the reaction mixture had cooled, an almost quantitative yield of the nearly pure 5-bromo-acid was obtained. In each case two crystallisations from glacial acetic acid yielded the pure acids.

6-Alkoxy-5-iodo-2-naphthoic Acids.—A solution of iodine monochloride was prepared by dissolving sodium iodide (0.1 mol.) in boiling glacial acetic acid (50 ml.) and adding this carefully, with stirring and cooling, to a solution of dichloramine-r (0.05 mol.) in warm glacial acetic acid (25 ml.). To the solution of the 6-alkoxy-2-naphthoic acid (0.1 mol.), dissolved in the minimum volume of glacial acetic acid at 80°, the solution of iodine monochloride (0.1 mol.) was added rapidly with stirring. Almost immediately, the iodo-acid began to crystallise, but the mixture was kept at 80° for 20 min. to ensure complete iodination. Two crystallisations from glacial acetic acid gave the iodo-acids in 85–90% yields. Further crystallisation from this solvent did not raise the m. p.

6-n-Alkoxy-5-iodo-2-naphthoic acids.

Alkyl	Found (%)			Formula	Required (%)		
	C	H	I		C	H	I
Methyl	44.0	2.7	38.5	C ₁₂ H ₉ O ₃ I	43.9	2.7	38.7
Ethyl	45.7	3.3	37.4	C ₁₃ H ₁₁ O ₃ I	45.6	3.2	37.1
Propyl	47.4	3.8	35.5	C ₁₄ H ₁₃ O ₃ I	47.2	3.65	35.7
Butyl	48.6	4.1	34.4	C ₁₅ H ₁₅ O ₃ I	48.7	4.1	34.3
Pentyl	50.1	4.4	32.9	C ₁₆ H ₁₇ O ₃ I	50.0	4.4	33.1
Hexyl	51.4	4.7	31.8	C ₁₇ H ₁₉ O ₃ I	51.25	4.8	31.9
Heptyl	52.5	5.0	30.6	C ₁₈ H ₂₁ O ₃ I	52.4	5.1	30.8
Octyl	53.6	5.3	30.0	C ₁₉ H ₂₃ O ₃ I	53.5	5.4	29.8
Nonyl	54.4	5.8	28.8	C ₂₀ H ₂₅ O ₃ I	54.6	5.7	28.9
Decyl	55.5	5.9	27.7	C ₂₁ H ₂₇ O ₃ I	55.5	5.95	27.9
Dodecyl	57.4	6.5	26.6	C ₂₃ H ₃₁ O ₃ I	57.3	6.4	26.35
Hexadecyl	60.2	7.4	24.0	C ₂₇ H ₃₉ O ₃ I	60.2	7.25	23.8
Octadecyl	61.5	7.7	22.6	C ₂₉ H ₄₃ O ₃ I	61.5	7.6	22.4

6-Alkoxy-5-nitro-2-naphthoic Acids.—To the 6-alkoxy-2-naphthoic acid (1 g.), dissolved in the minimum volume of glacial acetic acid at 55–60° (the hexadecyl and octadecyl ethers were used as a suspension in 50 ml. of the solvent), a solution of fuming nitric acid (4 ml.) in glacial acetic acid (4 ml.) was added with stirring. The temperature was raised to 75–80°, and kept there for 10 min., clear solutions then being obtained in all cases. When cold, the pale yellow, crystalline 5-nitro-derivatives were separated and, after being washed with glacial acetic acid and water, they were dried. The yields of crude material were 85–95%, but constant m. p.s were only attained after several crystallisations from glacial acetic acid (once), 95% ethyl alcohol (twice), toluene (once), and 95% ethyl alcohol, in this order.

6-n-Alkoxy-5-nitro-2-naphthoic acids.

Alkyl	Found (%)			Formula	Required (%)		
	C	H	N		C	H	N
Methyl	58.2	3.6	5.6	C ₁₂ H ₉ O ₅ N	58.3	3.6	5.7
Pentyl	63.4	5.7	4.8	C ₁₆ H ₁₇ O ₅ N	63.4	5.6	4.6
Octyl	66.2	6.8	4.1	C ₁₉ H ₂₃ O ₅ N	66.1	6.7	4.1
Nonyl	67.0	6.9	3.9	C ₂₀ H ₂₅ O ₅ N	66.85	7.0	3.9
Decyl	67.5	7.2	3.8	C ₂₁ H ₂₇ O ₅ N	67.6	7.2	3.75
Dodecyl	68.5	7.7	3.5	C ₂₃ H ₃₁ O ₅ N	68.8	7.7	3.5
Hexadecyl	71.1	8.6	3.05	C ₂₇ H ₃₉ O ₅ N	70.9	8.5	3.1
Octadecyl	71.9	8.9	2.85	C ₂₉ H ₄₃ O ₅ N	71.75	8.9	2.9

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