

*Mesomorphism and Chemical Constitution. Part I. The
n-Alkoxy-naphthoic Acids.*

By G. W. GRAY and BRYNMOR JONES.

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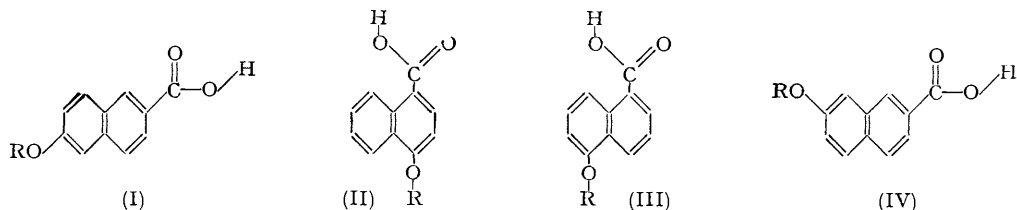
4- and 5-*n*-Alkoxy-1-naphthoic acids, and the 7-*n*-alkoxy-2-naphthoic acids exhibit no mesophases, whereas 6-*n*-alkoxy-2-naphthoic acids are mesomorphic. These results are discussed in relation to the structures of the acids, and the mesomorphic naphthoic acids are compared with the *p*-*n*-alkoxybenzoic acids and *trans-p*-*n*-alkoxycinnamic acids.

ALTHOUGH many mesomorphic compounds have been reported, little is known of the effect of changes in molecular constitution and shape on the degree of anisotropy in the melt. Inspection of the formulæ of mesomorphic compounds makes it clear that all the molecules are characterised by their predominant length. The molecules have a rod shape, which favours the linear molecular arrangement proposed by Friedel (*Ann. Physique*, 1922, **18**, 273) for the smectic and the nematic state. Such molecules will have a strong tendency to lie with their long axes parallel, and this will be accentuated by any dipoles in the molecule. Only few molecules broader than benzene have been found to be mesomorphic (Vorländer, *Trans. Faraday Soc.*, 1933, **29**, 907), and insufficient evidence exists to show what effect increase in breadth has on mesomorphism. One of the few established facts is that a nematic phase of 27° in *p*-*n*-pentyloxybenzoic acid is eliminated by 3 : 5-dichlorination—here a substantial increase in breadth destroys the mesomorphism.

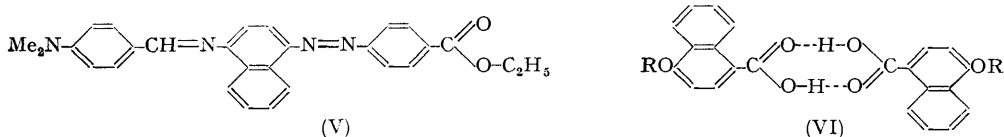
More is known about the general effect of systematic increments in molecule length. Bennett and Brynmor Jones (*J.*, 1939, 420) and Weygand *et al.* (*J. pr. Chem.*, 1940, **155**, 332, *Ber.*, 1938, **71**, 2399; *Naturwiss.*, 1931, 27, 28) prepared homologous series of *n*-alkoxy-compounds, *e.g.*, *p*-*n*-alkoxybenzoic acids, *trans-p*-*n*-alkoxycinnamic acids, and homologues of *p*-azoxy- and *p*-azo-anisole. These investigations show that when the alkyl chains are short the systems are either non-mesomorphic or nematic. As the chain length is increased, smectic properties begin to appear, and, as the smectic phase lengths increase, the nematic phase lengths decrease with each successive chain increment, until in the hexadecyl and the octadecyl ethers smectic phases alone are usually found. Among these systems no systematic effect of chain length on phase length was observed.

In an endeavour to enlarge the existing knowledge of the effect of breadth on mesomorphism, the alkoxy-naphthoic acids were examined. These were chosen for their similarity in molecular constitution to the series studied by Bennett and Jones (*loc. cit.*), and because alterations in the relative positions of the alkoxy- and the carboxy-group

change the effective molecular breadths and the linearity of the molecules. A brief preliminary report of the general behaviour of some of these acids has already been made (Gray and Brynmor Jones, *Nature*, 1951, **167**, 83). Four types have now been examined, and of these the 6-*n*-alkoxy-2-naphthoic acids (I) alone are mesomorphic, whereas the 4- (II) and the 5-*n*-alkoxy-1-naphthoic acids (III) and the 7-*n*-alkoxy-2-naphthoic acids (IV) are not mesomorphic. For the last two this may be attributed to the fact that the



molecules are not rod-shaped, since the axes of carboxy- and alkoxy-groups are not in line. This is particularly true when the dimer is considered. The 4 : 1-acids are essentially linear, but they are also very broad. Nevertheless, Vorländer (*loc. cit.*) has reported that ethyl 4'-*p*-dimethylaminobenzylideneamino-1'-naphthylazobenzoate (V), which is the same breadth, is mesomorphic. On this basis, these acids might be expected to show mesophases, particularly as their melting points are lower in seven cases than the upper clearing point of 197° for (V). It is possible that the acid dimer, which will be the effective unit in the crystal lattice, is as in (VI). This represents a molecule which is half as broad again as (V), which contains only one naphthalene ring. However, even if the dimer is the same breadth as (V), mesomorphism may be made impossible by the fact that the two naphthalene rings cause such imbrication in the molecule that the closest packing in the crystal lattice is not one in which the molecules lie parallel.



The mesomorphism of the 6-*n*-alkoxy-2-naphthoic acids is however to be expected, since the molecules and the dimers, although broader than the *p*-*n*-alkoxybenzoic acids, are both long and rod-shaped. Furthermore, the molecules are very similar in shape to the *trans-p*-*n*-alkoxycinnamic acids which are mesomorphic (Bennett and Brynmor Jones, *loc. cit.*).

These results make it highly improbable that any other *n*-alkoxy-1- or -2-naphthoic acid would exhibit mesomorphism, since any other relative distribution of alkoxy- and carboxy-groups would result in even greater deviations from linearity. The molecules would indeed be similar to *o*- or *m*-alkoxybenzoic acids, which show no mesophases.

The thirteen 6-*n*-alkoxy-2-naphthoic acids (methyl-decyl, dodecyl, hexadecyl, and octadecyl) are mesomorphic. The usual behaviour of a homologous series is shown by the fact that the lower members (methyl-octyl) are nematic, while the intermediate members exhibit both phase types, and the higher ethers (hexadecyl and octadecyl) are purely smectic. The corrected melting points, the smectic-nematic, and the smectic-nematic-isotropic transition points are tabulated below.

As is true to a lesser extent in the corrected constants for the *p*-*n*-alkoxybenzoic acids (Gray and Brynmor Jones, *J.*, 1953, 4179), fluctuations and an absence of regularity are observed in the nematic and in the overall phase lengths along the series. In both series however, after the onset of smectic properties, the nematic phase length decreases gradually to zero as the smectic phase length increases. The only exception to this is the octadecyl ether, which, compared with the hexadecyl ether, has a reduced phase length. The smectic phase of the nonyl ether is monotropic: that is, the solid melts at 147.5° to the nematic state, but, on cooling, passes through a smectic phase which appears at 140°

Alkyl group	Temp. of transition to			Phase length of	
	smectic	nematic	isotropic	smectic	nematic
Methyl	—	206°	219°	—	13°
Ethyl	—	213	224	—	11
Propyl	—	208	208.5	—	0.5
Butyl	—	198	208.5	—	10.5
Pentyl	—	179.5	199	—	19.5
Hexyl	—	147	198.5	—	51.5
Heptyl	—	163	192	—	29
Octyl	—	161.5	190	—	28.5
Nonyl	(140°)	147.5	183.5	(7.5°)	36
Decyl	139	147	181	8	34
Dodecyl	119	158.5	174	39.5	15.5
Hexadecyl	107	—	160.5	53.5	—
Octadecyl	114	—	159	45	—

just before the crystals of the solid appear. In the Table, the transition of 140° and the phase length of 7.5° are in parentheses, since they relate to a monotropic effect; the length of the phase is indeed a negative amount relative to the lengths of the enantiotropic phases.

In both series, when the constants are plotted against the number of carbon atoms in the alkyl chain, the upper transition points lie on two smooth curves, the upper curve corresponding to the acids with an even number of carbon atoms in the alkyl chain, and the lower to those with an odd number. This behaviour is common to many homologous series where the molecules pack together so that their long axes are parallel. It is believed that the alternations arise through variations in the packing of the terminal methyl group for odd and even members (Malkin, *Trans. Faraday Soc.*, 1933, 29, 977).

Since only these general similarities between the two series may be admitted, it is now necessary to compare the different series more specifically: that is, a criterion of the degree of mesomorphism is essential so that it may be decided which of two series is the more mesomorphic. The length of a phase is an unsuitable measure of mesomorphism since it indicates only the degree of separation of the lower m. p. and the upper transition point. The m. p. does determine the temperature at which the mesophase appears, but is a measure of the stability of the crystal lattice rather than of that of the mesophase. Two very similar compounds, which would be expected to have similar degrees of mesomorphism, may give widely different phase lengths because their crystal types and their internal energies are not the same, and give rise to different m. p.s. This means that the m. p. may be affected by the crystal type, and by polymorphic changes which are quite unrelated to the stability of the mesophase. Such factors may vary along a homologous series and result in irregularity of both m. p. and phase length. This in fact is most often the case. The phase length is therefore an unreliable criterion because of the influence of external factors upon the m. p. Objections of this kind do not apply to the upper transition points, which determine the temperature at which the thermal agitation destroys the linear orientation of the mesophase, through weakening of the intermolecular forces. This temperature is a direct measure of the stability of the mesophase. Therefore, a compound of m. p. 150° and upper clearing point 250° is less mesomorphic than another of m. p. 250° and upper clearing point 251°, since the phase of the latter is capable of resisting thermal breakdown at a higher temperature. This criterion of greater or smaller degrees of mesomorphism has been used in the comparison of the relative behaviours of many mesomorphic compounds.

From the Table it is clear that the most mesomorphic member is 6-ethoxy-2-naphthoic acid, with upper transition point 224°. In this series the general trend is for the upper transition points, and consequently the mesomorphism, to decrease as the alkyl chain length increases. Such behaviour may result from a decrease in intermolecular cohesion per unit length of the molecule as the chain length increases and the system becomes more paraffinic in character. The result will be a reduced thermal stability of the mesophase. Thus, mesomorphism decreases with increasing molecular length along a homologous series, since the cohesion is not maintained in proportion as the length is increased. This occurs with a general increase in phase length, which is therefore an unreliable guide to mesomorphic behaviour.

When the smectic-nematic and the smectic-isotropic transitions are plotted against the number of carbon atoms in the chain, the points are found to lie on a smooth curve

which rises to the smectic-isotropic transition at 160.5° of the hexadecyl ether. Since the stability of the smectic phase cannot increase indefinitely, the curve then falls slightly to 159° , the smectic-isotropic transition for the octadecyl ether. This decrease is in keeping with the general decrease in mesomorphic stability along the series. In the *p-n*-alkoxybenzoic acids, the smectic-nematic and the smectic-isotropic transitions also lie on a smooth curve, which rises from heptyl to hexadecyl and then falls slightly to octadecyl.

The upper transition points for 6-*n*-alkoxy-2-naphthoic acids are higher than those for *p-n*-alkoxybenzoic acids with the same alkyl groups, by an average of 47° , and the former are therefore the more mesomorphic. Thus, despite their smaller molecular breadths (6.8 \AA) the benzoic acids are less mesomorphic than the naphthoic acids (breadth 7.9 \AA). Moreover, the molecules of the naphthoic acids are longer by 2.2 \AA , but, unlike the increases in a homologous series, this greater length results from the presence of the second aromatic ring of the naphthalene nucleus. This will contribute more to the intermolecular cohesion than a single benzene ring, and so enhances the thermal stability. The effect is made clear by comparing members of each series in which molecule lengths are approximately the same. For example, 6-ethoxy-2-naphthoic acid (length 14.3 \AA), upper transition point 224° , is considerably more mesomorphic than *p-n*-pentylloxybenzoic acid (length 14.82 \AA), upper transition point 151° .

For the same reasons, the *trans-p-n*-alkoxycinnamic acids are more mesomorphic than the *p-n*-alkoxybenzoic acids, whereas the 6-*n*-alkoxy-2-naphthoic acids are more mesomorphic than the cinnamic acids. Naphthoic and cinnamic acids containing the same alkyl group will be of the same length, and the greater mesomorphism of the former must be due to the presence of the second aromatic ring of the naphthalene nucleus compared with the ethylenic bond in the cinnamic acids.

Experimental.—The physical constants for the 6-*n*-alkoxy-2-naphthoic acids were obtained in an electrically heated instrument (Gray, *Nature*, 1953, 172, 1137), and are corrected for exposed stem. Enantiotropic polymorphic transitions were also determined with this instrument; the following data were obtained, the stable solid at room temperature being termed solid I.

The butyl and pentyl ethers exhibit a monotropic polymorphic transition.

Alkyl group	Heptyl	Octyl	Nonyl
Transition of solid I to solid II	105°	160.5°	115°

In polarised light, the nematic phases in all cases were highly threaded or were made up of homogeneous areas which contained threads. The smectic phases did not give well-defined focal-conic groups, but appeared as fine, mottled mosaics consisting of minute focal-conics.

UNIVERSITY COLLEGE, HULL.

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