Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

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To cite this article: G. W. Gray (1966): The Influence of Molecular Structure on Liquid Crystalline Properies, Molecular Crystals, 1:2, 333-349

To link to this article: http://dx.doi.org/10.1080/15421406608083277

Molecular Crystals. 1966. Vol. 1, p. 333–349

Printed in Great Britain

The Influence of Molecular Structure on Liquid Crystalline Properties

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Received October 18, 1965

Abstract—The influence of molecular structure upon liquid crystalline properties has received considerable attention, particularly with regard to the effects upon liquid crystalline transition temperatures of introducing lateral substituents into suitable aromatic molecules. The results from such investigations are reviewed. The effects of changing the terminal substituent in the molecule of a liquid crystalline compound are less clear, and results are presented which show that the smectic and nematic properties are affected quite differently by the same substituents. The situation with regard to terminal substituents is discussed and illustrated by reference to homologous series of liquid crystalline compounds. It is concluded that no single order of terminal group efficiency can be expected to apply to all systems, as the nature of the molecule into which the terminal substituent is introduced plays an important part in determining the effect of the substituent on the liquid crystalline properties.

When molecular structure is varied widely within a group of suitable compounds, the liquid crystalline properties change markedly. For example, the liquid crystalline transition temperatures will vary extensively, and the type and number of liquid crystalline states may be different. In such cases it is difficult to relate the observed changes in liquid crystalline behaviour to the numerous molecular parameters which have been altered. For this reason, in studying the effect of molecular structure on liquid crystalline properties, it is often profitable to examine the effects of making relatively small changes in the molecular structure of one particular type of liquid crystalline compound, i.e., retaining the greater part of the molecular skeleton unaltered. In this paper, it is the intention to review some of the work which has been done along these lines, highlighting some of the conclusions which have been reached as regards introducing lateral substituents into liquid crystalline systems, and considering the situation with respect to the effects of modifying the terminal groups in liquid crystalline systems.

The temperature of a given transition may be used as an index of the thermal stability of a liquid crystalline state. Thus, an increase in the temperature of a nematic-isotropic transition reflects an increase in the thermal stability of the ordered arrangement of molecules in that nematic state, and this may be regarded as a direct result of some change in molecular structure. First of all, let us consider whether it is justifiable to make comparisons of like liquid crystalline transitions and to relate the differences to changes in molecular structure. Certainly, it would not be particularly useful to try to do this for ordinary melting temperatures (solid to isotropic liquid), but at the various transitions between smectic, nematic, and isotropic liquid states, much less profound changes in molecular order are involved, and a more obvious correlation between structural cause and temperature effect would be anticipated. This conclusion is justified when we consider the regular changes in liquid crystalline transition temperatures which occur as a homologous series is ascended and the fact that predictions as to the effects of changes in molecular structure on liquid crystalline transition temperatures are often borne out by experiment.

Before considering particular cases, we should envisage the changes in molecular order which occur at certain transitions involving liquid crystals, paying particular attention to the types of intermolecular attraction which appear to govern the changes. In the smectic state, the molecules (rod-like) are arranged parallel to one another, in layers; the long axes of the molecules lie normal or tilted with respect to the layer interfaces, and the cohesive forces operating across the interfaces are weak, i.e., under suitable conditions, layer flow is permitted. In the nematic state, the layer arrangement no longer exists, and the molecules are simply arranged parallel, but without any definite arrangement of the ends of the molecules. Consider now the changes:

Smectic to nematic—Primary terminal attractions between the molecules have already been loosened to allow layer flow in the smectic state. At the transition, the primary lateral attractions must loosen, allowing interpenetration of the layers.

Nematic to isotropic—Residual lateral and residual terminal attractions loosen giving disorder.

Smectic to isotropic—Primary lateral, residual lateral, and residual terminal attractions loosen giving disorder.

Bearing these points in mind, let us look at some effects of changing molecular structure on liquid crystalline properties. In all cases, the changes in structure are such that the number of molecular parameters being varied is as small as possible.

Structural Change Leading to Increase in Molecular Breadth

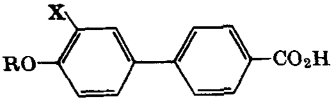
Such a change is most readily achieved by introducing lateral substituents into the molecule. Such substituents will affect the situation in the following ways:

(a) by broadening the molecule. This will tend to decrease the thermal stabilities of the smectic and nematic states, as a result of the increased lateral separation and the decreased lateral attractions;

(b) by increasing the polarity and polarizability of the molecule. This will tend to increase the smectic and nematic thermal stabilities because of the resulting increase in lateral attractions.

Of these two opposing effects, the first always predominates, unless the substituent does not exert its full breadth-increasing effect. Only when a substituent occupies some pocket in the side of a molecule has substitution been observed to increase liquid crystalline thermal stability; the 5-halogeno-6-n-alkoxy-2-naphthoic acids[1] and the 4-*p*-n-alkoxybenzylideneamino-3′-fluorobiphenyls[2] provide examples of this kind.

The normal state of affairs is typified by the 3′-substituted 4′-n-alkoxybiphenyl-4-carboxylic acids,[3] in which the full size effect of the substituent X operates.



When the nematic-isotropic transition temperatures (° C) for say the n-octyl ethers are plotted (Fig. 1) against the molecular diameters (defined as the diameter of the narrowest cylinder through which the molecule could pass, flexible parts such as alkyl chains being assumed not to interfere), the points lie on a smooth, steeply falling curve.† When such a graph for these systems was first published,[4] a predicted nematic-isotropic transition temperature of 235° was used in the case of X = Me. It is gratifying to report that the 3′-methyl-4′-n-octyloxybiphenyl-4-carboxylic acid has since been prepared, and the transition temperature is in fact 237°. Similar plots are given by the nematic-isotropic transition temperatures for other sets of substituted liquid crystalline compounds. Thus, despite the different polarities of the substituents, the main effect is that which the substituent has in separating the long axes of the molecules. These facts support the view that dipole-dipole interactions are not of great importance in the nematic melt; the significance of the added polarizability of the substituent is more difficult to assess, because this will increase roughly in proportion to the size of the substituent. However, the situation seems to be reasonably accounted for in terms of the idea that only residual interactions of an attractive kind retain the order in the nematic

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† It should be noted that 3′-nitro-4′-n-octyloxybiphenyl-4-carboxylic acid exhibits no nematic properties and the smectic-isotropic transition temperature of 214° has been used in Fig. 1 and for both sets of figures for NO_2 in Table 1. Although this transition temperature may be compared with other smectic-nematic transition temperatures, the smectic-isotropic transition temperature for the nitro-acid should not at first sight be comparable with the nematic-isotropic transition temperatures for the other derivatives. However, when nematic properties cease to appear at a particular member in an homologous series, the smectic-nematic and nematic-isotropic transition lines coincide, i.e., the smectic-isotropic curve is a continuation of the nematic isotropic curve. Looked at in this way, smectic-isotropic transition temperatures may be compared with nematic-isotropic transition temperatures.

melt, and that the increased ease of randomization on substitution is a function of the increased separation of the long axes of the molecules in the nematic melt.

As shown in Fig. 2 for the smectic-nematic or smectic-isotropic changes of the 3′-substituted 4′-n-alkoxybiphenyl-4-carboxylic acids, molecular diameter is not the sole criterion, the points for

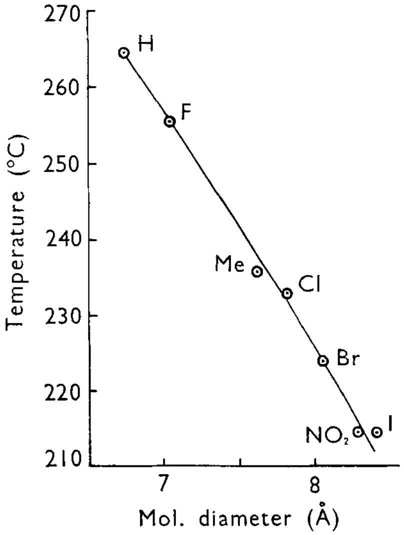


Figure 1. A plot of molecular diameter (Å) against the nematic-isotropic transition temperatures (° C) for 4′-n-alkoxybiphenyl-4-carboxylic acid and its 3′-substituted derivatives. The point for NO_2 is obtained using the smectic-isotropic transition temperature of 214° for the 3′-nitro-derivative (see footnote, p. 224).

X = H and Me lying below a line drawn through the points for X = F, Cl, Br, and I, and the point for $X = NO_2$ lying well above the line. The smectic-nematic transition temperature in the case of the acid in which X = Me has been found to be 213° (originally predicted[4] as about 210°). Similar distributions of the points have been found for the same types of transition for other sets of substituted liquid crystalline compounds. The dipole moment of the C—X bond seems therefore to be important. When this is weak (C—H or C—Me), the points lie below the line defined by the points for the halogeno-substituted acids (C-Hal, moderately dipolar), and when this is strong (C—NO_2), the point lies well above the line. In the smectic layers, dipole moments acting across the long axes of the molecules will reinforce one another, and be of importance in enhancing the lateral attractions which retain the order. The greater importance of such dipoles in counteracting breadth effects of substituents in the smectic state can now be appreciated, because in the nematic state such dipoles may lead to both attraction and repulsion, and the net effect may be very small.

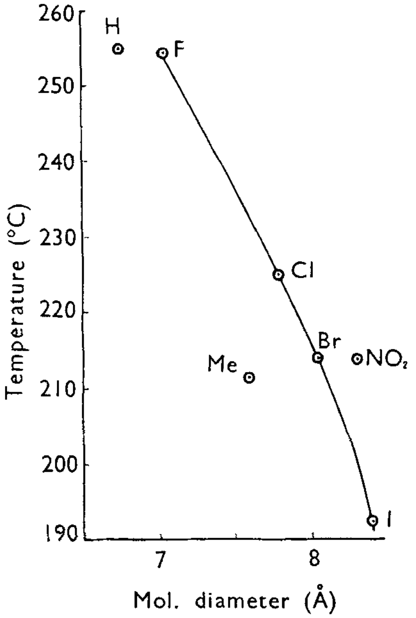


Figure 2. A plot of molecular diameter (Å) against the smectic-nematic or smectic-isotropic transition temperatures (° C) for 4′-n-alkoxybiphenyl-4-carboxylic acid and its 3′-substituted derivatives.

Of the two effects which a lateral substituent may have on liquid crystalline thermal stability, the breadth increasing effect dominates the situation as far as the nematic state is concerned, whilst a combination of breadth and dipolar effects is important when considering the smectic state. The greater influence of the dipole moment of the substituent in the smectic state is illustrated well in the case of the 5-substituted 6-n-alkoxy-2-naphthoic acids[1] where the breadth effects are very small. Thus, 5-chloro- and -bromo-substituents increase and a 5-iodo-substituent decreases the nematic thermal stability, but 5-chloro-, -bromo-, *and* -iodo-substituents increase the smectic thermal stability relative to the parent acid.

This does not mean that a given dipolar substituent will always affect the smectic thermal stability less than the nematic. The dipolar effect of the substituent itself and interactions between other dipolar parts of the molecules will be inversely proportional to a power of the distance of separation. Thus, for large substituents exerting their full breadth increasing effects, the counteracting dipolar effect may be small compared with the decreased interactions arising from the breadth effect upon other dipolar interactions. We can see from the figures in Table 1 for the 3′-substituted 4′-n-alkoxybiphenyl-4-carboxylic acids (cf. Figs. 1 and 2), that, amongst the halogens, only for X = F and Cl is the effect on the smectic state smaller. With the large nitro-group, the large dipole effectively counteracts the breadth effect, and again the smectic state is less affected. But, for the methyl group, despite its smallness, the reverse is true, because of its weakly dipolar nature.

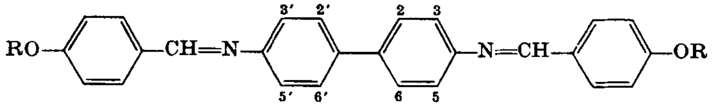
TABLE 1 3′-Substituted 4′-n-Alkoxybiphenyl-4-carboxylic Acids

	F	Cl	Br	I	NO_2	Me
Decrease in smectic thermal stability (°)	0.5	30	41	62.5	41	42
Decrease in nematic thermal stability (°)	9	31.5	40.5	50.5	50.5	27.5

Thus, the relative effect of a substituent on the smectic and nematic thermal stabilities depends on the size and polarity of the substituent, and also upon the nature of the molecule into which it is introduced.

We would now anticipate that if our lateral substituent exerts a steric effect which still further increases the intermolecular separation, much greater decreases in thermal stability would accompany the substitution, and the smectic state would suffer more than the nematic state. The recent work on 2- and 2′-substituted 4-*p*-n-alkoxybenzylideneaminobiphenyls[5] and 4,4′-di-(*p*-n-alkoxybenzylideneamino)biphenyls[6] has shown this clearly, e.g., the decrease in thermal stability associated with the small fluoro-substituent may be as high as 60° for the smectic and 50° for the nematic states.

TABLE 2 Observed and Predicted Average Decreases in Liquid Crystalline Thermal Stability for some Di-, Tri-, and Tetra-substituted 4,4′-Di-(*p*-n-alkoxybenzylideneamino)biphenyls[7]



Substitution	Average decrease (C_8–C_{10}) Smectic Calc.	Average decrease (C_8–C_{10}) Smectic Obs.	Average decrease (C_7–C_{10}) Nematic Calc.	Average decrease (C_7–C_{10}) Nematic Obs.
3,3′-DiCl	180°	181°	96.8°	94.2°
3,3′-DiBr	223.8	203.9	116	112.4
3,3′-DiMe	220.4	—	96	90.6
2,5-DiCl	—	—	132.5	134.6
2,5-DiBr	—	—	157.2	157.7
2,5-DiMe	—	—	133.4	131.5
2,3′-DiCl	—	—	132.5	126.4
2,3′-DiMe	—	—	133.4	127.1
2,2′-DiCl[a]	—	—	132.5	160.2
2,6-DiCl[a]	—	—	132.5	152.9
2,2′-,6-TriCl	—	—	229	222.1
2,2′,6,6′-TetraCl[b]	—	—	284	> 253.5

[a] Probable extra steric effects not allowed for in calculated figures.
[b] Based on n-heptyl ether only.

Finally, concerning lateral substitution, the work on di-, tri-, and tetra-substituted 4,4′-di-(*p*-n-alkoxybenzylideneamino)biphenyls[7] is of interest. In general, these are purely nematic systems, and the nematic-isotropic transition temperatures should depend on the degree of separation of the long axes of the molecules. Therefore, if we know the decreases in thermal stability which accompany substitution in the 2- and 3-positions, one might predict, on a simple additivity basis, the decreases which should accompany the introduction of these substituents in sets of two, three, etc. This is in fact possible with surprising accuracy, as shown by the figures in Table 2. The observed and calculated average decreases in liquid crystalline thermal stability agree very well, and where discrepancies are larger, there is reason to believe that extra steric effects are operating. With the exception of the 3,3′-dimethyl derivative, in those cases in which no smectic properties are observed, calculations show that the smectic-nematic transition temperatures would be very low, often below 0° and always very much below the melting points of the compounds.

With a fairly rational picture in mind as regards the effects of broadening the molecule of a liquid crystalline compound, let us consider next the effect of modifying the molecule in another way.

Changing the Nature of the Terminal Substituent

The situation here has been studied less fully and systematically, but Tables 3, 4 and 5 give some results which have been obtained by varying the nature of a *p*-substituent.

TABLE 3 4-*p*-Substituted-benzylideneamino-4′-methoxybiphenyls

Substituent	Nematic-isotropic transition temp.	Substituent	Nematic-isotropic transition temp.
H	176°	F	265.5°
Me	279	Cl	295
MeO	318	Br	294.5
n-PrO	296	NO_2	308
n-PnO	274	NMe_2	293.5
s-PrO	256	$NHCOCH_3$	345

TABLE 4 4-*p*-Substituted-benzylideneamino-4′-n-octyloxybiphenyls

Substituent	Smectic-nematic transition temp.[a]	Nematic-isotropic transition temp.
H	170.5°[a]	—
Me	178	222°
MeO	167.5	249.5
n-PrO	201	242
n-PnO	214	234
s-PrO	178	211
F	230[a]	—
Cl	261.5[a]	—
Br	267.5[a]	—
NO_2	169	231 (decomp.)[b]
NMe_2	214	225
$NHCOCH_3$	283	292.5

[a] Smectic-isotropic transition temperature when no nematic-isotropic transition temperature is quoted.

[b] 10° higher than the value quoted elsewhere.[8]

TABLE 5 4′-Substituted-Biphenyl-4-carboxylic Acids

Substituent	Nematic-isotropic transition temp.	Substituent	Nematic-isotropic transition temp.
H	(m.p. 222°)	n-PnO	275°
Me	275.5	F	265
Et	275	Cl	290
s-Pr	256	Br	(m.p. 306)
t-Bu	(m.p. 280)	I	(m.p. 312)
MeO	300	NH_2	(m.p. 245)
EtO	301.5	CN	315
n-PrO	287	NO_2	(m.p. 339)
n-BuO	284.5	Ph	331

Using the data in Tables 3–5, the substituents may be arranged to give orders of group efficiency in promoting liquid crystalline properties.

Smectic

$NHCOCH_3$ > Br > Cl > F > NMe_2 = n-PnO > n-PrO > Me
= s-PrO > H > NO_2 > MeO

Nematic

(i) *Methoxy anils* (Table 3)

$NHCOCH_3$ > MeO > NO_2 > n-PrO > Cl > Br > NMe_2
> Me > n-PnO > F > s-PrO > H

(ii) *Octyloxy anils* (Table 4)

$NHCOCH_3$ > MeO > n-PrO > n-PnO > NO_2 > NMe_2 > Me > s-PrO > H

(iii) *Biphenyl acids* (Table 5)

Ph > CN > EtO > MeO > Cl > n-PrO > n-BuO > Me > Et
= n-PnO > F > s-Pr > H

It is noted that all substituents enhance the nematic thermal stabilities, whilst nitro- and methoxy-substituents lower the smectic thermal stabilities. Moreover, the latter two substituents are high in the orders of group efficiency for nematic states. Below are given the simplified group efficiency orders, based on the substituents contained in the group efficiency order published earlier by Dave and Dewar[9] whose work centred around the behaviour of certain mixed liquid crystalline systems.

Nematic

NO_2 > MeO > NMe_2 > Me > Cl > Br > H (Dave and Dewar[9])
MeO > NO_2 > Cl > Br > NMe_2 > Me > H (Methoxy anils, Table 3)
MeO > NO_2 > NMe_2 > Me > H (n-Octyloxy anils, Table 4)
MeO > Cl > Me > F > H (Biphenyl acids, Table 5)

Smectic

Br > Cl > F > NMe_2 > Me > H > NO_2 > MeO (n-Octyloxy anils, Table 4)

The first three nematic orders are broadly similar, but the fourth is rather too limited to comment upon; the smectic order is quite different. Moreover, the arrangement of the terminal groups within these orders reflects no very obvious trend in the properties of the terminal groups. Before attempting to analyse these orders further, it seemed therefore that it might be wise to consider more carefully the effects on liquid crystalline transition temperatures of increasing the length of a simple terminal n-alkyl chain. Plenty data exist for such systems, and it is firmly established that increase in alkyl chain length gives regular changes in liquid crystalline transition temperatures. When such transition temperatures are plotted against an axis representing chain length, one of a limited number of plots is obtained. These have been fully illustrated elsewhere.[8] The commonest situation is that in which the smectic-nematic transition temperatures—which do not alternate—lie on a curve which rises steeply at first, then more gradually, and finally coincides with the falling nematic-isotropic transition lines, of which there are two, one for odd and one for even carbon chains. The smectic-nematic curve may sometimes fall slightly before it merges with the nematic-isotropic transition lines, and for certain series, the nematic-isotropic transition line may rise with increasing alkyl chain length, the points alternating for odd and even carbon chain members.

Previously we had good reason to believe that the carbon chain might adopt a castellated conformation, but preliminary results of X-ray studies of the crystalline states of some liquid crystalline compounds now make this unlikely, and we now favour the zig-zag conformation for the chain. This certainly allows an explanation of the absence of alternation for the smectic-nematic transition temperatures, since an added methylene unit does not affect the *lateral* attractions differently, whether the chain is even or odd, provided that the chain axes are normal to the layer interfaces.

From a range of homologous series, we can obtain the change in smectic-nematic transition temperature on passing from the C_8 to the C_{10} homologue. If we plot these differences against the average transition temperature for these homologues, we find that approximate straight lines are obtained, the slopes depending on the nature of the liquid crystalline system—carboxylic acid, mono-anil, or di-anil. The smallest increases in smectic-nematic transition temperature are found when the average transition temperatures are high, and the largest increases when the average transition temperatures are low. It may be concluded that when the lateral attractions between the molecules are high (giving high smectic-nematic transition temperatures), the increased lateral attractions arising from lengthening of the alkyl chain are relatively small in their effect, and vice-versa. Thus, increasing the alkyl chain length when the smectic-nematic transition temperature is low gives quite a pronounced increase in the transition temperature.

The increased lateral attractions arising from the polarizability of the lengthening alkyl chain cannot however account for the *fall* in the smectic-nematic transition line which sometimes precedes merging of this curve with the nematic-isotropic curve. Considering the overall shape of the smectic-nematic curve, we have to conclude that with increasing chain length, interpenetration of the layers becomes more difficult and subsequently more easy. This we consider is because the depth of flexible alkyl chain constituting the surface of the smectic layer is becoming greater. Only a partial interpenetration of the layers is necessary to destroy smectic properties, and it is readily imagined that this may occur more easily with very long alkyl chains which are of a "fluid" nature. Certainly a combination of this effect with that from the increasing lateral attractions would account for the observed shape of the curve.

Consider next the nematic-isotropic transition lines; for these transitions, four factors need to be considered as the chain lengthens.

(1) The longer molecules will be less readily rotated out of the ordered state.

(2) The overall polarizability increases with each added methylene unit.

(3) The frequency with which readily polarizable aromatic parts of the molecules lie next to one another in the fluid nematic melt will decrease, i.e., the residual lateral attractions will tend to decrease.

(4) Each methylene unit forces apart polarizable centres in the molecules, and decreases the residual terminal attractions.

(1) and (2) would increase the nematic-isotropic transition temperatures, and (3) and (4) would decrease the nematic-isotropic transition temperatures.

Thus, if aromatic and other readily polarizable parts of the molecules do not give rise to reasonable attractions, (1) and (2) may predominate, giving a rising transition line, and vice versa. In keeping with this view is the fact that rising transition lines are found in series in which the transition temperatures are low, i.e., when the residual interactions are weak. Thus, we find that when we plot the change in nematic-isotropic transition temperature in passing from C_7 to C_{10} against the average transition temperature for the four homologues, a straight line is given for a particular type of liquid crystalline compound (carboxylic acid, mono-anil, or di-anil), large decreases occurring at high temperatures and large increases at low temperatures.

The alternation of nematic-isotropic transition temperatures is less readily dealt with on the basis of a zig-zag alkyl chain conformation. If for shorter alkyl chains, this chain extends strictly along its own axis (dotted line in Fig. 3), then the terminal methyl groups present different faces to one another or to other end groups in the molecule depending on whether the chain is even or odd. The different attractive forces resulting could affect the energy of the system and account for an alternation of the transition temperatures. With the higher homologues, the alkyl chain may be forced (curved arrow in Fig. 3) into line with the main axis defined by the more rigid aromatic parts. The methyl-other end group contact would then gradually become the same in nature for odd and even

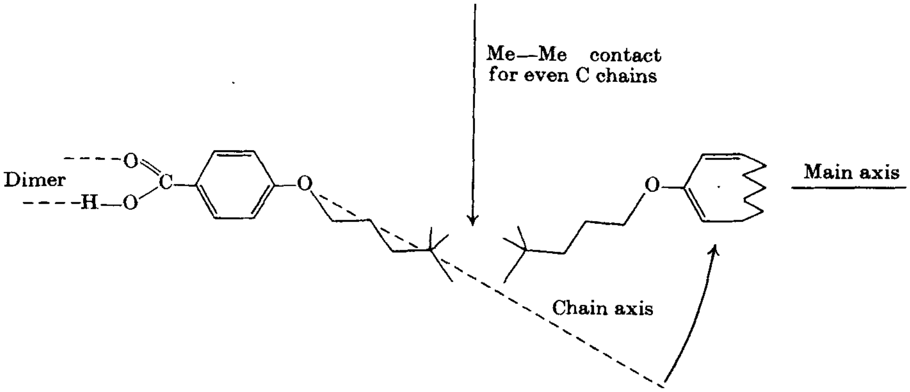


Figure 3. A diagrammatic representation of the possible relative orientation of terminal methyl groups in an end-to-end packing of the molecules of n-alkyl aryl ethers such as the *p*-n-alkoxybenzoic acids.

carbon chains, explaining the petering out of the alternation as the series is ascended.

Summarizing the situation, we may say that extending an alkyl chain affects:

Smectic thermal stability in two opposing ways,

(a) by enhancing primary lateral attractions
(b) by "softening" the layer surfaces
both effects applying irrespective of the system.

Nematic thermal stability by two pairs of opposing effects, of which three (2, 3, and 4) of the separate effects will differ in importance depending on the nature of the system.

Bearing these points in mind, if we therefore vary our terminal substituent by changing its type, e.g., as for the sets of substituents in Tables 3, 4 and 5, it is not suprising that different orders of group efficiency are found for the smectic and nematic states of the same system, and that differences in the details of the orders are observed for the nematic states of different systems.

Considering the nematic group efficiency orders in a general way, we can now appreciate that polarizable groups such as Ph, and polar groups such as CN, OMe, and NO_2 increase the length of the molecule and the extent of the polarizable parts of the system, and from both points of view would be expected to enhance the nematic thermal stability. Low in the efficiency order are substituents like fluoro- (small and of low polarizability), s-Pr (not highly polarizable and may broaden the molecule), and weakly polar alkyl groups and longer chain or branched alkoxy groups which do not make very effective contributions to the polarizability of the system. In the middle of the order lie the moderately polarizable halogeno-substituents (Cl and Br) and the group NMe_2, which appear to affect the length and polarizability of the system to an intermediate degree.

It is however clear that factors (1) and (2) above, i.e., the length and overall polarizability effects, are always important, because all the groups have raised the nematic-isotropic transition temperatures relative to the system having hydrogen in the terminal position.

The group $NHCOCH_3$ favours both the smectic and the nematic states, and it is possible that hydrogen bonding is of importance in this case in retaining the order in both states.

Most groups appear to enhance the smectic thermal stability, and this again can be considered in terms of the increased lateral attractions between the molecules, i.e., none of the substituents is long enough or low enough in polarizability to give the second effect of a long chain alkyl group, the "softening" effect on the layer surfaces. The order Br > Cl > F suggests the polarizability effects are important in this connection. Only NO_2 and OMe groups slightly diminish the smectic thermal stability relative to the parent compound. Indeed, this would suggest that certain orientations of dipoles can have a disadvantageous effect upon smectic thermal stability. Thus, the dipole moments associated with terminal nitro-groups are directed along the axis of the molecule. Moreover, these dipoles lie in line (Fig. 4) in the smectic state, and a net repulsive force may operate, reducing lateral attractions.

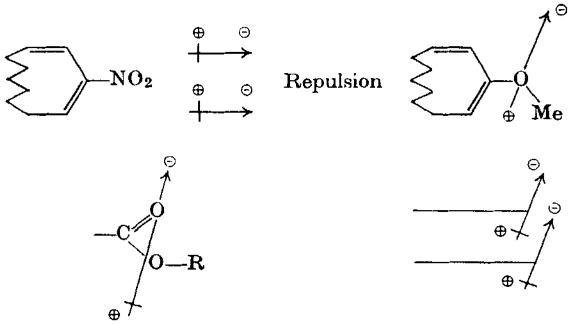


Figure 4. The orientation of the dipole moments for substituents such as $-NO_2$, $-OMe$ and $-CO_2R$ situated terminally in a molecule.

In the case of the OMe substituent, one normally considers that the C—O—Me dipole operates at an angle across a molecule in which the group is terminally situated. Whether such an orientation of dipoles will lead to attraction or repulsion in the smectic state will depend upon the exact dipole orientation and the angle of tilting of the molecules with respect to the layer interfaces. The effect must be quite critical, because groups such as CO_2R, terminally situated in an ester molecule, give a strong dipole moment directed across the long molecular axis, and yet these groups are strong promoters of smectic properties.

The situation regarding terminal substituents in liquid crystalline systems therefore requires further exploration by the study of a more extensive range of terminal substituents, and by the establishment of the group efficiency orders for more widely different systems. Of course, the relationships will be nothing more than empirical correlations until they are put onto some form of mathematical basis which relates the energy and entropy of the ordered liquid crystalline states to the various parameters which define the molecules. Unfortunately, the molecules of liquid crystalline compounds are fairly complex, and this represents a substantial problem in any attempt to relate molecular structure to liquid crystalline properties on anything more than a qualitative basis.

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