The Chemistry of Liquid Crystals

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The chemistry of liquid crystals

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The nature of the liquid crystal phases formed by different compounds and the thermal and other physical characteristics of these phases are strongly affected by the stereochemistry and structure of the molecules. Precise structure–property correlations of an embracing nature cannot yet be quantified, but even a qualitative understanding of such relations is desirable from many standpoints, including that of the achievement of still better liquid crystal materials for the ever widening range of applications that is emerging for these ordered but fluid systems. By means of a range of selected examples, an attempt is made to illustrate not only those areas where generalizations seem possible, but also others wherein the properties of the materials are much more difficult to understand, to such an extent that doubt must be cast on at least some theoretical concepts of the liquid crystal state.

Introduction

This paper is concerned with the way in which particular features of molecular structure have been found to influence the liquid crystal properties – the type(s) of liquid crystal phase and the liquid crystal transition temperatures – of a system. Considering liquid crystals in their broadest sense, this is a vast subject and it is necessary to begin by narrowing down our objectives, as shown in figure 1.

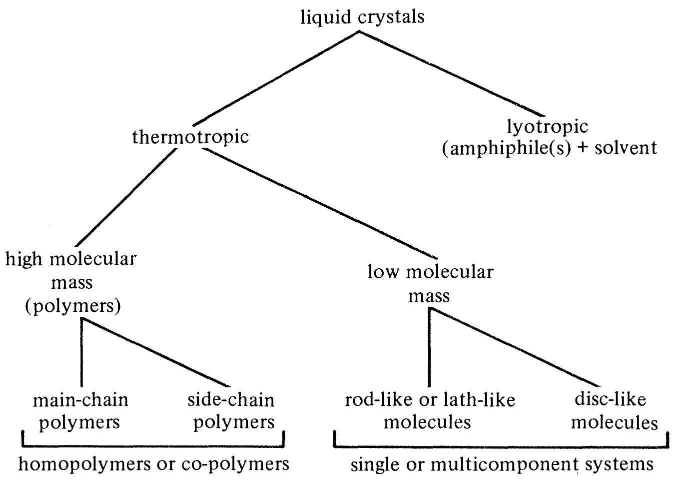


Figure 1. Subclassifications of liquid crystal systems.

With regard to figure 1, the following points should be made.

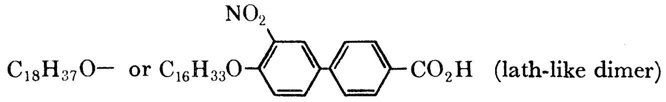
1. Lyotropic liquid crystal systems composed of amphiphilic compounds and solvent will not be considered further, and attention will be concentrated upon thermotropic systems that form their liquid crystal phases as a result of temperature change: heating or cooling.

2. Thermotropic liquid crystal systems may be of either high molecular mass (polymer

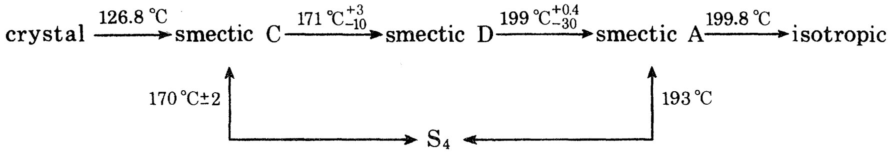
systems) or low molecular mass. Because the former are the subject of a subsequent presentation at this meeting, I shall deal here only with low molecular mass systems.

3. Low molecular mass liquid crystal systems may themselves be divided into those involving elongated, rod-like molecules and those involving disc-shaped molecules. It is my intention to deal only with the rod-like molecular systems, for the discotic systems are the subject of Professor Chandrasekhar's contribution to this symposium.

My theme will be to stress how very sensitive liquid crystal properties are to small perturbations of molecular structure, with the result that sweeping generalizations are simply not possible. The situation is certainly not quantifiable. We are in fact concerned with how well rod-shaped molecules are disposed to fit together into a smectic or nematic liquid crystal lattice, and our ability to comprehend exactly how molecular structure, shape, polarizability and flexibility influence such three-dimensional packing is, to say the least, limited.



Phase sequence for C_{16} homologue (Demus *et al.* 1978, 1980)



S_D, optically isotropic, viscous, cubic;
S_4, birefringent (discotic?) (Lydon 1981).

FIGURE 2. The phase behaviour of some smectic D materials.

Consider for example the rod-like molecules of the dimeric 4′-alkoxy-3′-nitrobiphenyl-4-carboxylic acids shown in figure 2. The elongated dimeric molecules appear to have exactly the right structure to form smectic or nematic thermotropic phases of the classical kind involving statistically parallel alignments of the rods. The C_{16} and C_{18} homologues do indeed form such phases, but injected between their ordinary S_C and S_A or isotropic phases lies an optically isotropic cubic phase or, alternatively, depending upon the experimental conditions relating to the heating–cooling cycles, a different phase (S_4), which could possibly be discotic in nature. Lydon (1981) has rather neatly tried to rationalize this apparently contradictory situation by proposing that the elongated dimeric molecules can, under suitable conditions of temperature, form disc-like aggregates that may then stack up to form columns. These columns may then either arrange themselves parallel to give a columnar discotic phase or form jointed rod structures, two of which, as pointed out by Luzzati & Spegt (1967) and Tardieu & Luzzati (1970), may interconnect to form a structure with overall cubic symmetry – a structure that would be compatible with the properties of the S_D phase (Tardieu & Billard 1976). This illustrates how judgements of phase behaviour based on an over-simplistic view of molecular structure and packing can be very misleading.

The unexpected discotic behaviour of diisobutylsilanediol (Bunning *et al.* 1980, 1982) provides another interesting example of this kind.

The above examples relate to major effects arising from the manner in which molecules pack together. If we consider that subtle features of molecular shape and packing may influence the subtleties of the phase behaviour of liquid crystals, the magnitude of the problem of establishing exact structure–phase correlations for thermotropic liquid crystal systems is realized.

ROD-LIKE MOLECULAR STRUCTURES

The importance of an elongated, rod-like molecular shape in relation to liquid crystal phases was clearly established early in the century. Some typical compounds that exhibit thermotropic liquid crystal phases are shown in figure 3.

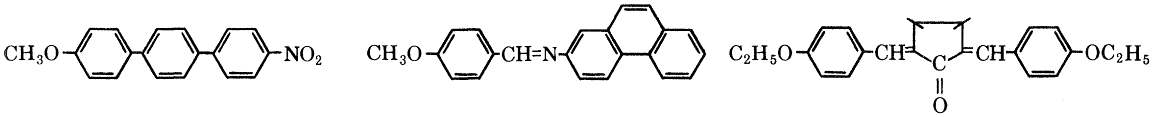


FIGURE 3. The structures of some typical compounds (nematogens) that form nematic phases.

The structural relation is very clear, for as can be seen from the formulae in figure 3, the molecules contain rings and double bonds, which help to prevent the molecules from adopting nonlinear conformations or configurations that would militate against the parallel packing of rods needed for formation of liquid crystal states. The concept of a rod-like molecular structure as a necessary requirement for the formation of liquid crystal phases has therefore become generally accepted and applies to smectic, nematic and cholesteric phases.

(*a*) *Smectic phases*. With the exception of the S_D phase, smectic phases are lamellar in nature. Smectic phases (in the plural) is written because we must remember the complexities that arise as a result of the polymorphism of smectic systems. Many structural variants of the smectic phase are known, dependent upon how the rod-like molecules are arranged in the smectic lamellae, the tilt angle of the rods with respect to the lamellar planes, and the degree of correlation of structure from layer to layer. Table 1 summarizes the state of current knowledge, showing the division of smectic systems into (1) liquid crystal smectic phases with no or low correlation of structure between layers, and (2) crystal type smectic phases with extensive interlayer correlations. Subdivisions within these categories depend upon molecular tilt and packing within the layers.

TABLE 1. SMECTIC POLYMORPHIC TYPES

liquid crystal smectics			*crystal-type smectics*		
no or low correlation of order between layers			long-range correlation of order between layers		
type	lamellar order	tilt	type	lamellar order	tilt
S_A	none	no	S_B	yes	no
S_B (hexatic)	yes	no	S_E	yes	no
S_C	none	yes	S_G; $S_{G'}$	yes	yes
S_F	yes	yes	S_H; $S_{H'}$	yes	yes
S_I	yes	yes			

(*b*) *Nematic phases*. Here we are involved with a simple non-lamellar, statistical parallel packing of rods.

(*c*) *Cholesteric phases*. These phases are simply spontaneously twisted nematic phases, the twist arising from the optically active nature of the chiral molecules, or alternatively from the

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chirality of suitable solutes dissolved in a nematic host. Cholesteric phases are therefore formed by nematogenic molecular systems that are optically active. Therefore from a structural standpoint, nematogenic and cholesterogenic compounds can be considered together.

The relative smectic–nematic tendencies of a compound

Even if we ignore the problems of smectic polymorphism, it is not easy to make more than general comments about the relative smectic–nematic tendencies that a compound may possess. The question is apparently a most basic one, but it is in fact very subtle, for we are attempting to judge features of molecular structure that influence not simply whether the molecules will pack with their long axes parallel, but whether they will do so in a manner such that their ends lie in planes, as distinct from an interdigitated nematic arrangement. This is clearly not a simple matter.

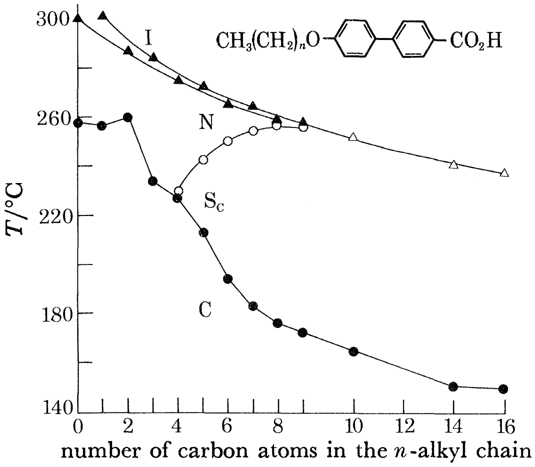


Figure 4. The transition temperatures and the sequence of liquid crystal phases exhibited as a function of chain length n, for a homologous series of carboxylic acids.

However, it did seem clear – at least until recently – that lengthening the alkyl chain of a terminal n-alkyl or n-alkoxy substituent did strongly promote smectic character through a mutual affinity of neighbouring alkyl chains. Numerous examples of this are known, and one showing the phase distribution in a homologous series is shown in figure 4. However, even this generalization is not completely true. Consider the bicyclohexyl compounds – members of the CCH series (Pohl *et al.* 1978) – of the structure shown in figure 5. For this series, smectic properties *decrease* as R increases in length, and as explained by Brownsey & Leadbetter (1981) a particular packing situation has been favoured by a propitious combination of the best anti-parallel correlation of the cyano groups for this alicyclic system and the similar sizes of the terminal groups. The behaviour can be comprehended, but it is doubtful that it could have been predicted.

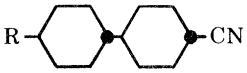


Figure 5. The general structure and an unusual pattern of behaviour for the bicyclohexyl compounds known as the CCH materials. Smectic properties diminish as R = alkyl increases in length.

SMECTIC SYSTEMS

The question now arises as to molecular structural features that may favour particular smectic types from the range of possible smectic polymorphic modifications. As yet no clear relations are obvious, perhaps not surprisingly because we are now attempting to relate molecular structure to detailed aspects of particular lamellar packings. We are in fact almost attempting to predict solid crystal structure from molecular structure, and we are all well aware that even the ascent of a homologous series of alkyl-substituted compounds can cause dramatic changes in *crystal* lattice type. Similarly the ascent of a homologous series of mesogens can cause most marked fluctuations in the types of smectic phase formed. This is therefore a very difficult area on which to comment at present, when even the addition or removal of one CH_2 group in a terminal chain can dramatically alter the smectic phase type(s) exhibited.

Only in smectic C phases have clear attempts been made to relate molecular structure to the tendency of the compound to give the tilted, disordered lamellar structure that this phase adopts. In line with structural studies made by de Jeu (1977), there is no doubt that terminal alkoxy groups in aromatic mesogens favour formation of tilted S_C phases rather than orthogonal S_A phases. Because alkyl analogues of such materials are often S_A in character, models relating the tendency of the molecules to tilt (with respect to the lamellar planes) to the existence in the molecules of terminal outboard dipoles associated with the alkoxy substituents have been proposed (McMillan 1973); the molecules may or may not also carry a lateral central dipole. However, it is known that certain esters (Goodby *et al.* 1977) containing no significant terminal dipoles and only a central dipole do form S_C phases. These S_C phases do admittedly persist until lower temperatures than those of the analogous esters with terminal alkoxy substituents, so there is no doubt that terminal outboard dipoles do *enhance* S_C character, but they do not appear to be *essential* to the formation of the phase. Allowance for all these observations and their consequences in relation to McMillan's theory of S_C phases have been made by Van der Meer & Vertogen (1979).

NEMATIC–CHOLESTERIC SYSTEMS

Until comparatively recently, most nematic–cholesteric materials studied in relation to the changes in phase transition temperatures brought about by change in molecular structure were aromatic in type, and these polarizable, rigid rings became regarded – wrongly as it emerges – as rather important to the formation of thermally stable liquid crystal phases. Through the study of such aromatic systems, certain ground rules were, however, established. These (Gray 1976) may perhaps usefully be summarized briefly here.

(*a*) *Some established structural relations for rod-shaped aromatic molecules*

(i) *Extension of the length of the rod-shaped molecule*

(1) *Addition of rings or multiple-bonded units to extend the rigid core of the molecule.* As can be seen from the examples given in figure 6, such extensions of the core structure result in significant increases in the nematic–isotropic liquid transition temperatures (T_{NI}).

(2) *Lengthening the terminal chain of an n-alkyl or n-alkoxy substituent.* The important point here is that although the effect on T_{NI} as the series is ascended varies from system to system (Gray 1962, 1976), the effects within a given homologous series are always regular. When the T_{NI} values are quite high, two falling T_{NI} curves may be drawn and reflect a regular, diminishing

alternation between odd and even members of the series. This common pattern of behaviour is evident in figure 4. This pattern changes, however, for systems exhibiting lower T_{NI} values. For example, for the well known series of PCH compounds (Eidenschink *et al.* 1977), the curves now rise, but the alternation effect is similar. Other systems can, however, show a combination of these two types, and this is found for the 4-*n*-alkyl-4′-cyanobiphenyls (Gray 1978), for which the initially falling T_{NI} values reach a minimum and then rise again. The alternation effect is again pronounced.

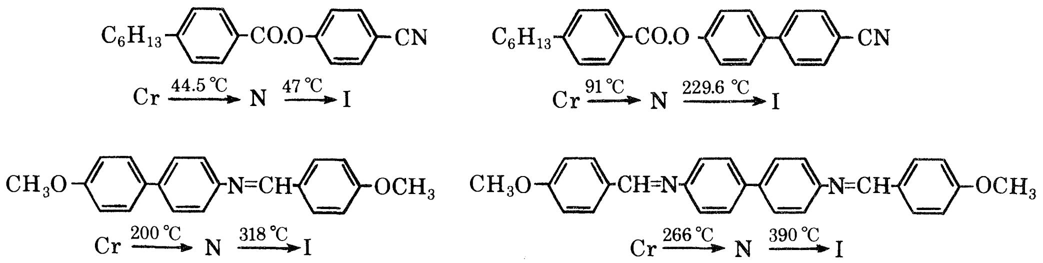


FIGURE 6. Data illustrating the enhancement of the nematic–isotropic liquid transition temperature (T_{NI}) associated with extending the core structure of a mesogen.

These results are not simple to interpret, and require (de Jeu *et al.* 1973) a combination of effects: the influence of the chain (odd or even) upon $\Delta\alpha$ (the anisotropy of the molecular polarizability) and the effect of temperature upon the molecular length:breadth ratio through its influence in causing deviations of the chain from an ideal all-*trans*, zig-zag conformation.

It is noted that a very striking effect arises (Gray & Harrison 1971 *a*, *b*) if the chain carries a bulky group such as phenyl at its end. Extremely large alternation effects (100–200°) occur, apparently as the ring moves on-axis and then off-axis for odd and even homologues.

(ii) *The effect of different terminal groups on* T_{NI}

A nematic terminal group efficiency order has been established for aromatic systems by their effects on T_{NI}: it is Ph > $NHCOCH_3$ > CN > OCH_3 > NO_2 > Cl > Br > $N(CH_3)_2$ > CH_3 > F > H. The high position occupied in the order by a terminal cyano group is noted, as is the higher position of alkoxy relative to alkyl. Any group is apparently superior to hydrogen in promoting T_{NI}. A different order exists for smectic phases.

(iii) *The effect of different linking groups in the core structure*

Figure 7 summarizes the order established for a number of different linking groups when these are used in molecules of the structure indicated. It is noted that a direct bond between the two benzene rings is the least effective linking unit.

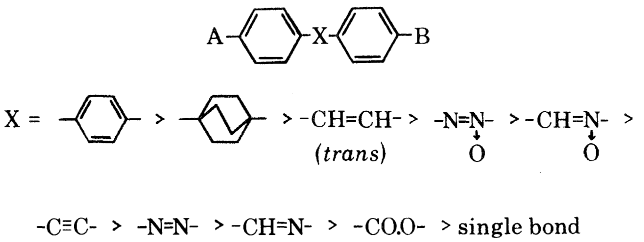


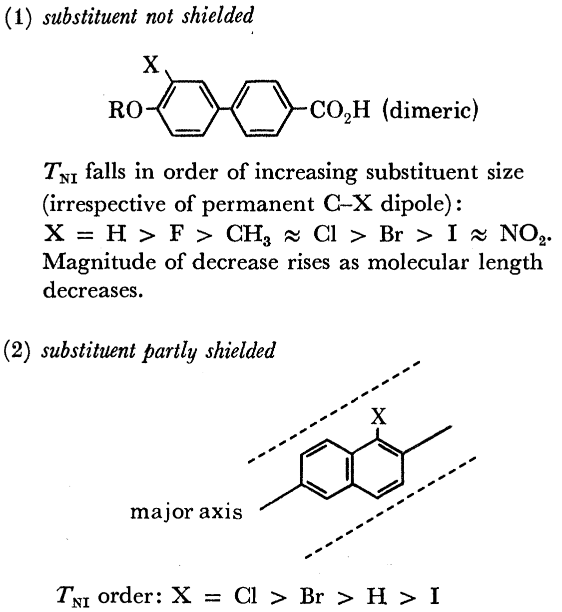
FIGURE 7. The relative effects of different linking groups between the aromatic rings in the core of the mesogen upon the nematic–isotropic liquid transition temperature (T_{NI}) (in order of decreasing T_{NI}).

(iv) *The effects of different lateral substituents in the core structure*

These effects were established by studies of acids of the structure shown in figure 8 (top).

The results are entirely consistent with maintaining a high molecular length:breadth ratio. The depressing effect of a lateral substituent (X) upon T_{NI} is proportionately related to the size of the substituent, and the permanent dipole of the ring–X bond is *not* a contributing factor. The T_{NI} depression is greatest for a given X if the molecule is short.

(1) *substituent not shielded*



T_{NI} falls in order of increasing substituent size (irrespective of permanent C–X dipole):
$X = H > F > CH_3 \approx Cl > Br > I \approx NO_2$.
Magnitude of decrease rises as molecular length decreases.

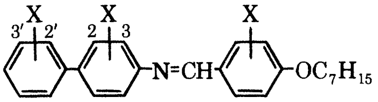
(2) *substituent partly shielded*

T_{NI} order: $X = Cl > Br > H > I$

FIGURE 8. A summary of the effects of different lateral substituents in the core of a mesogen upon the nematic–isotropic liquid transition temperature (T_{NI}).

TABLE 2. ENHANCED EFFECTS OF LATERAL SUBSTITUTION

(extra) molecular twisting (steric effect)



X	T_{NI}/°C	ΔT_{NI}(H → Cl)/°C	
H	163.5		
3Cl	96	67.5	
2′Cl	52	111.5	enhanced twist
2Cl	45	118.5	enhanced twist
3′Cl	smectic	—	

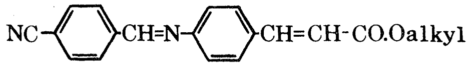
As would now be expected (figure 8, lower part), a lateral substituent that for some structural reason does not broaden a molecule, as in suitable derivatives of naphthalene, can enhance T_{NI}. This is consistent with the length:breadth ratio's being maintained, but with a more efficient occupancy of space between the parallel-packed rod-shaped molecules.

Special cases exist for systems in which the lateral substituent not only broadens the molecule but also exerts a twisting steric effect, or as in the Schiff bases shown in table 2, an extra twisting effect (the Schiff base linkage is itself not planar). The resulting increase in molecular thickness depresses T_{NI} very strongly. The much greater effect of the sterically twisting 2- and 2′-chloro substituents, relative to that of the 3-chloro substituent, is obvious.

(v) *The effects of branching of a terminal alkyl chain*

The effects are again well established (Gray & Harrison 1971*a*, *b*) for systems such as those shown in table 3. The branching methyl group diminishes in its depressing effect upon T_{NI} on being moved towards the free end of the chain, but the very large effect of the 1-methyl substituent implies that a steric effect may operate here. Because cholesteric compounds are often produced (Gray & McDonnell 1975) by using chiral alkyl groups, which are necessarily branched, such effects are clearly important to the molecular engineering of cholesterogens.

Table 3. Chain branching

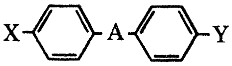


alkyl	T_{NI}/°C	comment
$—CH_2CH_2CH_2CH_2CH_3$	136.5	
$—\underset{\substack{\vert \\ CH_3}}{CH}CH_2CH_2CH_2CH_3$	< 20	large effect
$—CH_2\underset{\substack{\vert \\ CH_3}}{CH}CH_2CH_2CH_3$	112	gradual recovery
$—CH_2CH_2\underset{\substack{\vert \\ CH_3}}{CH}CH_2CH_3$	103	
$—CH_2CH_2CH_2\underset{\substack{\vert \\ CH_3}}{CH}CH_3$	119.5	

These, then, are some general effects established over the years for liquid crystal systems composed of aromatic molecules. Simple as some of the conclusions are, these rules have been applied usefully and they contributed to the discovery of the 4-alkyl- and 4-alkoxy-4′-cyanobiphenyls (Gray *et al.* 1973), which have been fundamental to the development of a liquid crystal display industry producing electro-optic displays of good quality and high lifetime capability. Table 4 shows how the rules were used. Central groups (A) such as $—CH{=}N—$, azo and azoxy were known to confer both colour and chemical–photochemical instability upon the compounds. Such groups were eliminated by directly linking the two rings, i.e. by a single bond. The depressing effect upon T_{NI} was countered by using for Y a group high in the nematic efficiency order, i.e. a cyano group (also needed for the strong positive dielectric anisotropy ($\Delta\epsilon$) needed for twisted nematic displays). The group X was chosen to be *n*-alkyl or *n*-alkoxy, and the resulting model systems were as formulated at the foot of table 4, and in several cases they represented the structures of compounds giving stable, colourless nematic phases at room temperature.

The interest aroused in these systems has resulted over the years in their very intensive study, and it has emerged that the high position of the cyano group in the T_{NI} efficiency order arises from the antiparallel association of the molecules. This was first demonstrated by Leadbetter *et al.* (1975), and occurs to minimize dipole–dipole repulsions between cyano groups. The situation for the biphenyls is shown in figure 9. For other cyano-substituted mesogens, the core overlap is only partial (PCH materials), and as already discussed, in the CCH systems, only the two atoms of the cyano groups are involved in the antiparallel overlap.

TABLE 4. DESIGN FOR A LOW-MELTING STABLE NEMATOGEN

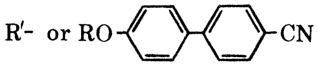


(1) For maximum stability, A = single bond.
Consequence: very low T_{NI}.

(2) Promote T_{NI} by using a group Y high in nematic terminal group efficiency order,

e.g. Y = CN.

(3) Use X = alkyl or alkoxy to promote nematic order and maintain low melting point; this also gives a selection of homologues.



$R' = C_5H_{11}$: $\mathrm{Cr} \xrightarrow{22\,^{\circ}\mathrm{C}} \mathrm{N} \xrightarrow{35\,^{\circ}\mathrm{C}} \mathrm{I}$

The thrust that the availability of the biphenyls gave to the display industry has naturally provided an incentive to produce alternative materials that might have modified properties that could be advantageous for other display forms. Of greatest significance in this respect has been the experimentation involving replacement of benzene rings by alicyclic rings.

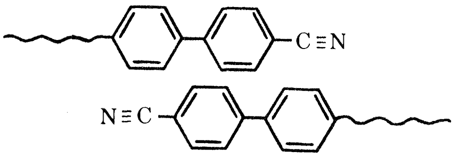


FIGURE 9. Antiparallel pairing or correlation of two molecules of a 4-alkyl-4′-cyanobiphenyl.

(*b*) *Nematogens containing alicyclic rings*

The first development in this area occurred through the work of Deutscher *et al.* (1977) who used the *trans*-1,4-disubstituted cyclohexane ring with its collinear but non-coaxial 1,4 bonds, substituting this for the benzene ring in the acid moiety of esters of the general structure shown at the bottom right of table 5. That is, ring A was changed from benzene (BZ) to cyclohexane (CH). This led to the development by Eidenschink *et al.* (1977) (Merck group, Darmstadt) of the cyclohexane analogues of the cyanobiphenyls: the *trans*-1-alkyl-4-(4′-cyanophenyl)cyclohexanes (the PCH series). Later, the 1,4-disubstituted bicyclo(2.2.2)octane ring was used by the Hull University group (Gray & Kelly 1980, 1981 *a*, *b*) in similar esters and cyanobicyclic systems to produce the compounds at the bottom of table 5, where ring A is bicyclooctane (BCO). The results in table 5 show that, for both types of system, T_{NI} falls from BCO to CH to BZ, i.e. the T_{NI} order is as shown at the top of figure 10.

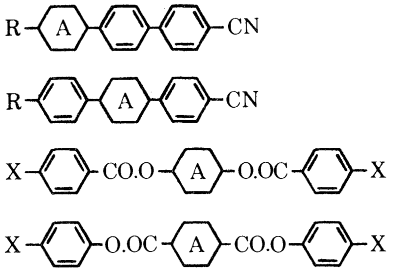
This order has been verified now for over 20 structurally different systems (Gray 1981; Carr *et al.* 1981), so that it applies widely, and not only to cyano compounds and simple esters.

However, for the cyano compounds shown at the foot of table 5, it has been demonstrated (D. A. Dunmur & A. E. Tomes, personal communication 1981; Ibrahim & Haase 1981) that the order of the anisotropy of the molecular polarizability ($\Delta\alpha$) is that shown in figure 10, and is not the same as the T_{NI} order.

T_{NI} order:
BCO > CH > BZ (20 systems)

order of $\Delta\alpha$:
BZ > BCO > CH (cyanobiphenyl type)

few exceptions (to T_{NI} order):



BCO > BZ > CH

BZ > BCO

BZ > BCO > CH

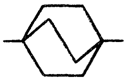
FIGURE 10. Data relating to the effects of cyclohexane and bicyclo(2.2.2)octane rings in the core structures of mesogens.

TABLE 5. USE OF ALICYCLIC RINGS

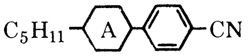
(1) *trans*-1,4-disubstituted cyclohexane

collinear
not coaxial

(2) 1,4-disubstituted bicyclo(2.2.2)octane



collinear
coaxial



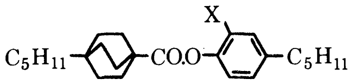
A	T_{NI}/°C	T_{NI}/°C
BCO	100	61.5
CH	55	48
BZ	35	26

We must therefore conclude that either the molecular interactions that determine T_{NI} are not solely a function of the anisotropic London dispersion forces, or the true significance of the London dispersion forces is not revealed by the experimental measurement of $\Delta\alpha$.

It is noted in figure 10 that some four exceptions to the general T_{NI} order are known. In the first, there is an inversion of the positions of BZ and CH; in the second, the position of CH is not clear, but BZ and BCO are inverted; in the last two, BZ rises above BCO > CH. The first may reflect differences in the extent of antiparallel overlap in the 'dimers' but, in the other three, $\Delta\alpha$ could be severely affected by the interruption of the extensive conjugated system that is possible when A = BZ.

Because the order BCO > CH > BZ cannot be explained in terms of $\Delta\alpha$ or antiparallel correlation effects,† it is proposed that ring flexibility may be of significance. The cyclohexane ring is flexible, and this may assist in the achievement of an energetically economical close packing of the molecules – superior to that when ring A = BZ, but minimized to some extent by the non-coaxiality of the 1,4 bonds and the possibility that over-flexing of the ring can cause the 1,4 bonds to depart from strict collinearity through the adoption of skewed or twisted ring conformations. The BCO ring is also quite flexible, involving a twisting, concertina-like movement about the 1,4 bonds. Coupled with the bulk of the BCO ring, this could assist in efficient close packing of the molecules and efficient filling of space, giving a stable nematic state. Note that, for the BCO ring, the above motion of the ring does not lead to any deviation from collinearity of the 1,4 bonds. It is possible then that the BCO ring gives a particularly favourable combination of strict collinearity of its 1,4 bonds and sufficient flexibility of the ring structure, so favouring the nematic potential for a phase composed of molecules containing the ring, except in the few exceptional cases mentioned above.

Table 6



X	T_{CN}/°C	T_{NI}/°C	Δε
H	31	64.5	−0.6
F	26	65	−0.95
Cl	35.5	41	—
Br	14.5	27	—
CN	27.5	29.5	−3.2

The BCO ring makes possible a wider range of structural possibilities.

It is interesting to record that the rules of thumb summarized earlier for aromatic nematogens can still be applied usefully for such systems. As shown in table 6, the bulk of the BCO ring shields the molecular broadening effect of 2-substituents in the phenolic moiety of the BCO esters of the structure shown (Gray & Kelly 1981*c*). Whereas a 2-fluoro substituent substantially decreases T_{NI} in the corresponding esters derived from the benzoic acids and cyclohexanoic acids, in BCO esters the effect is minimal, and T_{NI} may increase by up to 2 K for some homologues. Thus Δε can be made more negative without paying a significant penalty in T_{NI}. Larger groups such as 2-Cl, 2-Br and 2-CN *do* depress T_{NI}, but much less than in the benzoate and cyclohexanoate esters, so that such BCO esters still show enantiotropic nematic phases, with a strong negative Δε, particularly in the 2-cyano substituted BCO ester.

Such observations have led to the examination of other cycloaliphatic materials such as the cyclohexenyl compounds **1** and **2** in table 7. In compound **1** (Sato *et al.* 1979) the vinylic association of the double bond with the benzene ring promotes Δα (not incidentally considered to be unimportant, but just one factor in several), and this may contribute to the enhanced T_{NI} relative to the analogous PCH compound, **4**. In compound **2** (Osman & Revesz 1982) the stereochemistry of the molecule is adverse, and models show that an efficient close packing of molecules will not readily be achieved. Note that T_{NI} for compound **2** is monotropic, and this is conventionally indicated in parenthesis in table 7.

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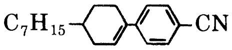
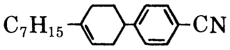
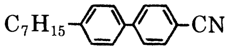
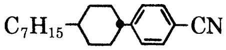
† PCH compounds and their BCO analogues are similarly antiparallel paired.

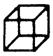
Table 7. Cyclohexene systems

1		$N \xrightarrow{61\ ^\circ C} I$
2		$(N \xrightarrow{5\ ^\circ C} I)$
3		$N \xrightarrow{42\ ^\circ C} I$
4		$N \xrightarrow{59\ ^\circ C} I$

(*c*) *Nematogens containing cubane rings*

Our own explorations of novel cycloaliphatic rings have included the cubane system, and, as will emerge, the results from this work reinforce the view that flexibility of rings and collinearity of bonds in the ring structures play a most significant role in determining T_{NI}. Although, as shown by the data in table 8, the dimensions of the cubane ring (strictly collinear 1,4 bonds) are in all ways intermediate between those of benzene and bicyclo(2.2.2)octane, the results shown in table 9 clearly illustrate (Gray *et al.* 1981) that replacement of a benzene or a cyclohexane or a bicyclooctane ring by a cubane ring in any system so far studied very markedly depresses T_{NI}. In fact, the cubane ring is a very bad unit to incorporate in the core structure of a mesogen.

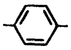
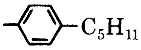
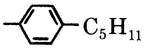
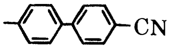
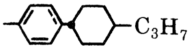
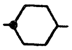
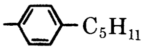
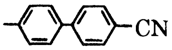
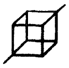
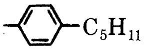
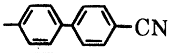
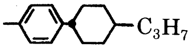
Table 8. Diameters of cylinder of rotation (ångströms)

	$C_1\cdots C_4$	$H\cdots H$ (width)	$C\cdots C$ (width)
	2.78	4.31	2.41
	2.68	4.59	2.53
	2.55	5.61	2.88

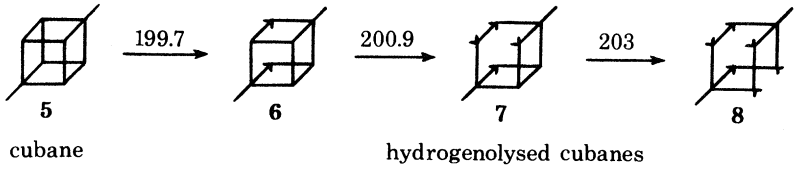
Cubane is always intermediate.

Table 9. C_3H_7-ring-CO.OY

(Examples from Gray *et al.* (1981).)

ring	Y	T_{CN}/°C	T_{NI}/°C
		14	20
		29	55
		142	289
		156	221
		32	(29)
		94	249
		51	[−60]
		107	171
		101	116

Measurements of $\Delta\alpha$ for cubanes have not yet been made, but calculations of strain energy reveal that the high strain energy of the ring (650.8 kJ mol^{-1}) means that the cubane system is highly rigid. This strain energy is relieved if bonds in the cubane system are cleaved by hydrogenolysis, and it is very interesting to see that if the right bonds are successively cleaved, as shown in figure 11, we progress from cubane (**5**), to the dihydrocubane (**6**), to the tetrahydrocubane (**7**) and eventually obtain the hexahydrocubane (**8**), which is none other than bicyclo(2.2.2)octane. The data given in figure 11 also show that the strain energy is relieved in roughly equal amounts in the steps involved. As stated earlier, this emphasizes that the BCO ring is low in strain energy (47.2 kJ mol^{-1}) and quite flexible, and that the dihydrocubane and tetrahydrocubane rings might represent better core units than cubane itself, although the 1,4 bonds in the dihydrocubane and tetrahydrocubane do now deviate somewhat from collinearity (22° for the dihydrocubane and 12° for the tetrahydrocubane system). A balance will therefore be involved between the two factors, increased flexibility raising and non-collinearity depressing T_{NI}.



structure **8** is equivalent to

bicyclo(2.2.2)octane

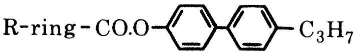
above each arrow is the relief in strain energy (kilojoules per mole) associated with the particular hydrogenolysis step

1,4-bond angles: dihydrocubane, 22°; tetrahydrocubane, 12°; cubane and BCO, 0°.

FIGURE 11. Hydrogenolysis of the cubane system in three steps yields the bicyclo(2.2.2)octane system with progressive relief in strain energy.

So far, only mesogens of the dihydrocubane system have been successfully prepared (K. J. Toyne *et al.*, unpublished results). Hydrogenolysis to the tetrahydrocubane ring has been successfully achieved, but rigid purification of an intermediate product required for the production of suitable mesogenic esters is still being carried out. However, as shown by the data in table 10, T_{NI} does increase on passing from a cubane ester to a dihydrocubane ester. Despite the nonlinearity of the bonds, therefore, the dihydrocubane ring is superior to cubane, and this could reflect the greater flexibility of the ring. Presumably this again gives a more efficient packing of the molecules with better space filling, resulting in stronger London dispersion forces than might be expected.

TABLE 10



R-ring-CO.O-C_6H_4-C_6H_4-C_3H_7

ring	T_{CN}/°C	T_{NI}/°C
cubane	110	118
dihydro	80	134
tetrahydro	?	?
BCO	131	232

As said earlier, it is felt that these results stress the need to take molecular flexibility and quite fine detail of stereochemistry into account, and it will be most interesting to see whether the tetrahydrocubane ring does in fact generate T_{NI} values intermediate between those of the dihydrocubane system and the known high values of the BCO analogues.

(*d*) *Other cases of interest*

In case the above discussion leads to the view that phase behaviour can readily be related to molecular structure, provided that thought be given to the situation, it is salutary to end with two examples that stress that we have still a great deal to learn.

(i) *Comparisons of some cyano-substituted bicyclic nematogens*

The cyano-substituted compounds under consideration here have the structures shown in figure 12 and the terminal substituent remote from the cyano group is in all cases an *n*-alkyl group with five carbon atoms, i.e. $n\text{-}C_5H_{11}$. The data include unpublished results by R. Eidenschink of E. Merck, Darmstadt, and D. Lacey and S. M. Kelly of Hull University.

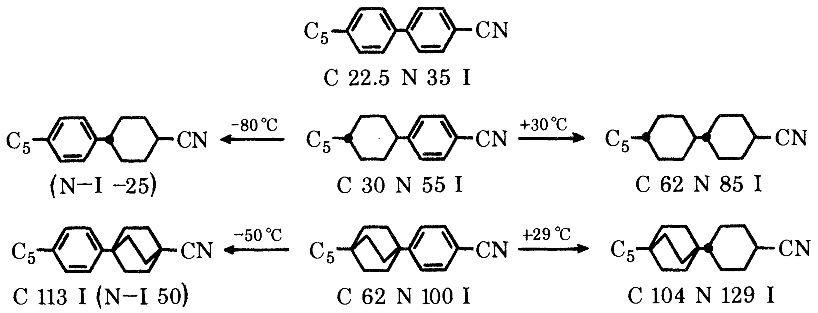


FIGURE 12. Structural variants of cyano-substituted bicyclic materials and the effects upon the nematic–isotropic liquid transition temperature (T_{NI}).

The three compounds in the central vertical block of figure 12 are the cyanobiphenyls, the PCH compounds and the corresponding BCO compounds, and the T_{NI} values show the normal increase on passing from BZ to CH to BCO. Moving to the right, we have the bicyclohexyl (CCH) and the bicyclooctylcyclohexyl analogues. The result of converting the ring carrying the cyano group from benzene to cyclohexane is a marked increase in T_{NI}. The effect could arise from the different antiparallel correlation situation in these alicyclic nitriles (only the cyano groups may be overlapped, giving a 'dimeric' situation). However, a similar situation could be argued for the compounds on the left side of figure 12 – also alicyclic nitriles – achieved by inverting the alicyclic ring and the aromatic ring in the appropriate compound in the central block. Now, however, the T_{NI} values are very low. Satisfactory explanations for these effects are difficult to find, but it is noted that:

(1) the isolated, unconjugated cyano group, with a strong localized dipole moment, is only well tolerated in the fully alicyclic systems;

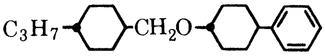
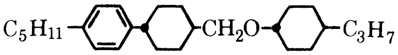
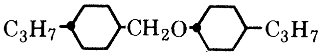
(2) the highest T_{NI} values arise when the molecule can be divided into one high and one low polarizability part. Conversely, a sequence of low, high, low then high polarizability units – as in the left-hand structures – is apparently unfavourable to a stable nematic order.

(ii) *Mesogens with aliphatic ether functions*

Evidence accumulated (Gray 1981) from a range of systems has shown that whereas an alkoxy function linked to an aromatic nucleus favours a high T_{NI} value, an alkoxy group linked to alkyl or cycloalkyl gives a very low T_{NI} value. These conclusions have stemmed from studies of ethers whose molecules carry additional aromatic rings, and the first two examples (Osman 1982) recorded in table 11 show the large depressions in T_{NI} when the $-CH_2O-$ function is substituted for $-CO.O-$. However, the purely aliphatic ether – the third compound in table 11 – has a much more respectable T_{NI} value relative to the ester (Osman 1982). Therefore the isolated, unconjugated, dipolar ether function appears to be best tolerated in a purely alicyclic system, and this reminds us of conclusion (1) in § (*d*) (i) above. It therefore seems possible that, in both instances, interactions between aromatic rings and localized dipoles in neighbouring molecules may result either in repulsive interactions or in attractive forces that favour a non-ideal alignment for the formation of a nematic phase; in either case, the result is a lowering of the resistance of the nematic phase to the disaligning effects of increasing temperature.

TABLE 11

(Osman (1982).)

	T_{NI}/°C	T_{NI}(ester)/°C	ΔT/°C
	(22)	(69.5)	−47.5
	87.7	177.3	−89.6
	17.5	36.6	−19.1

The purely alicyclic ether tolerates satC–O–satC quite well:
compare satC–CN link in CCHs and BCOCHs.

CONCLUSIONS

Whatever the true explanations may be for some of the unusual effects described above, it is clear that studies of alicyclic mesogens have in recent years revealed a range of new factors that need to be taken into account when assessing the effects of molecular structural change upon liquid crystal transition temperatures, and theory must now move to accommodate the new facts.

The author wishes to express his gratitude to members (past and present) of his research group on whose work he has drawn for the purposes of this article. The names over the years would be many, but particular thanks for the more recent results quoted are due to Dr K. J. Toyne, Dr D. Lacey, Mr N. Carr and Mr S. M. Kelly.

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