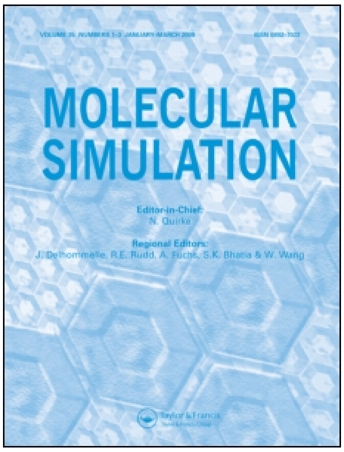

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Structure-Property Relationships in Liquid Crystals: Can Modelling do Better than Empiricism?

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STRUCTURE-PROPERTY RELATIONSHIPS IN LIQUID CRYSTALS: CAN MODELLING DO BETTER THAN EMPIRICISM?

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This paper reviews the relationships observed experimentally between the physical properties of liquid crystals and the molecular structures of the constituent molecules, and reports molecular mechanics calculations designed to provide a predictive and interpretative basis for structure/property relationships in liquid crystals. The calculations are of the minimum energy configurations of dimers of interacting liquid crystal molecules, and the geometry of the dimers, relative orientation of molecular dipoles and the extent of parallel correlation are related to liquid crystal properties. A large number of structural types are examined and the results discussed in terms of dipole correlation, apolar angular correlation, chiral twist sense and transition temperatures of liquid crystals.

KEY WORDS: Structure-property relations, liquid crystals, molecular mechanics

1. INTRODUCTION

Liquid crystals are thermodynamically stable phases that exist between the solid crystalline and isotropic liquid states, they are consequently sometimes known as mesophases and molecules that form such phases are called mesogens. A number of different liquid crystal phases of different symmetries have been discovered [1], but all are characterised by partial orientational order and positional disorder of constituent molecules. The existence of orientational order means that the molecules themselves must be anisometric (usually prolate or oblate), and liquid crystal phases have anisotropic dielectric, optical, elastic and transport properties. Disorder in the positions of molecules is dynamic, so that liquid crystal phases are fluid, but viscosities and other properties depend on the degree of translational order. The simplest liquid crystal phase is the nematic in which the orientations of molecules are partially ordered, but there is a complete absence of long range positional order. Smectic phases [2] have translational order in one direction and are layered structures, while columnar liquid crystal phases [3] are translationally ordered in two directions, with molecular positions disordered along the third direction. The structures of some basic liquid crystal phase types are illustrated in figure 1. If the molecules are chiral, i.e. they possess a left or right handedness, then orientationally ordered phases can develop a macroscopic helical structure. The pitch of the helix depends on the molecular species, but is of the order of 100 nm.

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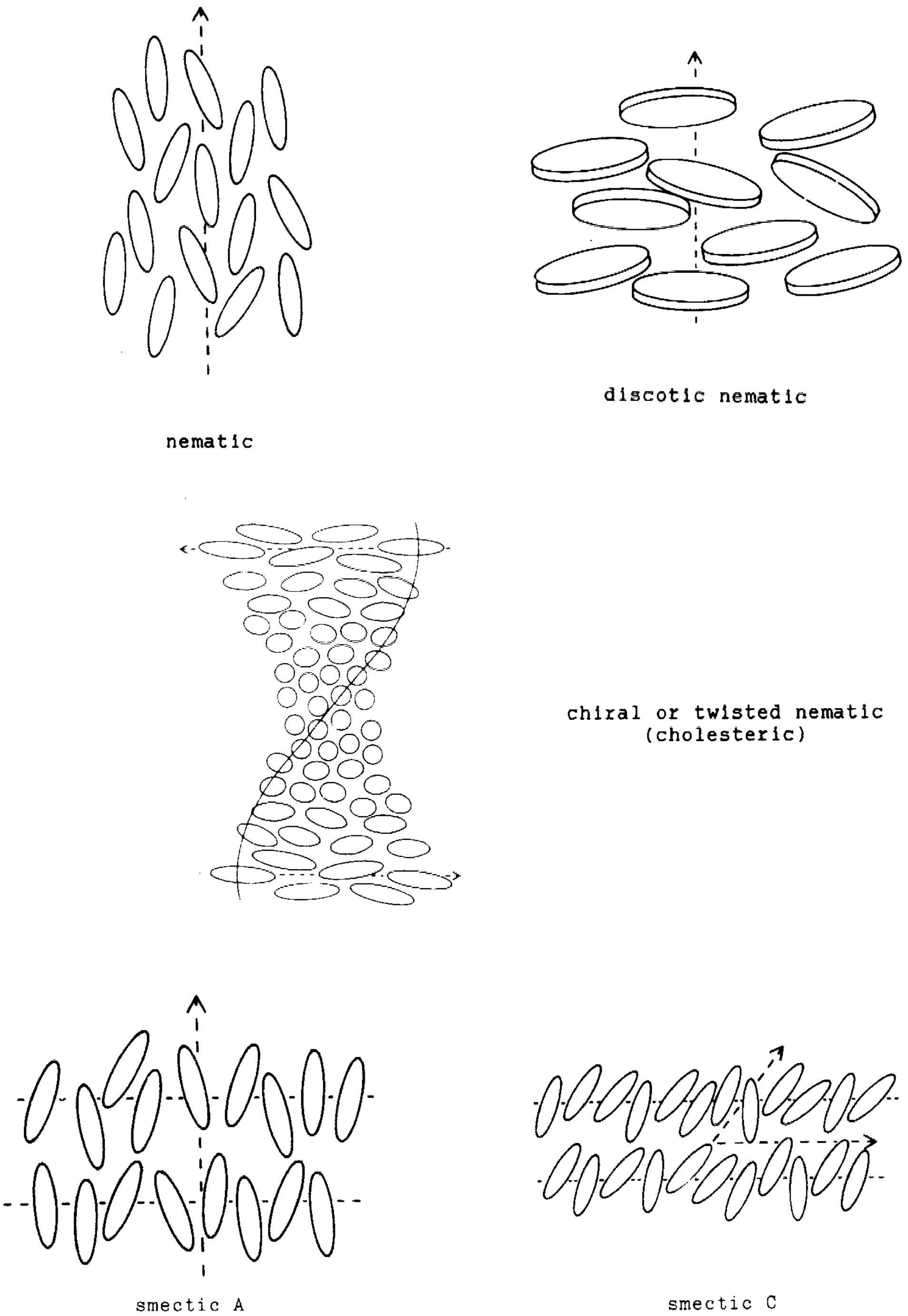


Figure 1 Liquid crystal phase types.

When crystals of a mesogenic compound are heated, they melt to a liquid crystal phase. Most of the crystal stabilisation energy is absorbed at the melting point, and the enthalpy changes associated with liquid crystal/liquid crystal or liquid crystal/isotropic liquid phase transitions are small. For example the nematic/isotropic transitional enthalpy is of the order of 1 $\mathrm{kJmol^{-1}}$, which is about 10 times less than the latent heat of fusion. From a theoretical point of view the small stabilisation energy of liquid crystal phases has advantages and disadvantages. The liquid crystal phase can be regarded as a perturbation of the liquid state, and by focussing on exclusively liquid crystalline properties, simple mean field theories provide a fairly successful description of some aspects of liquid crystal behaviour [4]. More sophisticated van der Waals theories have also been developed [5]. The anisotropic electric permittivity, magnetic susceptibility and birefringence can also be reasonably explained using mean field theory [6]. In fact for any physical property that is proportional to the molecular number density, i.e. a single particle property, mean field theory works reasonably well. For those phenomena that depend directly on molecular interactions, such as elastic properties, transport properties and dipole-dipole correlation, mean field theories fail. A problem which results from the small stabilisation energy of liquid crystals is that small changes in the molecular structure and hence molecular interactions of mesogens can dramatically affect the thermodynamic stability of the liquid crystal phases, and can change the phase structure and transition temperatures. Subtle changes in structure may also have a drastic influence on some physical properties.

In the past 15 years much of the stimulus for research into liquid crystal materials has come from the demands of the liquid crystal display industry [7]. The operation of various types of liquid crystal devices depends critically on the physical properties of the materials, and much research has gone into the preparation of liquid crystals with closely defined physical properties. As has been pointed out, this is not such an easy task. Engineering molecules with particular structures is fairly straightforward, but the prediction of the resultant liquid crystal properties is much more difficult. Accumulation of data on many compounds has enabled some empirical rules to be established which relate liquid crystal behaviour to molecular structure. The fact that these work suggests that appropriate theoretical models can be formulated which should do at least as well as the empirical rules.

This paper is concerned with the problem of describing the detailed influences of molecular structure on liquid crystal properties. To take account of all aspects of the structure and short range interactions requires a very detailed potential energy function and this can be provided by the empirical force fields developed for molecular mechanics calculations [8]. The complexity of the potential means that only interactions between small numbers of molecules can be considered (two in this work), but this must be better than trying to relate liquid crystal behaviour to the structures of isolated molecules. It is hoped that a consequence of this work will be the formulation of real intermolecular potentials which can be used in more extensive calculations of the properties of liquid crystal phases. Simulations of liquid crystals based on hard particle interactions [9], molecules on a lattice [10] or molecules interacting with simple model potentials [11] have been made and are providing a better understanding of the broad features of liquid crystal phase stability. However these methods will not be able to explain the details of liquid crystal behaviour without much more complex potentials which accurately model the details of molecular structure. Modelling is also important in simulating various macroscopic phenomena in liquid crystals. The static and dynamic [12] electro-optical properties of liquid crystals can only be described by simulation methods, the parameters of which are values for components of the permittivity tensor and viscoelastic tensors and the principal refractive indices. These are only available from measurements at present, but ultimately should be capable of prediction from the techniques to be described in this work.

The structure of the paper is as follows. In the next section we will outline some of the structure property relationships that have been established for liquid crystals. Our application of the molecular mechanics method to the calculation of interactions between molecules will be described in section 3, and in section 4 we give the results for a number of model mesogens.

2. MESOPHASE PROPERTIES AND MOLECULAR STRUCTURE

The most desired objective in establishing structure/property relationships in liquid crystals is to be able to predict the type of mesophase and the corresponding transition temperatures from the molecular structure. The difficulty of achieving this has not deterred attempts, and a number of general rules have been formulated, at least for nematic and some smectic phases. Normally the criterion for mesophase stability is the transition temperature to the isotropic liquid, T_{NI} for nematics and T_{SI} for smetics. This has some justification since the energy parameter in Maier-Saupe mean field theory [4] is proportional to T_{NI}. However a material with a potentially high T_{NI} or T_{SI} may not be liquid crystalline if the crystal melting point is higher, so melting occurs directly from the crystal to the isotropic liquid; in such circumstances a metastable liquid crystal phase may be revealed by supercooling a liquid phase. The thermodynamic stability of a mesophase depends on both the liquid crystal transition temperature and the crystal melting point: empirical structure/property correlations address the former, but we have very little information about the latter. For the purposes of discussing the effect of molecular structure on liquid crystal properties, it is necessary to introduce an archetypal mesogenic structure, see figure 2. The effect of varying the nature of the ring system, the linking group or terminal group on the nematic phase stability can be summarised by [13, 14, 15]:

Ring systems

Bicyclo-octane > cyclo-hexane > benzene

Linking groups

$-CH{=}CH- > -CH{=}N(O)- > -C{\equiv}C- > -N{=}N- > -CH{=}N- > -COO- > -$

Terminal groups

$-NHCOCH_3 > -CN > -OCH_3 > -NO_2 > -Cl > -H$

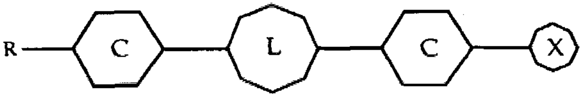


Figure 2 Schematic structure of a liquid crystal molecule C = ring system, L = linking group, X = terminal substituent, R = terminal alkyl or alkoxy chain.

A major effect of terminal alkyl or alkyoxy chains is to lower the crystal melting point; the length of the chain also influences the mesophase transition temperature, but not always in the same way. It is usually observed that increasing the chain length will enhance the stability of smectic phases with respect to nematic phases, except that the reverse happens with alkyl bicyclohexyl-nitriles. The number of carbon atoms (odd or even) is usually reflected by the mesophase transition temperatures, which exhibit an alternation with the number of carbon atoms. This so-called "odd-even" effect is observed for a number of properties, and a theoretical model has been introduced [16, 17] to explain it. Although attempts have been made to explain the relative stability of different smectic phases in terms of molecular structure [18], there are many exceptions, and the rules are not sufficiently well-established to justify model calculations.

The electric permittivity is approximately a single particle property, and the dielectric anisotropy $\Delta\varepsilon$ increases with molecular dipole moment μ according to:

$$\Delta\varepsilon = \frac{\mathrm{NLFS}}{\varepsilon_o}\left[\Delta\alpha - \frac{F\mu^2}{2kT}(1 - 3\cos^2\beta)\right] \tag{1}$$

where N is the number density and L and F are internal cavity and reaction field factors. $\Delta\alpha$ is the polarisability anisotropy, $S = 1/2\langle 3\cos^2\theta - 1\rangle$ is the orientational order parameter [θ is the angle between a molecular long axis and the average orientation direction of the molecules], and β is the angle between the dipole moment direction and the molecular long axis; varying the angle β can change the sign of the dielectric anisotropy. For many polar liquid crystals local dipole-dipole correlation is also important in determining the dielectric properties and their temperature dependence. Thus predominantly anti-parallel dipole association reduces the permittivity anisotropy and mean permittivity, and their dependence on temperature. Parallel dipole association has also been detected [19] and is important in ferroelectric liquid crystal phases. Both parallel and anti-parallel dipole correlation result from short range interactions between molecules, and are critically dependent on details of molecular structure. Local dipole correlation can be quantified by measurements of the Kirkwood correlation factor defined as:

$$g_1 = 1 + \sum_{i \neq j} \langle P_1(\cos\theta_{ij})\rangle \tag{2}$$

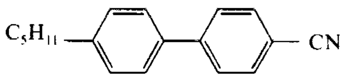
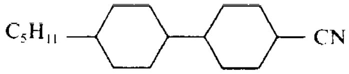
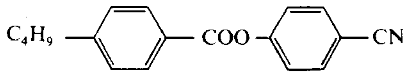
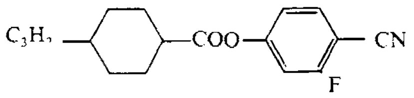
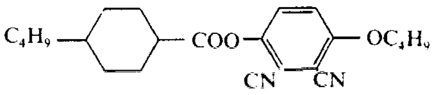
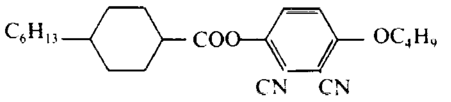
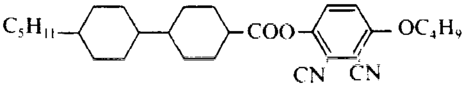
θ_{ij} is the angle between molecular dipoles on molecules i and j; $g_1 < 1$ indicates anti-parallel or anti-ferroelectric dipole ordering, while $g_1 > 1$ results from local ferroelectric or parallel dipole ordering. Some typical values of g_1 measured for mesogens of different structures are listed in Table 1. Those molecules with strongly dipolar groups co-linear with the molecular alignment axis have $g_1 < 1$, and this can be explained by dimer formation [20]. The dimers do not have any chemical integrity, but represent an average short range structure for interacting molecules.

Kirkwood's dipole correlation factor is a measure of short range polar order, but it is useful to introduce a quantity which measures apolar short range orientational order. This is the quantity g_2, defined by:

$$g_2 = 1 + \sum_{i \neq j} \langle P_2(\cos\theta_{ij})\rangle \tag{3}$$

g_2 can be measured by light scattering [21, 22] or less directly through the Kerr electro-optic effect [23]. Calculations of g_2 from theory [24] or computer simulation

Table 1 Dipole correlation factors for different mesogens

mesogen	$g_I(T_{NI})$
	0.5(35°C)
	0.6(88°C)
	0.7(42°C)
	1.3(18°C)
	3.9(76°C)
	3.3(88°C)
	1.8(150°C)

$g_I < 1.0$ = anti-parallel dipole order
$g_I > 1.0$ = parallel dipole order

[25, 9] are useful in showing the growth of short range orientational order, which becomes long range at a liquid crystal phase transition.

A characteristic of all liquid crystals is their ability to transmit a torque i.e. they have non-zero torsional elastic constants. For the nematic phase there are three elastic constants, which measure the energy associated with splay (k_{11}), twist(k_{22}) and bend (k_{33}) elastic strains. These are illustrated in figure 3. As defined the elastic constants are macroscopic quantities, but for small strains they can be related to angular derivatives of an intermolecular potential function or distribution function [26]; in fact elastic constants provide a very direct measure of the angular dependence of intermolecular forces. The relationship between elastic constants and molecular structure is an outstanding problem in the field of liquid crystals. To a first approximation the elastic constants depend on the square of the order parameter, emphasising the two particle nature of elastic properties. Saupe, Nehring and Gruler [27, 28] using mean field theory proposed that:

$$k_{ii} = C_{ii}S^2 / V_m^{7/3} \tag{4}$$

where C_{ii} is a molecular parameter including short range interactions, and V_m is the molar volume. For anisotropic dispersion forces between spherical particles, Saupe

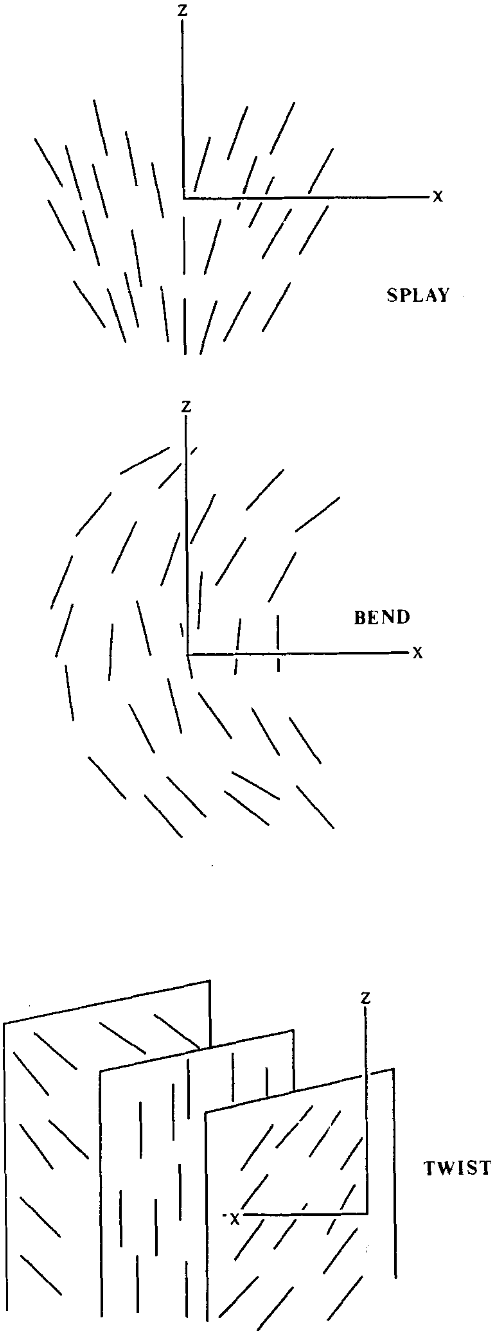


Figure 3 Representation of splay, twist and bend elastic deformations in a nematic liquid crystal.

and Nehring predicted that $k_{11}: k_{22}: k_{33}$ are in the proportions 5:11:5. Unfortunately this is not borne out by experiments, which find the relative size of elastic constants to be $k_{33} > k_{11} > k_{22}$. Molecular shape has been included in models proposed by Priest [29] and others [26, 30, 31], and the general conclusion is that k_{33}/k_{11} should be an increasing function of the molecular length:width ratio (L/W). Even this is not confirmed by experiment, since k_{33}/k_{11} often decreases with increasing alkyl chain length in a homologous series, while k_{33}/k_{11} has no systematic dependence on molecular structure when different homologous series are compared. A detailed study [32] of mesogens containing a double bond in the terminal alkyl chain showed that the position of the double bond influenced k_{33}, but did not affect the van der Waals volume nor L/W of the molecule. More recent work on related systems [33] has shown that a correlation can be established between k_{33}/k_{11} and the length:width ratio of equilibrium ensembles of 12 molecules. The latter have been determined using molecular mechanics calculations on molecular clusters. Although the method to be described in this paper should be applicable to the calculation of elastic properties, we have not yet attempted this.

A feature of chiral nematics is the formation of a helical structure perpendicular to the average alignment direction. The sense (left or right) and pitch of the helix is determined by the molecular structure of the chiral mesogen and the intermolecular interactions. However there is no general relation between the sign and size of the molecular optical rotation, as measured in solution or in the isotropic liquid phase, and the pitch sense and pitch length of the helix. Observations by Gray and McDonnell [34] established a relationship between the location of a chiral centre in a terminal alkyl chain and the sense of the helix in the chiral nematic phase. It was found that the sense of the helix alternates as the chiral centre is moved along the alkyl chain. Furthermore changing the absolute configuration of the chiral centre resulted in a change of sign of the pitch sense. If the chiral nematic forms a tilted smectic phase on cooling, either directly or through an intermediate smectic A phase, then the tilt direction describes a helix in the smectic phase having the same sense as in the chiral nematic phase. Additionally symmetry constraints now require that there is a component of the dipole moment normal to the tilt direction and in the plane of the smectic layer. In a twisted structure the direction of this net dipole moment rotates

Table 2 The effect of absolute configuration, position of chiral centre and the sign of the inductive effect at the chiral centre on the sign of optical rotation and the direction of spontaneous polarization in chiral smectic C liquid crystals.

absolute configuration	*position of chiral centre*	*sign of inductive effect*	*sign of optical rotation*	*direction of spontaneous polarization*
S	o	+I	(−)	P_s (+)
S	e	+I	(+)	P_s (−)
R	o	+I	(+)	P_s (−)
R	e	+I	(−)	P_s (+)
S	o	−I	(+)	P_s (−)
S	e	−I	(−)	P_s (+)
R	o	−I	(−)	P_s (+)
R	e	−I	(+)	P_s (−)

o = chiral centre removed from the core by an odd number of carbons,
e = chiral centre removed from the core by an even number of carbons,
+I and −I indicate positive and negative inductive effects at the chiral centre.

with the helix, but if the helix is unwound by external forces a macroscopic ferroelectric polarisation develops. This phenomenon is the basis of fast-switched chiral smectic C displays that are currently under development. Once more the magnitude of the ferroelectric polarisation and its direction with respect to the tilt direction and layer normal depend on the molecular structure. Investigations by Goodby and others [35, 36] showed that the direction of spontaneous polarisation was linked to the twist sense of the helix. If the inductive nature of a group or atom attached to the chiral centre is changed, then there is an opposite relation between pitch sense and the direction of spontaneous polarisation. These rules are summarised in Table 2 adapted from Goodby [37]. It must be pointed out that some doubts have been raised [38, 39] concerning the validity of these rules, since materials have been discovered for which the sign of the spontaneous polarisation changes with temperature. Such behaviour cannot be rationalised from the rules in Table 2.

3. APPLICATION OF MOLECULAR MECHANICS TO THE CALCULATION OF LIQUID CRYSTAL PROPERTIES

Molecular mechanics has become established as a useful tool for determining the structures of complex molecules. The method has been well-described [40]; basically it consists of formulating a potential energy function for the molecule which models bond stretches, bond bends, torsional energy, non-bonded and electrostatic interactions. The total energy of the system of interacting atoms is then minimised by varying the internal geometry. This minimum steric energy is the difference between the energy of the minimised geometry and the hypothetical structure which has all the bond lengths, bond angles, torsion etc. at their equilibrium values. It has no absolute significance, but it is useful as a basis for comparing the relative stability of different structures. There is considerable choice of functional form for the potential and potential parameters: we have used the MM2 potential [41], which has been widely used for modelling the structures of small organic molecules, to model the internal structure of mesogenic molecules.

Since in this work we are interested in calculating intermolecular interactions, the molecular mechanics method has been extended to calculate the minimum energy of clusters of non-bonded molecules. In order to provide some basis for the empirical structure/property relationships discussed above, the intermolecular potential must take account of the detailed molecular geometry of the interacting molecules i.e. their shape, molecular volume and length:width ratio. The effects of different groups and their location in the mesogen requires that the chemical identities of constituent atoms or groups of atoms must be recognised in the intermolecular potential. To model effects attributable to dipole–dipole interactions, the potential must also include terms to describe electrostatic and induction forces. We have used a Lennard-Jones 12–6 potential to model van der Waals interactions between atoms on different molecules, together with a coulombic term to take account of electrostatic intermolecular forces. For molecules with less than 50 atoms, partial atomic charges were obtained from *ab initio* calculations using the program GAMESS, employing a minimal basis set (STO-3G). Semi-empirical calculations (CNDO, INDO, MNDO and MINDO) were carried out for molecules with more than 50 atoms. These different methods of calculation do produce slightly different partial charge distributions. To investigate the effect on our results of changing the partial charges, we carried out the dimer minimisation with different sets of partial charges. We found that there was a negligible effect on the minimum energy configurations of the dimers; the energy differences between parallel and anti-parallel configurations changed slightly, but not enough to affect our conclusions. An induction force term was not included, as simulations on proteins and other molecules [42] have suggested that dipole-induced dipole contributions can be assimilated into the parameter of the L-J r^{-6} term. The van der Waals parameters of our intermolecular potential function have been taken from the work of Jorgensen [43], who has simulated a number of liquids comprised of small organic molecules. To cut down on the number of interacting atom pairs we have used the extended atom approximation, which replaces hydrogen atoms by an "extended" atom to which they are attached. Clearly this model cannot take account of hydrogen-bonded interactions, but we assume that these are unimportant for most thermotropic liquid crystals. The intermolecular potential used in our calculations is given below:

$$E = \sum_a \sum_b \left[\frac{A_{ab}}{r_{ab}^{12}} - \frac{C_{a.b}}{r_{ab}^{6}} + \frac{q_a q_b}{4\pi\varepsilon_0 r_{ab}} \right] \tag{5}$$

where *a* refers to atoms on molecule *i* and *b* refers to atoms on molecule *j*. In order to calculate the minimum energy configuration of interacting pairs of mesogens, the internal structure was fixed at that determined by MM2, and the pair energy was minimised using the program (LMIN) written at Sheffield [44]. Attempts to use MM2 to model pairs of interacting molecules without constraints on the internal molecular geometry were unsuccessful [45], but the more versatile packages such as AMBER [51] should allow internal flexibility to be included in the calculations. To find the lowest energy minimum, molecules were given a number of different starting positions (typically 120), and in each calculation the molecules were moved along the maximum potential energy gradient until an energy minimum was found. From the results of 120 calculations the global minimum for the two molecules was determined. Calculations on pairs of molecules cannot be used to make predictions of the bulk properties of liquid crystals, but the liquid crystal environment of interacting molecular pairs can be simulated by an average potential of suitable symmetry. In principle the symmetry of a nematic, smectic or chiral liquid crystal environment can be modelled by a suitable choice of potential. In the work reported here we have modelled a nematic environment using a potential of the form:

$$E_{nem} = -\sum_i b(3\cos^2\theta_i - 1) \tag{6}$$

where θ_i is the angle between a molecular axis and the uniaxial symmetry axis of the nematic, known as the director. The molecular axis is usually selected to be the "long" axis for rod-like molecules or the "short" axis for disc-like molecules. These terms only have precise definitions for moelcules with uniaxial symmetry: for most molecules the long or short axes are selected through consideration of molecular geometry. In our calculations the molecular axis is a direction parallel to the bond linking the rings of the rigid core. The parameter b in the nematic potential is adjustable, so that the effects of a variable ordering potential on the configuration of molecular pairs can be observed. Finally for ease of computation we have fixed the director to be along the axis of one of the molecules of a pair.

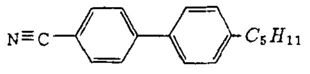
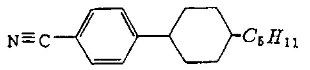
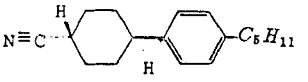
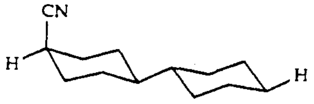
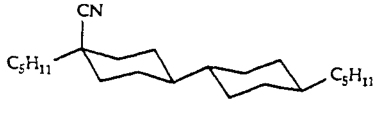
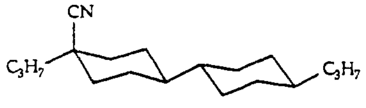
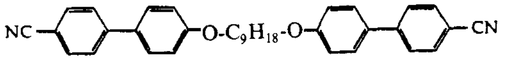
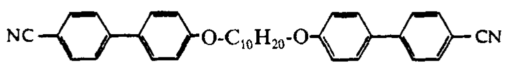
4. RESULTS AND DISCUSSION

Some preliminary results of applying molecular mechanics to the interpretation of structure/property relationships in liquid crystals have already been presented [45]. In this paper we extend the calculations to a number of new systems, and some different aspects of liquid crystal behaviour.

(i) Dipole Association

Calculations on dimers of CCH5 and CB5 (see Table 3 for structures and acronyms) have already been reported [45], and they confirmed the preference for antiparallel association of these mesogens already detected experimentally. The strength of as-

Table 3 Structures and acronyms of some anisotropic cyano-compounds

acronym	*structure*
CB5	
CCH5	
PCH5	
revPCH5	
ACCHNC	
CCN55	
CCN33	
BCBO9	
BCBO10	

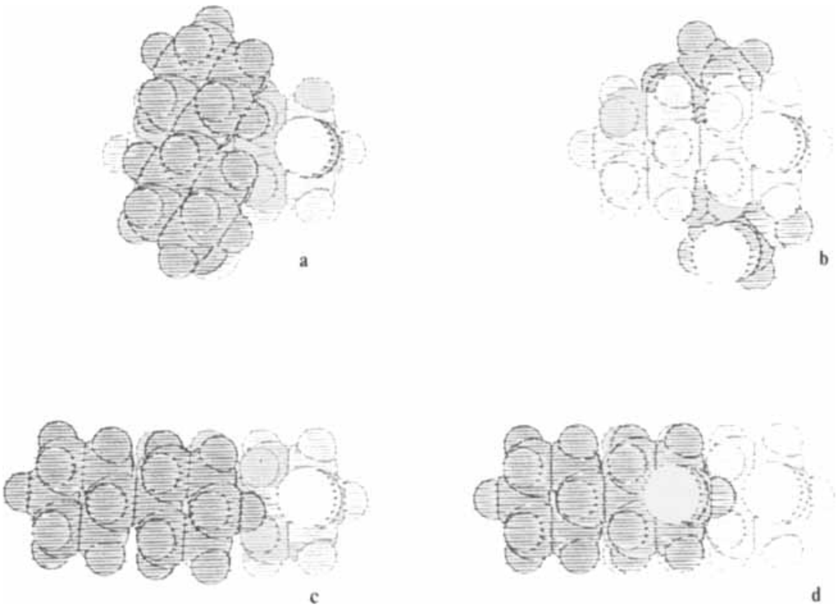


Figure 4 Dimers of ACCHNC a) lowest energy antiparallel dimer, potential energy = − 43.01 kJ/mol. b) lowest energy parallel dimer, potential energy = − 37.24 kJ/mol. c) lowest energy anti-parallel dimer with a mean field of 10.46 kJ/mol applied, potential energy = − 45.59 kJ/mol. d) lowest energy parallel dimer with a mean field of 10.46 kJ/mol applied, potential energy = −44.37 kJ/mol. (See colour plate I.)

sociation, as determined by the relative magnitude of the dimer energies was greater for CB5 than CCH5, which is also in accord with experiment [22].

Recent experimental and theoretical work [19, 46, 47] has suggested that parallel dipole association or ferroelectric order might be preferred for rod-like mesogens with transverse dipoles, or disc-like molecules with dipoles along their short axes. We have carried out molecular mechanics calculations on a number of model compounds to investigate the possibility of ferroelectric order in liquid crystals.

The molecule ACCHNC was selected as a model for a rod-like mesogen with a transverse dipole. In the absence of a nematic potential the dimer with antiparallel dipoles was considerably more stable than that with parallel dipoles. On application of an external ordering potential, the configurations of the most stable dimers changed and the energy difference between parallel and antiparallel dimers became smaller; these results are summarised in figure 4. Other model systems were constructed replacing the cyclohexyl rings by benzene rings, but no compound was found which favoured parallel association of the transverse dipoles. A variety of molecules based on a disc-like structure were also investigated, and of these only 1, 3, 5 tri-*a*-cyano-hexa-methyl cyclohexane (compound a) figure 5 showed a preference for parallel dipole association. Substitution of ethyl or phenyl groups onto the cyclohexane ring caused the antiparallel dipole dimer structure to be stabilised due to increased apolar interactions. Our calculations on strongly dipolar molecules have not yet predicted a

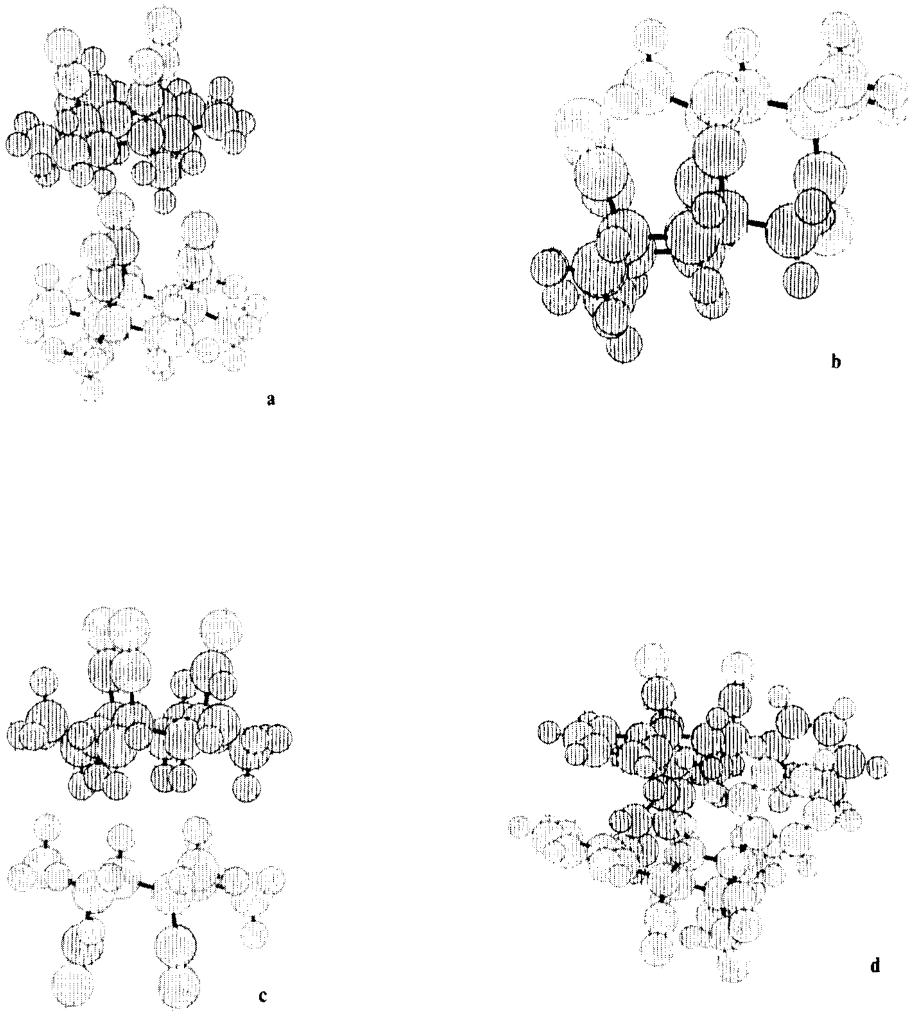


Figure 5 Dimers of disc-like molecules with axial dipoles a) lowest energy parallel dimer of 1, 3, 5-tri-*a*-cyanohexamethylcyclohexane. b) lowest energy antiparallel dimer of 1, 3, 5-tri-*a*-cyanohexamethylcyclohexane. c) lowest energy antiparallel dimer neglecting partial charges of 1, 3, 5-tri-*a*-cyanohexamethylcyclohexane. d) lowest energy antiparallel dimer of 1, 3, 5-tri-*a*-cyanohexaphenylylcyclohexane. (See colour plate II.)

suitable mesogen which prefers ferroelectric order, however we have shown that structural effects on dipole association can be quantitatively modelled. Calculations on more complex structures were limited by constraints on computer time, but it is likely that a structure can be devised which satisfies the requirements for nematic and ferroelectric order.

(ii) Apolar Orientational Correlation

If an isotropic liquid is maintained at a temperature a few degrees above a transition

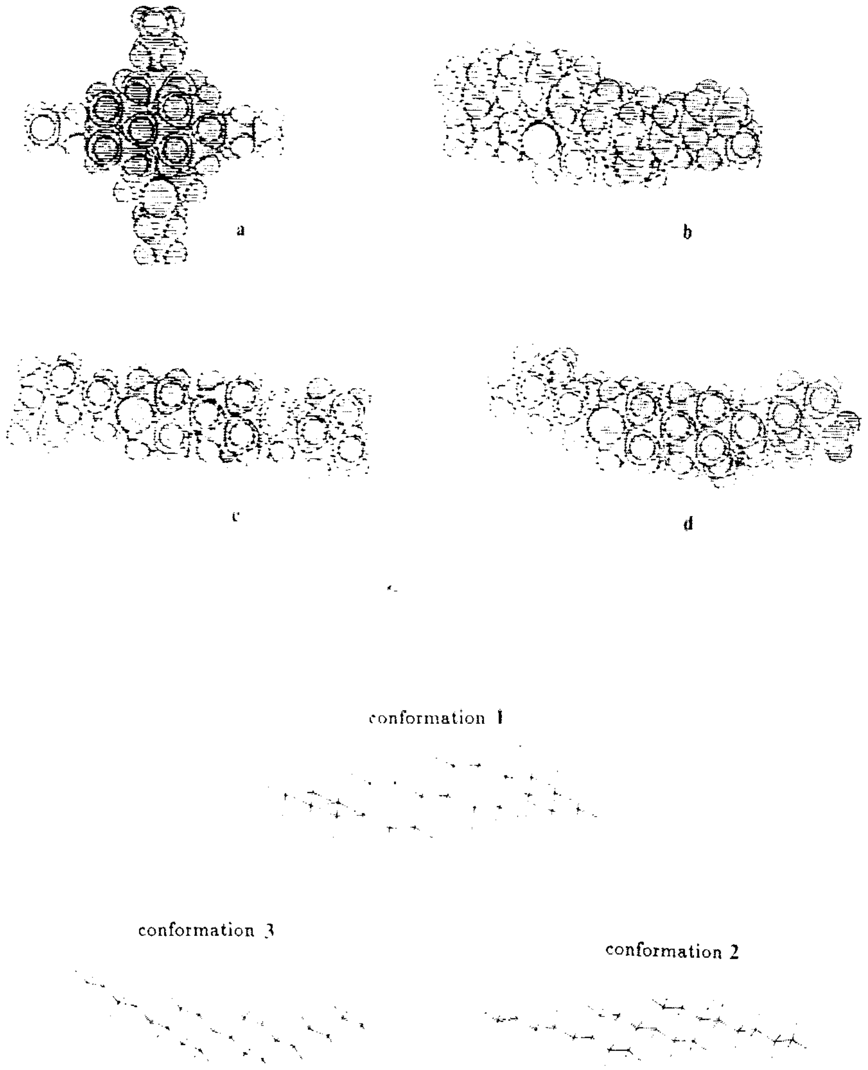


Figure 6 Lowest energy dimers of CCN33 and CCN55 a) lowest energy arrangement for two molecules of CCN33, potential energy = − 50.1 kJ mol. b) lowest energy arrangement for two molecules of CCN55 (conformation 1), potential energy = − 58.9 kJ mol. c) lowest energy arrangement for two molecules of CCN55 (conformation 2), potential energy = − 64.64 kJ mol. d) lowest energy arrangement for two molecules of CCN55 (conformation 3), potential energy = −68.52 kJ/mol. (See colour plate III.)

to a liquid crystal phase, it strongly scatters light and possesses an anomalously high Kerr constant. Both these observations can be interpreted in terms of strong apolar angular correlation as measured by g_2. On reducing the temperature further, the value of g_2 diverges as the liquid crystal phase transition is approached. Calculations of g_2 for a model system provide a useful indicator of its propensity for forming an orientationally ordered liquid crystal phase. For dimers a value of g_2 is obtained from the angle between the molecular axes in the minimised energy configuration. As explained previously, account can be taken of the liquid crystal environment by observing the dimer energy and g_2 as an external ordering potential is applied.

The effect of alkyl chain length on the angular correlation of molecules was demonstrated by calculations on CCN33 and CCN55, which differ by 2 carbon atoms in each of the terminal alkyl chains. Results for the lowest energy configurations for the all *trans* conformations of CCN33 and CCN55 are shown in figure 6, where it is seen that only CCN55 has parallel orientation of long molecular axes. The effects of generating different conformations for CCN55 are also illustrated in the figure 6.

Alternation in liquid crystal transition temperatures and the magnitudes of other physical properties down a homologous series has already been noted. This effect is particularly strong in the so-called siamese twin molecules discovered by Luckhurst *et al.* [48]. These consist of two mesogenic units separated by a flexible alkyl chain, and are a model for side-chain liquid crystal polymers. A mean field theory has been developed for these molecules [17] using Flory's rotational isomeric state model, and this predicts a strong alternation in liquid crystal transition temperatures for odd and even homologues. Our molecular mechanics calculations on these molecules reported earlier [45] confirm the increased orientational correlation for twin molecules with an even number of carbon atoms in the chain (see figure 7), and this has been further substantiated by light scattering measurements in the pretransitional region [49].

(iii) Twist Sense in Chiral Nematics

The formulation of empirical rules relating twist sense and the direction of spontaneous polarisation to the location of a chiral centre in a terminal alkyl chain prompted us to calculate the minimum energy dimer configurations for model chiral molecules. We chose the systems (S)-n-methyl-octylbiphenyl and (S)-n-methyl-octylterphenyl; these are not mesogenic, although their cyano-substituted derivatives do form chiral nematic phases. Only parallel dimers were considered, for which a twist sense can be easily visualised. In the case of n-methyl-octyl biphenyls, for $n < 4$ the preferred parallel dimer configurations are those in which the substituted methyl groups point away from each other, and an alternation of left- and right-handed dimers is found for $n = 1 \rightarrow 4$. For $n = 5$ or 6, the lowest energy parallel dimer structures are those with the methyl groups pointing towards each other, with the

Table 4 Preferred twist sense in parallel dimers of (*S*)-n-methyloctylbiphenyls and (*S*)-n-methyloctylterphenyls.

n	*biphenyls*	*terphenyls*
1	LH	LH
2	RH	RH
3	LH	LH
4	LH/RH	RH
5	RH	LH
6	LH	LH/RH

LH = left handed dimer more stable than right handed dimer,
RH = right handed dimer more stable than left handed dimer,
LH/RH = left and right handed dimers equally stable.

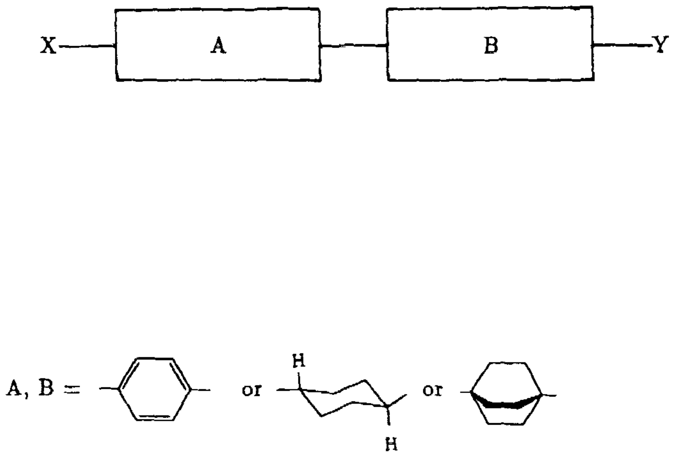
Figure 7 Lowest energy dimers for BCBO9 and BCBO10. BCBO9 dimer energies: a1) −114.68 kJ/mol, b1) −112.68 kJ/mol, c1) −92.09 kJ/mol, d1) −89.62 kJ/mol, e1) −83.89 kJ/mol, f1) −81.88 kJ/mol. BCBO10 dimer energies: a2) −108.53 kJ/mol, b2) −102.3 kJ/mol, c2) −95.60 kJ/mol, d2) −92.26 kJ/mol, e2) −90.21 kJ/mol, f2) −88.66 kJ/mol. (See colour plate IV.)

right handed dimer being of lowest energy for b = 5, and the left-handed dimer the most stable for n = 6. The change in alternation of twist sense at n = 4 can be explained by the balance of repulsive and attractive interactions of the methyl groups: the latter being dominant for n > 4. A similar behaviour was found for the corresponding terphenyls, except that the change in alternation of twist sense occurs for n = 6. Our results are summarised in Table 4.

(iv) Prediction of Phase Stability

The prediction of phase types and their relative stability is an objective of many theoretical studies of liquid crystals, but the present limited scope of molecular mechanics calculations makes predictions of macroscopic liquid crystal properties unreliable. Some information can be obtained on the relative tendencies of mesogens with different structures to form mesophases, but much more work is necessary before the results can be used with confidence. A striking example of the effect a small structural change can have on mesophase stability is observed with PCH5 and revPCH5 (Table 3). These molecules differ only in the positions of the phenyl and cyclohexyl rings. PCH5 has a nematic phase betwen 31°C and 55°C, while revPCH5 is not liquid crystalline, but has an estimated metastable nematic/isotropic transition at −25°C, well below the normal melting point. The physical properties of PCH5 and revPCH5 are similar, and the dipole moment and polarisability anisotropy of revPCH5 are almost identical [50] with those of CCH5, which has a nematic phase between 65°C and 88°C. The results of our calculations on PCH5 and revPCH5 have already appeared [45]. We found that there was little difference in energy or structure of dimers of PCH5 and revPCH5, but that dimers of PCH5 responded to a much lower orienting nematic potential than those of revPCH5.

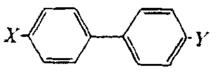
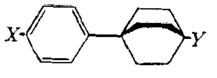
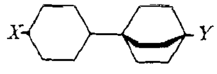
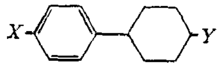
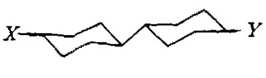
The effects of different ring systems on nematic phase stability have been extensively studied. We have carried out a series of molecular mechanics calculations on dimers of model compounds with the variety of ring systems illustrated in figure 8. Calculations were performed on the unsubstituted cores, disubstituted in the 4, 4′ positions with n-pentyl chains, and monosubstituted in a 4 position with a nitrile group. For biphenyl systems calculations were done both for coplanar rings, and for rings having a dihedral angle of 30°. A cyclohexane ring may adopt a number of conformations with respect to a phenyl ring, and there will be a large number of possible conformations of attached alkyl chains. We have carried out calculations for different core conformations, but in this paper we report results for which the angle between a phenyl ring and the adjacent axial C-H bond was fixed at 30° to maximise the intermolecular interactions, while alkyl chain conformations were assumed to be all *trans*. The energy barriers between chain conformations is low, and torsional angles are likely to vary as molecules interact in clusters. This is a major problem which we have not yet tackled, although it is within the capability of program packages such as AMBER [51] and CHARMM [52] run on suitably large machines with sufficient CPU time. Table 5 lists the minimum dimer energies for the various systems studied. With the one exception noted in the table, all model mesogens preferred antiparallel association. Terminal alkyl chains stabilise the anti-parallel configurations, but it must be remembered that this arises from increased attractive van der Waals forces between the molecules due to the assumed rigid alkyl chains; effects of chain flexibility have yet to be included. Dipolar terminal groups enhance the antiparallel energy, but not to the same extent as terminal alkyl chains. In a number of the calculations we



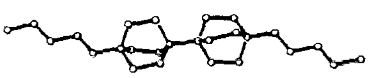
X, Y = CN or C_5H_{11}

Figure 8 Schematic of two-ring systems studied.

Table 5 Minimum dimer energies for different ring systems[I] (kJ/mol)

mesogen	$X = -$ $Y = -$	$X = C_5H_{11}$ $Y = C_5H_{11}$	$X = CN$ $Y = -$	$X = -$ $Y = CN$	$X = CN$ $Y = C_5H_{11}$	$X = C_5H_{11}$ $Y = CN$
	−37.4	−62.1	−45.7	-	−60.0	-
	−35.5	−57.4	−43.9	−37.0	II	II
	−34.8	−58.7	−39.7	−35.1	II	II
	−35.0[III]	−61.6	−42.6[IV]	−40.7[V]	−47.1	−46.8
	−33.6	−56.7	−39.7	-	−51.8	-
	−31.5	−51.7	−33.1	-	II	-

[I] these energies are highly conformationally dependent. All-*trans* conformations were used for all the chains and a similar ("MM2 minimised") molecular conformation was chosen for all molecules. The chosen molecular conformations were based on the lowest energy conformation of 4,4'-dipentyldi-[2, 2, 2]-bicyclooctane.



Further work is in progress on the effect of different molecular conformations on these energies.

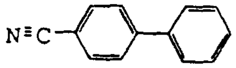
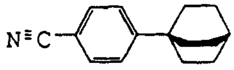
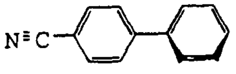
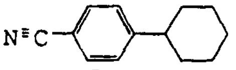
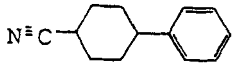
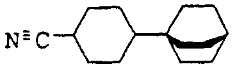
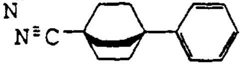
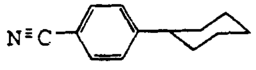
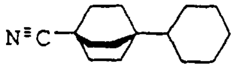
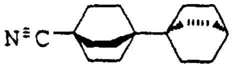
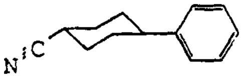
[II] calculations yet to be carried out.

[III] lowest energy dimer has a parallel configuration. The lowest energy anti-parallel dimer found has an energy of -34.6 kJ/mol.

[IV] this energy is increased to -36.3 kJ mol when the lowest energy core conformation is used.

[V] this energy is increased to -30.0 kJ mol when the lowest energy core conformation is used.

Table 6 Results for cyanosubstituted two-ring systems

molecule/conformation	*energy of lowest energy dimer /(kJ/mol)*	*angle between molecular axes /°*	*Boltzmann averaged angle /°*	*energy of lowest energy dimer (with nematic field of 10.5 kJ/mol) /(kJ/mol)*	*angle between molecular axes (with nematic field on) /°*
	−45.71	0.0	6.9	I	I
	−43.88	29.0	37.3	−51.85	18.4
 *II*	−43.67	15.6	20.2	−53.50	8.7
 *III*	−42.60	15.9	28.1	−52.06	14.0
 *IV*	−40.74	19.5	18.5	−49.90	1.5
	−39.70	1.5	33.8	−50.15	0.0
	−39.69	36.9	21.9	−49.86	1.5
	−39.96	13.9	34.2	−47.35	0.0
 *III*	−36.26	34.1	44.0	−42.71	26.9
	−35.05	14.5	30.8	−45.29	2.1
	−33.06	31.9	27.0	−42.64	2.1
 *IV*	−30.00	32.7	39.8	−39.40	7.6

[I] results not available
[II] inter-ring torsional angle of 30°
[III] maximum and minimum energy configurations of the same molecule
[IV] maximum and minimum energy configurations of the same molecule

were able to detect energy minima close to the global minimum with very similar dimer configurations. In a real system these other configurations also contribute to the average dimer structure, and must be included in our assessment of the relative nematic stability of different ring systems. This can be done by calculating the

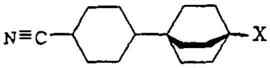
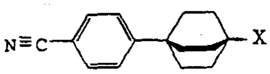
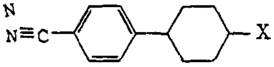
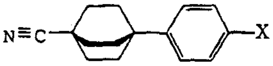
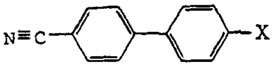
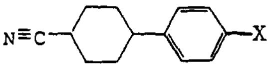
Boltzmann averaged angle between molecular axes including all energy minima. To illustrate this, calculations were performed for the cyano-substituted two-ring systems, and Table 6 lists the energy minima, angles between molecular axes in the global minimum configuration and the Boltzmann-averaged angle. The effect of a nematic potential on these dimers was determined with the results also given in Table 6. Although the stabilisation energy of dimers increased in the presence of a nematic potential and the angle between molecular axes in the dimers decreased, an external ordering potential has not dramatically changed the relative energies of the different ring systems.

5. CONCLUSIONS

In our review of empirical and theoretical aspects of structure/property relationships in liquid crystals, we have drawn attention to the large effects of small structural changes on macroscopic properties. A quantitative basis for explaining structure/property correlations can only be established if all details of the molecular structure are taken into account. This paper has described how the molecular mechanics method can be used to model the detailed intermolecular interactions responsible for liquid crystal behaviour. The method works well when describing short range interactions, particularly those that are observable in solution or in the isotropic liquid phase and which presage the behaviour in orientationally ordered liquid crystal phases. This has been illustrated by reference to dipole–dipole association and apolar angular correlation. The modelling of macroscopic properties of liquid crystals is more problematic. We have obtained encouraging results in simulating the alternation in pitch sense of chiral mesogens as a chiral centre is moved along a terminal alkyl chain. More extensive work is required using molecules with chiral axes and chiral planes to see if molecular mechanics can be used predictively. An outstanding problem in liquid crystals is to relate elastic constants to molecular structure. Torsional elasticity is a direct probe of the angle dependence of intermolecular forces, and molecular mechanics should be a useful tool to probe non-equilibrium elastic distortions between molecules: we have not yet attempted these calculations.

One objective of a molecular theory of liquid crystals is to predict the dependence of phase stability on molecular structure. This is a difficult problem because thermodynamic stability arises from many particle interactions, and while molecular mechanics can model the details of molecular structure, the method cannot as yet handle interactions between large numbers of molecules. In spite of this we have carried out calculations to investigate the relative nematic stability associated with different ring systems. Our results are summarised in Table 7. The relative ordering of ring systems in terms of dimer energies is only slightly affected by terminal substituents, and unfortunately does not accord with empirical observations. These suggest that the bicyclo-octane system is most effective at promoting liquid crystal behaviour, while the phenyl ring is least effective. The most serious disagreement between our calculations and the experimental results is found for CB5, which has an almost planar structure. The stabilisation energy for CB5 dimers results mostly from strong overlap of the aromatic rings; in a cluster of more than 2 molecules, dimers with perpendicular rings will dramatically reduce the stabilisation energy and may explain the experimental observation. This effect is specific to CB5 which contains 2 aromatic rings: the other ring systems studied are not planar, and so configurations

Table 7 Relative ordering of ring systems[I]

	ordering of T_{NI} for $X = C_5H_{11}$	*ordering of energies of lowest energy dimers*[II] *for X = –*	*ordering of Boltzmann averaged angles*[III] *for X = –*	*ordering of energies of lowest energy dimers*[II] *with nematic field on for X = –*
	1 (129°C)	3	3	3
	2 (100°C)	1	5	2
	3 (85°C)	4	2	4
	4 (55°C)	6	7	6
	5 (50°C)	5	4	5
	6 (35°C)	2	1	1
	7 (–25°C)	7	6	7

[I] minimum energy conformations used

[II] 1 = lowest energy, 7 = highest energy

[III] 1 = smallest angle, 7 = largest angle

with perpendicular rings on interacting molecules will not be so different in energy from those with parallel rings. In our work we have noted the importance of torsional motion, but have not included it in our present calculations. We have demonstrated that molecular mechanics can model subtle effects of molecular structure on local packing, but as yet are not sophisticated enough to account for the liquid crystal stabilities of different structures. Thus the answer to the question posed in the title of this paper has to be "no". It is to be hoped that developments in simulating clusters of molecules using the complex atom-atom potential introduced here will lead to such calculations having predictive capability for structure/property relationships in liquid crystals.

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Phippen (IBM UK Scientific Centre, Winchester, Hants), and correspondence with Dr M Schadt (F Hoffmann-La Roche, Basle, Switzerland) are gratefully acknowledged.

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