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Molecular mechanics modelling of structure/property relationships in liquid crystals

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Molecular mechanics calculations are reported of structure/property correlations in some liquid crystals. An atom-atom intermolecular potential is used to calculate minimum energy configurations of pairs of mesogenic molecules. Observed effects of dipole-dipole association, twist sense in chiral nematics and properties of flexible nematogens are confirmed by the calculations. It is concluded that molecular mechanics can be a useful technique for predicting liquid-crystalline properties of potentially mesogenic molecules.

1. Introduction

Intermolecular interactions are extremely important in liquid crystal chemistry. It is the anisotropy in molecular interactions that is responsible for the formation of mesophases in the first place; and it is the subtle differences in these interactions that occur with changes in temperature or changes in structure that account for the rich phase behaviour exhibited by these materials.

In this work our aim was to look at molecular association and intermolecular interactions in a quantitative way. Molecular mechanics was chosen as our tool to model interactions between mesogenic molecules and to provide a theoretical understanding of association and structure/property relationships in these systems. All the relevant bond bends, stretches and torsions, together with van der Waals and dipolar interactions, are parametrized by simple potential functions. The 'steric energy' can then be minimized using one of a variety of different techniques and the geometry of the system optimized [1-3].

For our initial study of interactions between liquid crystal molecules, we have neglected contributions from internal rotations and assume rigid structures for mesogens. This is clearly a questionable assumption, but we believe recent calculations [4, 5] of average structures of molecules in a mean field provides some support for our model.

The calculations that we have undertaken have focused on dimers of liquid crystal molecules. The approach has been to calculate the most favourable arrangement for dimers composed of mesogens by finding the minimum energy for the two molecules. The structure of the minimum energy dimers can give us information about the magnitude of the intermolecular interactions and the anisotropy of interactions. It is this anisotropy that causes molecular association to take place in specific ways. It should be stressed that these calculations are not aimed at calculating the structure of the mesophase based on the structure of dimers. Instead, we have used these calculations to investigate empirical structure/property relationships in liquid crystal chemistry, and to use them to give information about the nature of the molecular interactions that occur between the molecules that form the mesophase. If empirical relationships exist then there must be some theoretical basis for them.

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2. The molecular mechanics potentials and force fields

The potential chosen to model internal motion for molecules was the potential in the MM2 program. MM2 is available from the Quantum Chemistry Program Exchange [6]. It has been shown to be extremely useful in the modelling of small molecules (100 atoms and less), and has produced excellent results for single molecule properties such as structures, conformational energies and vibrational frequencies [7, 8]. The MM2 force field has been widely developed and is fairly comprehensive in its coverage of organic molecules.

Considerable work has been undertaken in the last few years on developing new potentials to model intermolecular interactions accurately. This work has been stimulated by the desire to calculate intermolecular interactions between proteins and substrates and to study intramolecular interactions in proteins. Most of the work has been based on the extended-atom approximation, which replaces a non-hydrogen atom and any hydrogens attached to it by a single extended atom. We have employed the extended-atom approximation for the van der Waals interactions in all the systems studied. In these systems hydrogen bonding is not an important effect, and we have not included a potential to model these forces.

We have used a Lennard-Jones 12–6 potential (1) to model van der Waals interactions; from a detailed consideration of various approaches [9–12] to the determination of potential parameters, the Jorgensen parameters derived from Monte Carlo simulations of simple liquids [12] were chosen:

$$En = \sum_i \sum_j \left(\frac{A_{i,j}}{r_{i,j}^{12}} - \frac{C_{i,j}}{r_{i,j}^{6}} + \frac{q_i q_j}{4\pi\varepsilon_0 r_{i,j}} \right), \tag{1}$$

where

$$A_{i,j} = (A_{i,i} A_{j,j})^{1/2}, \qquad C_{i,j} = (C_{i,i} C_{j,j})^{1/2}.$$

$A_{i,j}$ and $C_{i,j}$ can also be expressed in terms of the Lennard-Jones εs and σs: $A_{i,j} = 4\varepsilon_{i,j}\sigma_{i,j}^{12}$ and $C_{i,j} = 4\varepsilon_{i,j}\sigma_{i,j}^{6}$. The approach used to model the effects of dipolar interactions involves the use of partial charges. Each atom is assigned a partial charge, and these interact via a Coulomb potential (1). Partial charges can be calculated via a variety of means. The best approach is to perform a quantum-mechanical calculation with the largest computationally reasonable basis set. There are no terms in the potential for dipole-induced dipole effects, i.e. a cross-interaction term between the dispersive r^{-6} and the charge terms. Numerous simulations on proteins and other molecules seem to indicate that a 12–6 potential with a Coulomb term is sufficient to model the system without the need for a dipole-induced dipole term. This thinking has been applied in the current work and it is believed that any dipole-induced dipole effects will be absorbed into the other terms.

In a condensed phase molecules interact with their neighbours (short-range) and with the rest of the environment. For liquid crystals, interactions with the long-range orientationally ordered environment can be replaced by a mean field, which is a potential averaged over orientations of all molecules except the probe molecule; the potential has the macroscopic symmetry of the phase. To take account of the nematic environment, we added a nematic potential to the intermolecular potential of our interacting molecules. We are only interested in the effect of the nematic environment on the configurations of the dimers, so it was convenient to set the symmetry axis of the nematic potential along one of the interacting molecules. This is equivalent to having one of the molecules along the director axis of the nematic. To include the nematic potential in our calculations, it was necessary to define an angle $\theta_{i,j}$ between the interacting molecules. This was done by defining a unit vector **b** along the bonds linking the rings of the molecules, so that $\cos \theta_{i,j} = \mathbf{b}_i \cdot \mathbf{b}_j$, the energy could then be computed using

$$En = -B \sum_{j=2}^{N} \tfrac{1}{2}(3 \cos^2 \theta_{1,j} - 1), \tag{2}$$

where $\theta_{1,j}$ is the angle between the molecule j and molecule 1. In this way the molecules were able to move in cartesian space inside the minimization algorithm without the mean field constraining the working of the algorithm by fixing the coordinates of the molecules. The parameter B in (2) acted as a user-defined constant that could be tuned to see the effect of an increasing mean field. When the mean field was not required B was set equal to zero.

3. Computational details and analysis of results

As has been described above, the MM2 program is widely available and has been successfully used to predict structures of many organic molecules. However, the MM2 algorithm coped poorly with the problems of two-molecule calculations and moved the molecules only small distances before finding a minimum. Part of the problem was that the potential energy surface for the molecules was so complicated that it was pitted with small minima. MM2 would stop as soon as it came across one of these minima without searching for another lower minimum. In addition, repeated MM2 calculations were computationally fairly expensive. Another approach was therefore sought.

The program LMIN is a program written in the Chemistry Department at Sheffield by P. Smith [13]. It proved ideally suited for the calculations we required. The program calculates the intermolecular energy based on a user-supplied potential. It then calculates the gradient of the potential energy based on repeated small movements of the molecules in the three translational degrees of freedom and three rotational degrees of freedom. The program then moves the molecules down the maximum potential energy gradient to find a minimized energy. This program had two big computational advantages over MM2 in calculating forces between molecules. First, it did not stop immediately that a minimum in the energy was found. Instead, it looked for another lower minimum. Secondly, the fact that the program works with rigid molecules greatly cuts down the number of local potential energy minima. LMIN was adapted to include a mean field energy term for nematic and smectic mean fields, to calculate entropies and free energies of the final minima and to produce an output deck compatible with the molecular graphics program PLUTO.

Our computational approach for LMIN was first to calculate the energy minimized structure for a single molecule using MM2 and then to put these energy minimized structures into LMIN to run intermolecular calculations. In the calculations reported here only two molecules were used: other calculations using three or more molecules greatly increased the number of energy minima found by LMIN, and interpretation of the results was difficult. For almost all the molecules it was found that LMIN could not be relied upon to produce a single global minima for the intermolecular energy regardless of the starting position. As a consequence of this, it was necessary to commence the minimization calculation at many different starting positions to give the program the best chance of finding the global minimum for the surface.

In most cases 120 LMIN calculations were carried out from different starting positions, though some of the larger molecules required 240 calculations. The large number of calculations ensured that we found the global minimum for the surface, as well as the other lowest energy minima.

In comparing the minima found for particular molecules, we found in many cases that particular potential energy minima were much lower in energy than other minima. These were particularly useful in giving information about dipole and long-axis correlation. For example, in CB5 there was a distinct energy gap between antiparallel and parallel dipole dimers. To get a measure of long-axis correlation over the series of energy minima, it was possible to work out a weighting for each individual minimum based on the following equation, and thereby obtain a weighted average for the angle between molecular axes:

$$w_i = \frac{\exp - [(e_i - e_0)/kT]}{\sum_{j=1}^{N} \exp - [(e_j - e_0)/kT]}, \qquad (3)$$

where w_i is the weighting for the dimer, e_0 is the energy of the lowest energy dimer and e_i is the energy of dimer i. For some molecules there were several potential energy minima that were very close together but possessed different twist angles. In these cases a very poor axis correlation was exhibited.

In comparing the minima of different molecules, we considered both the energy of the lowest minimum for each molecule and the spread of energy minima. This gave information about the strength of interaction between the molecules. Also, a comparison of long-axis correlation exhibited by different molecules proved useful in our calculations on molecules with different ring systems.

4. Results and discussion

Our molecular mechanics calculations on liquid crystal molecules were aimed at tackling specific problems. We tried to make our model as realistic as possible using the best atom–atom potential parameters and partial charges from minimal basis set SCF calculations. The structures and acronyms of the molecules studied are given in table 1. As explained in §1, various effects of structure-dependent behaviour were investigated by molecular mechanics. These are described in the following separate sections. Our first applications were concerned with specific local effects which might reasonably be explained from a simple consideration of dimeric association. Some preliminary results are also included on the more complex problem of phase stability, where the influence of the environment on dimeric structures is simulated by a nematic potential.

4.1. *Dipole association in liquid crystals*

Recent work involving dielectric measurements on solutions of liquid crystal molecules in isotropic solvents has indicated the presence of both parallel and antiparallel dipole dimers [14–16]. Molecular mechanics calculations were carried out on dimers of CCH5 and CB5, which both have longitudinal dipoles. These calculations were aimed at providing a computational model to complement the experimental results. Trial calculations were also carried out on model molecules with strong transverse dipoles to investigate the possibility of local ferroelectric ordering.

The results for the calculations on CB5 and CCH5 are summarized in table 2 and figure 1; in the table values for the four lowest energy minima are given. The

Table 1. Molecular structures and acronyms.

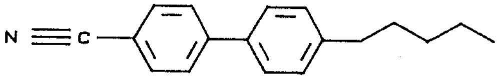
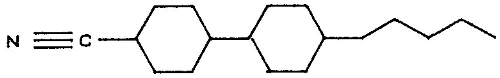
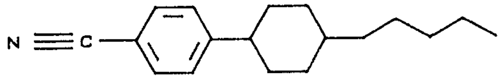
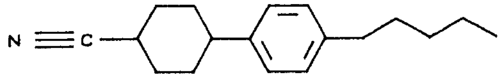
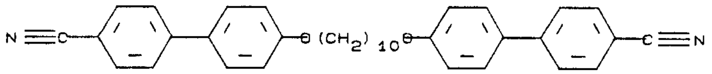
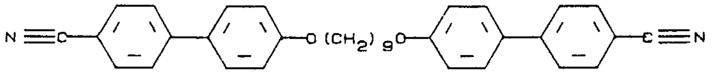
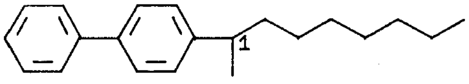
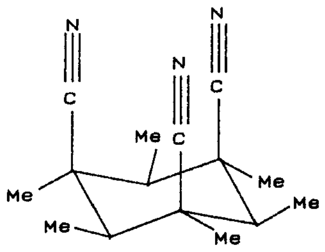
Material	Structure
CB5	
CCH5	
PCH5	
revPCH5	
BCBO10	
BCBO9	
1-methyloctylbiphenyl	
Bowl-shaped molecule	

Table 2. Four lowest energy minima for antiparallel and parallel arrangements of molecules for CB5 and CCH5.

Material	Antiparallel dimer/kJ mol^{-1}	Parallel dimer/kJ mol^{-1}
CB5	−60·04 −56·93	−56·16 −55·30
CB5, no partial charges	−59·42	−58·93 −56·55 −56·46
CCH5	−51·81 −51·01	−49·61 −48·71
CCH5, no partial charges	−52·31 −51·49	−51·36 −50·58

geometries of the molecular configurations corresponding to these minima were very similar for both the parallel and antiparallel cases. Thus the additional minima describe configurations only slightly perturbed from the parallel or antiparallel geometries of the lowest minima. For both CB5 and CCH5 two distinct potential energy minima were found that were considerably lower in energy than any other minima for these molecules. Figure 1 illustrates the antiparallel and parallel dipole minima for CB5. Table 2 shows that there is an energy gap that favours the antiparallel dipole dimer for both CB5 and CCH5. This energy gap disappears if the partial charges are removed from the calculations, even though the removal of charges produces a negligible effect on the spatial configuration of the dimers. This result indicates that it is the dispersive and repulsive forces that are the dominant factors in causing molecular association in these molecules, but the dipolar forces are important in determining the balance of parallel and antiparallel dipole dimers. These results fit in well with the solution measurements of Dunmur and Toriyama, who predict both parallel and antiparallel dipole dimers in their dielectric solution measurements [14, 15]. The strength of interaction is greater for CB5 than for CCH5. This is consistent with the larger association constant and orientational correlation found by Dunmur and Toriyama in their solution light scattering results [16].

In an effort to try and design a material that would form dimers with strong parallel dipole correlation, calculations were carried out on materials resembling bowls. Such bowl-shaped molecules have been shown in some circumstances to form columnar mesophases [17] that exhibit strong short-axis correlation. In these calculations the bowl-like shape was based on the cyclohexane ring. In order to produce parallel correlation, a strong parallel dipole was placed along the short axis of the molecule. In this case the strong dipole was produced by three cyano groups, each aligned parallel in three axial positions of the cyclohexane ring. Calculations were carried out on several molecules with a variety of different groups attached to the axial positions of the ring.

Our potential energy calculations produced a number of different dimers for the different molecules. We were particularly interested in dimers that exhibited strong short-axis correlation combined with parallel dipole correlation because these are good models for molecules that might form ferroelectric phases. The material shown in figure 2 was found to have the configuration with both strong short-axis correlation and strong parallel dipole ordering. It became clear that the precise arrangement of axial groups about the cyclohexane ring is important in determining relative energies of dimers. For example, three equatorial methyl groups did produce dimers with a similar configuration to that shown in figure 2—but not as the lowest energy minimum. Three methyls were evidently not enough to cause the molecules to want to align under each other, even though short-axis correlation was favoured. The calculations illustrated the large effect that small subtle changes in structure can produce on intermolecular interactions. They also show the way in which we can tune molecular interactions in order to get the desired effect on our dimers, in this case to produce parallel dipole ordering.

4.2. *Twist sense in chiral nematics*

One of the interesting and unexplained phenomena in liquid crystal chemistry occurs in chiral nematic mesophases. For many materials with chiral alkyl chains it has been found that moving the chiral centre down the chain by one unit but keeping the chirality the same causes a reversal in the twist sense of the helix describing the chiral nematic [18]. In fact a set of empirical rules has been developed in order to predict the twist sense for these materials. The rules depend on the absolute configuration at the chiral centre and the distance of the chiral centre from the core of the molecule. Additional rules were developed by Goodby [19], in order to predict the twist sense of the helix and the sign of the spontaneous polarization in chiral smectic C materials. Goodby suggested that the inductive effect at the chiral centre was also important in determining the sign of spontaneous polarization. Many chiral smectic C materials were synthesized that fitted in with Goodby's predictions [19] and gave credence to his rules. However, it was later discovered that other materials failed to fit in with the established pattern [20]. Molecular mechanics calculations were carried out on a number of chiral hydrocarbon materials. The aim of the calculations was to try to understand from a study of molecular interactions and preferred geometries of dimers the reason for the success of the rules governing twist sense.

Table 3. Favoured twist angle for chiral biphenyl materials.

Material	Twist sense†
(*S*)-1-methyloctylbiphenyl	LH
(*S*)-2-methyloctylbiphenyl	RH
(*S*)-3-methyloctylbiphenyl	LH
(*S*)-4-methyloctylbiphenyl	LH/RH
(*S*)-5-methyloctylbiphenyl	RH
(*S*)-6-methyloctylbiphenyl	LH

† LH, left-handed dimer more stable; RH, right-handed dimer more stable; LH/RH, left- and right-handed dimer equally stable.

Calculations were carried out on a series of alkylbiphenyl compounds, which acted as model chiral materials. The compounds used were chiral n-methyloctylbiphenyl compounds, all of which had the S absolute configuration at the chiral centre. All molecular structures were calculated using MM2, and coplanar ring systems were assumed in every case for simplicity. The results did indeed show an alternation in twist sense as the chiral centre was moved away from the rigid core as indicated in table 3. It was also found that the left-handed and right-handed structures were of equal energy when the chiral centre was at carbon atom 4, thereafter the twist sense changed. When a mean field was applied to the dimers, a reduction in the twist angle for the dimers occurred because the molecules naturally wanted to lie along the mean field. The effect on the relative stability of the dimers was that a reduction in the twist angle brought the methyl groups closer together. We should therefore expect to see the crossover point between the dominance of methyl attractive and repulsive effects to occur with the methyl further along the chain. This is indeed what is seen. When a mean field of $10{\cdot}46\,\mathrm{kJ\,mol^{-1}}$ was applied, the crossover point moved from $n = 4$, for no mean field, to a point in between $n = 4$ and $n = 5$. A mean field of $41{\cdot}84\,\mathrm{kJ\,mol^{-1}}$ moved the crossover to between $n = 5$ and $n = 6$.

4.3. *Long-axis correlation and phase stability—calculations with a nematic potential*

PCH5 and revPCH5 differ greatly in their liquid crystal phase behaviour. PCH5 shows a nematic phase that exists between 31°C and 55°C, but revPCH5 shows only

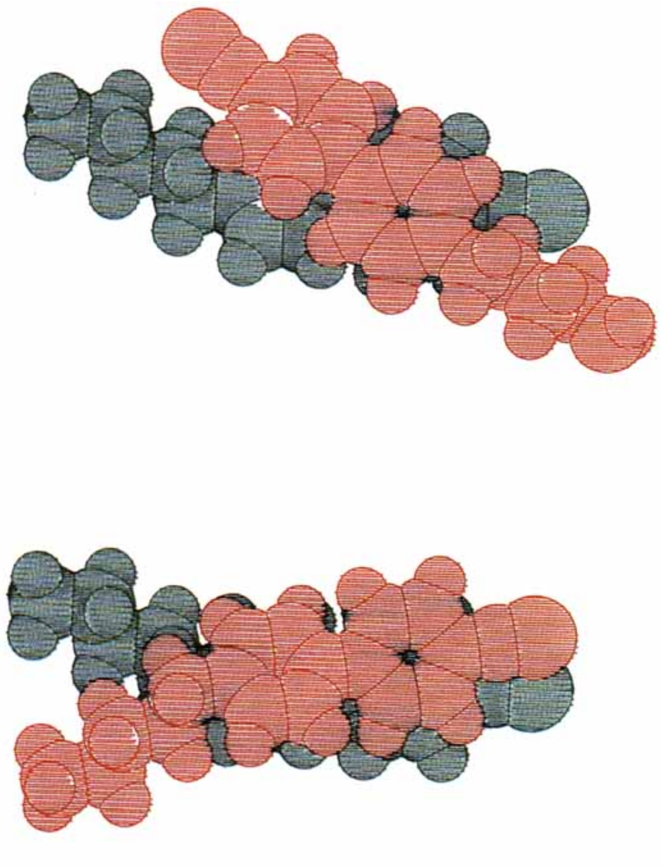


Figure 1. Antiparallel and parallel energy minimized arrangements of two CB5 molecules.

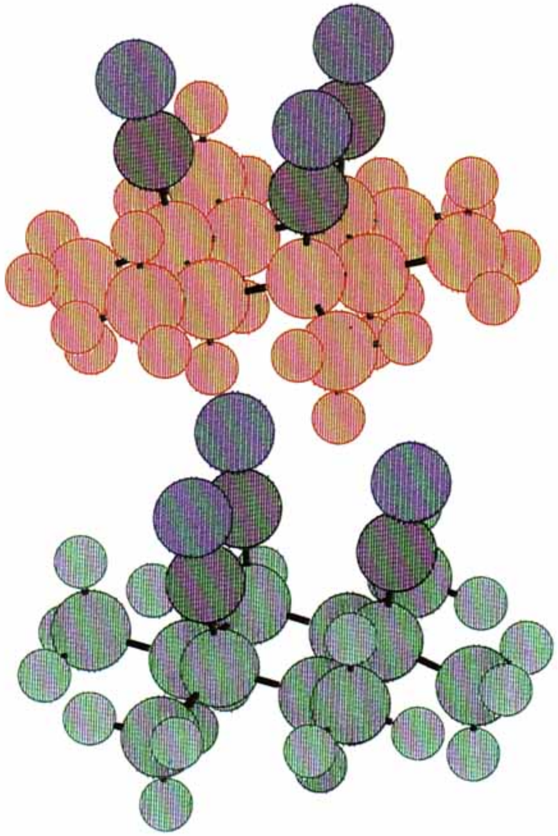


Figure 2. A dimer of a bowlic material showing parallel dipole alignment.

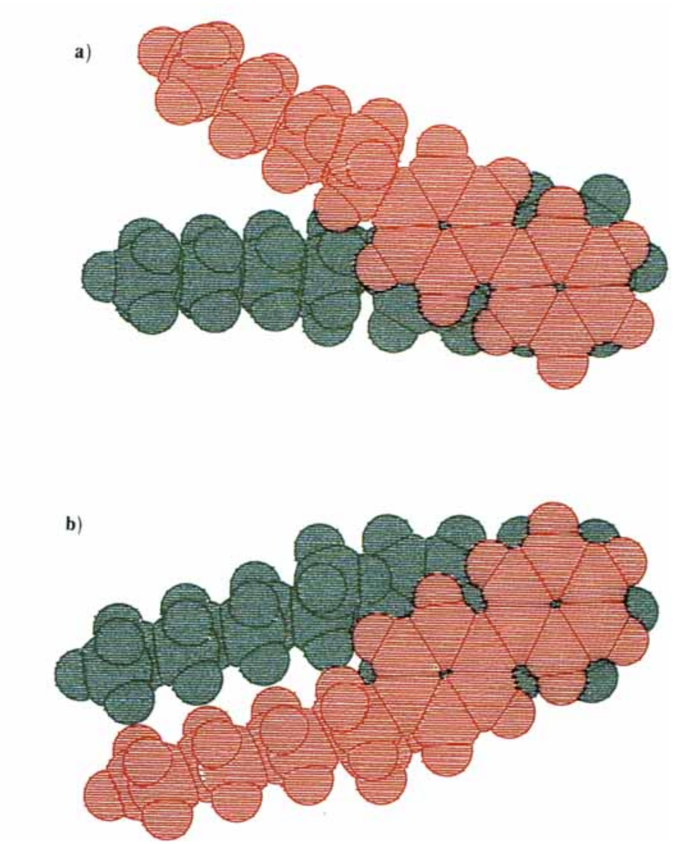


Figure 3. (*a*) (*S*)-1-Methyloctylbiphenyl dimer (left-handed). (*b*) (*S*)-2-Methyloctylbiphenyl dimer (right-handed).

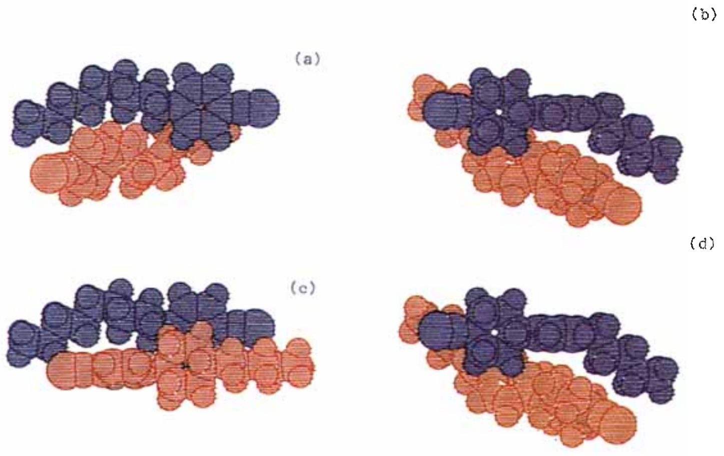


Figure 4. (*a*) Lowest energy PCH5 dimer with no mean field applied. (*b*) Lowest energy revPCH5 dimer with no mean field applied. (*c*) Lowest energy PCH5 dimer with a mean field of 8·37 kJ mol^{-1} applied. (*d*) Lowest energy revPCH5 dimer with a mean field of 8·37 kJ mol^{-1} applied.

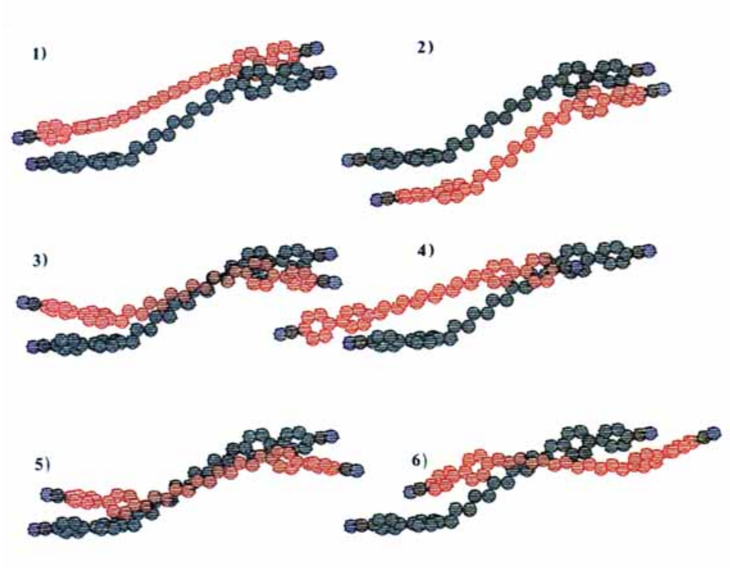


Figure 5. The six lowest energy dimer arrangements for BCBO10: (1) energy of minimum = $-108{\cdot}53\,\mathrm{kJ\,mol^{-1}}$; (2) $-102{\cdot}30\,\mathrm{kJ\,mol^{-1}}$; (3) $-95{\cdot}60\,\mathrm{kJ\,mol^{-1}}$; (4) $-92{\cdot}26\,\mathrm{kJ\,mol^{-1}}$; (5) $-90{\cdot}21\,\mathrm{kJ\,mol^{-1}}$; (6) $-88{\cdot}66\,\mathrm{kJ\,mol^{-1}}$.

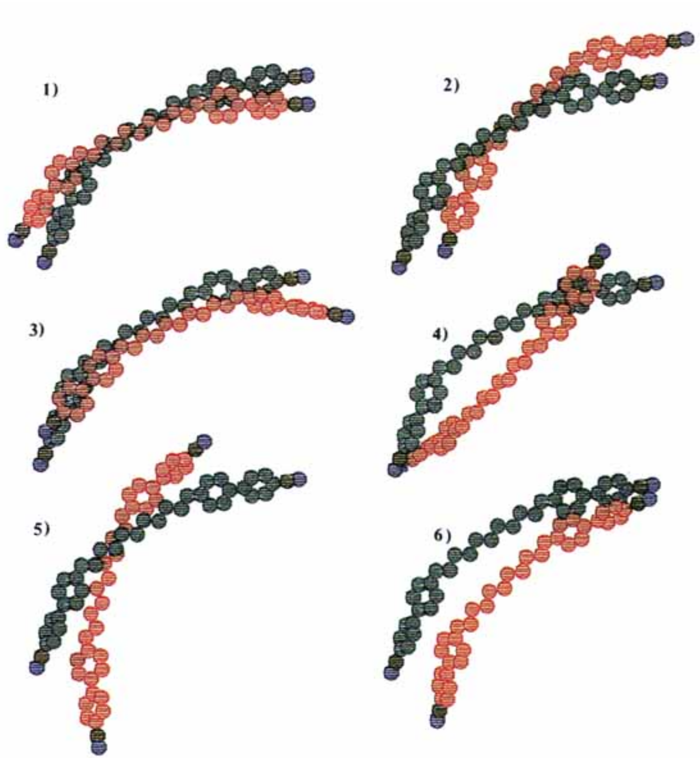


Figure 6. The six lowest energy dimer arrangements for BCBO9: (1) energy of minimum = $-114{\cdot}68\,\mathrm{kJ\,mol^{-1}}$; (2) $-112{\cdot}68\,\mathrm{kJ\,mol^{-1}}$; (3) $-92{\cdot}09\,\mathrm{kJ\,mol^{-1}}$; (4) $-89{\cdot}62\,\mathrm{kJ\,mol^{-1}}$; (5) $-83{\cdot}89\,\mathrm{kJ\,mol^{-1}}$; (6) $-81{\cdot}88\,\mathrm{kJ\,mol^{-1}}$.

a virtual transition at −25°C. The difference between the molecular structure is simply in the interchanged positions of the cyclohexane and phenyl rings. Calculations were carried out on dimers of each material, both with and without the application of a nematic mean field in order to see if the difference in intermolecular forces that causes this phase behaviour can be detected in the preferred arrangements of dimers.

The lowest energy dimers for these molecules in the absence of an ordering potential (figure 4) both had the same energy and neither exhibited strong orientational coupling, both molecules showing a preference for antiparallel dipole ordering. However, the application of a mean field of just $8{\cdot}37\,\mathrm{kJ\,mol^{-1}}$ produced strong orientational correlation in PCH5, but had little effect on revPCH5 (figure 4). A mean field of $41{\cdot}84\,\mathrm{kJ\,mol^{-1}}$ was required before strong ordering was obtained in the revPCH5 dimers.

These results provide a good qualitative explanation for the different phase behaviour of PCH5 and revPCH5. It seems to be the case that, despite the fact that the molecules contain the same constituent parts, it is the arrangement of these that is the key factor in influencing molecular association. The stabilization energy for revPCH5 dimers appears to result from strong localized interactions. In figure 4 the interactions are between the cyanocyclohexane unit and the alkyl chain, though in other higher energy dimer arrangements it is the interactions between phenyl rings that dominate. The application of a strong ordering potential is required to cause dimer arrangements with strong orientational coupling to become more stable than dimers with poor orientational correlation. In the PCH5 dimers the interactions are less localized. The stabilization energy for the dimer comes from all parts of the molecule. This inevitably means it is far easier for the PCH5 molecules to align parallel. Therefore the application of a small ordering potential causes strong orientational correlation.

4.4. *Twin molecules*

The synthesis of 'siamese twin' nematogens has been reported [21]—these comprise two mesogenic core structures joined together by a long alkyl chain. The materials are unusual because they break established ideas about the need for rigid cores and flexible terminal chains for molecules to form mesophases. The materials are also unusual because they exhibit extremely large 'odd–even effects' as the number of alkyl linking carbons in the chain are varied. It has been shown that molecules with even numbers of carbons in the chain exhibit much stronger ordering in their nematic mesophase than those with odd numbers of carbons [22]. We have carried out calculations on BCBO10 and BCBO9, in order to gain computational information about how these molecules interact.

The results for calculations on BCBO9 and BCBO10 were clear-cut. The six lowest-energy minima are shown in figure 5 for BCBO10 and figure 6 for BCBO9. Both molecules had two energy minima that were considerably lower in energy than any other minima. In all four of these minima we see evidence of strong interaction between the terminal cyanobiphenyl units. These forces dominate over the interactions between chains. The interaction energy for the lowest-energy BCBO9 dimers is about $6{\cdot}15\,\mathrm{kJ\,mol^{-1}}$ lower than for the corresponding BCBO10 dimers because it appears that, in ordering the two core units of BCBO9, the chains automatically come into a position where they can also interact to some extent. On the other hand, in BCBO10 the chains interact less strongly because the molecular arrangement for two molecules is such that when the core interactions are maximized the chains are not in a position to interact particularly strongly.

We can see that in both molecules the core units are strongly orientationally coupled, though it is really the shape of the molecules that is important. The BCBO10 molecular shape means than the terminal cyanobiphenyl units at the two ends of the molecules are well correlated with one another. However, the BCBO9 shape means that the terminal units are poorly correlated with one another. It should be stressed that these calculations have only taken into account the all-*trans* conformations for the chain, but these calculations clearly indicate that BCBO10 is likely to exhibit much stronger ordering than BCBO9. This result has already been found experimentally by light scattering measurements in our laboratory [22].

5. Conclusions

Attention has been focused on establishing relationships between the molecular structure of mesogens and their physical properties and behaviour in devices. Empirical rules have been formulated that suggest that molecular calculations could provide a quantitative basis for correlating structure and properties. It is important in such calculations to model intermolecular interactions as accurately as possible in order to account for the drastic changes in liquid crystal behaviour that can result from small alterations to molecular structure. The intermolecular potential used in this work is a full atom–atom potential, which includes repulsive forces, attractive dispersive forces and electrostatic interactions: the potential does not include dipole-induced dipole forces. For simplicity we have assumed that the molecules are rigid: this is certainly an inadequate description of alkyl chains, but further work could include torsional deformations within the framework of our molecular mechanics calculations.

The calculations presented here are only concerned with dimer interactions, and so only short-range effects can be modelled with confidence. Association of molecular dipoles is important in determining dielectric properties, the formation of smectic phases and possibly re-entrant phase behaviour. Our calculations on CB5 and CCH5 confirm experimental results on the relative strength of antiparallel dipole–dipole correlation in these materials. We have also shown that the molecular mechanics technique may be used to explore possibilities for local ferroelectric ordering in liquid crystals.

The calculations on model chiral nematics confirm experimental results that the twist sense alternates as a chiral centre is moved away from the core of a molecule. Other influences of substituent groups near the chiral centre [19, 20] can in principle be modelled by the molecular mechanics method.

Extension of our computational technique to clusters of more than two molecules would involve a large increase in computing time. Another way of accounting for multimolecular interactions, reported in this paper, is to model the environment of a dimer by an ordering potential of suitable symmetry. Thus the dimer interacts with the rest of the fluid via a two-particle pseudopotential. Application of this to a study of nematic phase stability of isomeric core structures suggests that the approach could be useful in planning stragegies for molecular engineering.

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