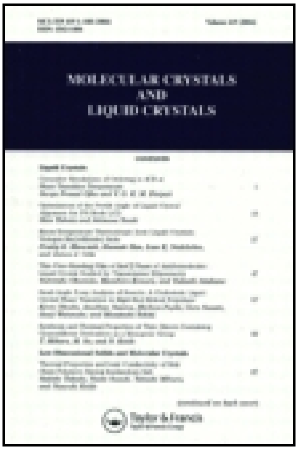

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Computer Simulation of Liquid Crystalline Molecular Asymmetry and its Link to Molecular Design

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Computer Simulation of Liquid Crystalline Molecular Asymmetry and its Link to Molecular Design

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The problem of identifying which molecular features of liquid crystals influence the formation of nematic and smectic phases is complex. Extensive simulation studies of steric and electric systems of thermotropic liquid crystals have had considerable success in simulating liquid crystal phase behaviour employing a variety of hard, soft and realistic models. We report here some links between molecular design of real liquid crystal molecules, using molecular properties calculated from semiempirical quantum techniques and the results of a series of simulation studies of steric and electric molecular asymmetry. The simulation studies allow electric and steric molecular properties to be considered separately, thus illuminating the effect of each.

Keywords: molecular design; computer simulation; semiempirical; asymmetry

1. INTRODUCTION

The link between the design of liquid crystal molecules and the simulation of liquid crystal phase behaviour represents a major challenge despite the substantial increase in the availability of computer processing time. Molecules that form calamitic liquid crystals (mesogens) are in general non-spherical with a rigid rod-like core with flexible end aliphatic chains, often with an overall zigzag molecular shape. To these steric and flexibility asymmetries are added the charge distribution and polarizability anisotropy asymmetries that influence phase behaviour. Simulation studies that involve realistic atom-atom potentials have been undertaken[1-4]. Typically the potential energy function, using some parameters from *ab initio* or semiempirical quantum techniques[5,6], will include bond stretching, bond bending and torsional terms to model flexibility, Lennard-Jones terms to model shape and polarizability anisotropy, and partial electronic charges on each atom. Such simulation studies have been limited by processor time to the order of one hundred molecules and have been undertaken at a few selected state points, commencing with ordered systems. They can provide valuable insights into the molecular features that influence liquid crystal phase behaviour but it can be difficult to distinguish the relative importance of the different terms in the potential energy function.

An alternative approach that has proved successful in studying trends in liquid crystal phase behaviour is to incorporate one asymmetry into an anisotropic potential, either a hard or a soft, Gay-Berne potential[7]. There is a considerable body of simulation work in this area covering a range of asymmetry, for example flexibility[8,9], electric dipole asymmetry[e.g.10-14], electric quadrupole asymmetry[15,16] and steric asymmetry[17].

Simulation studies of hard spherocylinders with flexible tails at one or both ends[8] have been found to stabilize the smectic A phase whilst those of a Gay-Berne core site with two flexible alkyl chains[9] have proved a useful tool in studying conformational distributions.

The addition of permanent dipoles, longitudinal or transverse, is very important because the inclusion of polar lateral or longitudinal substituents is a key element of molecular design. Extensive simulation studies of electric dipolar systems have been undertaken with soft and hard potentials. Soft Gay-Berne ellipsoids[10,11] with an axial electric dipole show short range antiparallel ordering, which is also seen in simulation studies of systems of dipolar hard spherocylinders[12]. The position of the dipole on the major axis was found to influence phase stability. The addition of transverse electric dipoles to a system of rod-like Gay-Berne particles[13] or to a system of hard spherocylinders[14] demonstrated the formation of chains and rings of dipoles in the smectic layer plane. Theoretical studies have predicted that tilted smectic C phases will be determined by dipole interactions[18], by quadrupole interactions[19-21] or by steric interactions[22,23]. In contrast to the results of the simulation of dipolar fluids the addition of axial electric quadrupoles to a system of Gay-Berne particles[15] has led to the simulation of a smectic C phase. Recently the simulation of longitudinal and transverse steric quadrupoles utilising multisite Gay-Berne particles to model zigzag (transverse steric quadrupole[24]) or hour-glass (longitudinal steric quadrupole[24]) shapes has led to the simulation of tilted smectic phases[25].

Whilst experimental measurements of molecular dipoles are available there are few experimental measurements or *ab initio* calculations in the literature of molecular electric quadrupoles[30]. Links between the phase behaviour of real molecules and the results of simulation studies of asymmetric fluids can be made through semiempirical programmes such as MOPAC[5]. We have studied molecules with unusual phase behaviour in the first instance followed by a more general discussion of some links between molecular properties and trends in series. Examples of unusual phase behaviour are the formation of a smectic D phase with cubic symmetry[e.g.26, 27] and of the ferrielectric and antiferroelectric phases formed by the achiral, triangular lath-like compound 1-propylbutyl 4'-(4''-*n*-nonyloxyphenylproprioloyloxy) biphenyl-4-carboxylate[28]. In section 2 the molecular properties of interest obtained from MOPAC are described and in section 3 they are compared with the results of simulation studies, followed by conclusions in section 4.

2. MOLECULAR PROPERTIES

Liquid crystal molecules are too large for accurate *ab initio* calculations of properties such as electric dipole and quadrupole moments. However, semiempirical quantum mechanical packages such as MOPAC are widely used to provide such information in addition to the more usual geometry optimization. MOPAC is adjusted to agree with experiment for a wide range of molecules and properties. For bromobenzene for example, the calculated value[5] for the dipole moment is 3.94 $\times 10^{-30}$Cm, an underestimate of 31% compared with experimental values of 5.67 $\times 10^{-30}$Cm. The calculations were done for a gas-phase optimized geometry obtained with the AM1 Hamiltonian as implemented in the MOPAC program. MOPAC calculates the dipole both as the expectation value of the dipole operator and as the derivative of the energy with respect to the electric field, (the method used to calculate the higher polarizabilities). There is no significant difference between these values.

For the molecules under consideration (Tables 1, 2 and 3) a quadrupole moment for the entire molecule was calculated from the partial charges using the form proposed by Buckingham *et al* [29] shown in equation (1).

$$Q=\frac{1}{2}\begin{pmatrix} \sum q_i(3x_i^2-r_i^2) & 3\sum q_i x_i y_i & 3\sum q_i x_i z_i \\ 3\sum q_i y_i x_i & \sum q_i(3y_i^2-r_i^2) & 3\sum q_i y_i z_i \\ 3\sum q_i z_i x_i & 3\sum q_i z_i y_i & \sum q_i(3z_i^2-r_i^2) \end{pmatrix} \tag{1}$$

where q_i is the partial charge, x_i, y_i and z_i are Cartesian co-ordinates relative to the inertial frame of reference and r_i is the position relative to the origin.

Table 1 compares the results of this calculation and *ab initio* and experimental calculations from MOPAC for the quadrupole tensor with experimental values[30] for some symmetric molecules. It can be seen that agreement is within 17% except for hexafluorobenzene where again there is an underestimate of 49%. The simulation studies with which comparisons are made[10-17] include a range of electric dipole and quadrupole values varying by more than this percentage and so

Molecule	Experimental $Q/10^{-40}\mathrm{Cm}^2$ (Ref. [30])			MOPAC $Q/10^{-40}\mathrm{Cm}^2$		
	Q_{xx}	Q_{yy}	Q_{zz}	Q_{xx}	Q_{yy}	Q_{zz}
Benzene $C_6H_{6\,(\mathrm{IB}^*)}$	-	-	-29.0	13.02	13.02	-26.0
Napthalene $C_{10}H_{8\,(\mathrm{QM}^*)}$	23.9	20.51	-44.4	26.69	21.51	-48.2
Hexafluorobenzene $C_6F_{6\,(\mathrm{IB}^*)}$	-	-	31.7	-7.87	-7.99	15.86
Anthracene $C_{14}H_{10\,(\mathrm{QM}^*)}$	34.7	26.5	-61.0	41.14	29.08	-70.2

TABLE 1 Molecular electric quadrupole moments calculated from MOPAC[5], from *ab initio* calculations and from experiment. For linear molecules the experimental values quote only the Q_{xx} value where x is the major symmetry axis. (IB* = induced birefringence, QM* = quantum mechanical calculation).

Molecule	Quadrupole Moment, $Q/10^{-40}\mathrm{Cm}^2$			Dipole Moment, $\mu/10^{-30}\mathrm{Cm}$		
				x	y	z
I	87.281	0.1963	28.512	-0.035750	-3.4638	-0.020169
	0.1963	-50.246	0.2607			
	28.512	0.2607	-37.035			
II	-81.704	-128.19	-36.129	-9.8132	-20.748	-0.11360
	-128.19	23.638	28.597			
	-36.129	28.597	58.066			
III	-105.49	-158.89	-39.178	-9.9973	-20.657	-1.2450
	-158.89	36.392	28.731			
	-39.178	28.731	69.096			
IV	-192.20	-22.029	-41.596	-13.25	-3.4108	-1.9352
	-22.029	141.61	14.967			
	-41.596	14.967	50.578			
V	-222.33	-17.207	-47.751	-13.128	-3.1128	-2.0183
	-17.207	156.09	16.094			
	-47.751	16.094	66.240			
VI	185.73	-21.478	-144.23	-17.386	-7.9608	-7.9682
	-21.478	-71.469	-10.418			
	-144.23	-10.418	-114.26			
VII	170.33	-0.4878	-145.57	-18.738	-7.1462	-8.6156
	-0.4878	-63.363	-5.7192			
	-145.57	-5.7192	-106.96			
VIII	193.51	14.476	-111.77	-19.132	-5.6758	-9.5196
	14.476	-76.562	-3.7609			
	-111.77	-3.7609	-116.95			
IX	183.62	-76.11	-44.81	-16.358	-11.227	-2.5740
	-76.11	-75.23	-28.77			
	-44.81	-28.77	-108.39			

TABLE 2 Molecule electric dipole and quadrupole moments calculated from MOPAC[5]. Structures are shown in Table 3. The MOPAC values are quoted in the inertial reference frame of the molecules, ordered x, y and z from the smallest to the largest moment of inertia.

encompass any deviation between experiment and calculation. The results of the MOPAC[5] calculation of dipole and quadrupole moments for the liquid crystal molecules considered here are shown in Table 2 with their structures shown in Table 3. All are referred to the centre of mass as origin so that only the first moment, the dipole, is uniquely defined[30,32].

The use of a central electric multipole as a single asymmetric term in a hard or soft potential allows comparison with the overall shape of the real molecule. Its effect on the self-assembly of systems of

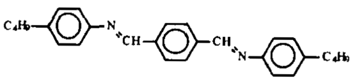
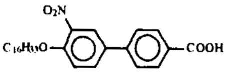
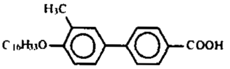
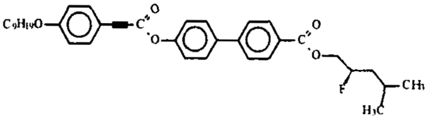
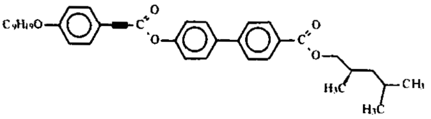
Molecular Structures	
I	
II	
IV	
VI	
IX	

TABLE 3 Molecular Structures from Table 2. Structures III and V are the same as II and IV respectively except that $-C_{16}H_{33}$ is replaced by $-C_{18}H_{37}$. Structures VII and VIII have fluorine replaced by chlorine and bromine respectively.

thousands of molecules can be studied but this method cannot include atom-atom interactions. Realistic atom-atom potentials studied in far smaller systems either include Van der Waals' functions and bond or atom electrostatics or alternatively a distributed multipole analysis where the exact electron density is decomposed into a set of multipoles centred in different parts of the molecule. The latter method reproduces the field created by molecules in a wide region of space and only fails at short distances[31,32].

3. RESULTS AND DISCUSSION

The effect of the transverse electric quadrupole moment on the formation of liquid crystal mesophases has recently been investigated by means of a computer simulation study[16]. A simple model of the molecular interaction employed the addition of a transverse, point quadrupole of varying magnitude to a Gay-Berne potential. A large transverse quadrupole was seen to destabilise the nematic phase and stabilise the smectic A phase. At a sufficiently large value of the transverse dipole a smectic D phase with cubic symmetry was formed on cooling the system, allowing the formation of the favoured 'T' arrangements of quadrupoles in-plane. At present few compounds[e.g.26, 27] are known to exhibit a cubic lattice and little is known about the detailed molecular arrangement. They should probably be labelled 'D' rather than smectic 'D' if the phase has overall cubic symmetry. Some compounds have a strong, lateral ring–NO_2 or –CN dipole and associated quadrupole. It may be the latter that is critical in determining the structure. In order to investigate this Table 2 shows MOPAC calculations of the dipole and quadrupole moments for the molecules that do form a D phase, structures II and III, and for structures IV and V with the lateral ring–NO_2 group replaced by a –CH_3 group. Structures IV and V do not form a D phase. Both the y component of the dipole moment and the yx component of the quadrupole moment are markedly increased in structures II and III compared with structures IV and V. Since simulation studies of transverse dipole moments have shown in-plane chains and rings[13,14] whereas simulation studies of transverse quadrupole moments have shown the formation[16] of a D phase it seems that it may be the increased transverse electric quadrupole favouring the D phase formation.

Goodby[28] *et al* also investigated the effect of changing the polarity of the chiral centre in the (S)-2-chloroalkyl esters incurred by the exchange of a halogen atom for the methyl substituent at the chiral centre. They found that by changing the substituent from fluorine to chlorine to bromine the smectic A* temperature range increases. The substitution has the effect of increasing the transverse dipole and quadrupole of the molecule. Table 2 shows calculations of the electric dipole and quadrupole moment for this series (structures VI-VIII) and for a molecule with the halide group replaced by a methyl group (structure IX) Goodby[28] *et al* inferred that the stabilisation of the smectic A* phase was the result of either increasing polarizability or increasing steric hindrance due to the halogen substituent's increasing Van der Waals' radius. The structures VI-VIII all have a large x direction dipole moment component and a large xz transverse quadrupole component. Structure IX in contrast has a large x and y dipole moment component and large yx and yz transverse quadrupole components for the optimized geometry. While the electronic structure is different from the optimized geometry of the halogenated esters no trend is apparent in the series of three halides that can be linked to the extended smectic A* region. The increased Van der Waals' radius does reflect a trend from fluorine though chlorine to bromine and in this case the effect may be steric.

Steric effects have been seen to simulate real liquid crystal behaviour in two other interesting cases. Goodby[28] *et al* inferred that the formation of a ferrielectric and antiferroelectric phase may be stabilized by the biaxial nature of the achiral, triangular lath-like compound 1-propylbutyl 4'-(4''-*n*-nonyloxyphenylproprioloyloxy) biphenyl-4-carboxylate. Simulation studies have been undertaken[17] of systems of three-site Gay-Berne molecules arranged in a lath-like triangle, constituting a longitudinal steric dipole. The molecules are found to self-assemble into a bi-layer system as the temperature is lowered. The simulation study reinforces the theory that antiparallel ordering within the bi-layer in this case is due to steric effects, as predicted by Goodby[28] *et al* . Bi-layer antiferroelectric stripe domains have also been simulated with axial dipoles[10] but not as yet an antiferroelectric phase.

Structure I, TBBA, has long been of interest in terms of molecular design since it forms a smectic C phase. This has variously been attributed to the transverse dipole, seen in Table 2, or to the molecule's zigzag shape. Studies of a fluid of three-site Gay-Berne zigzag molecules (transverse steric quadrupoles) formed a rippled but not tilted phase. The model utilised a rotation of 20° of the central site with respect to the two end aromatic rings based on a minimized geometry for the molecule. Recently the study has been repeated with a rotation of 30° of the central site and in this case tilted phases have been observed[25]. No tilted phases have yet been simulated with transverse dipolar fluids, again reinforcing the theory that it is a steric effect that is driving the formation of the phase, if a transverse steric quadrupole is sufficient.

CONCLUSIONS

Semiempirical quantum mechanical packages such as MOPAC are widely used to provide information on molecular properties such as electric dipole and quadrupole moments in addition to the more usual geometry optimization. The simulation of longitudinal steric dipoles and of transverse steric quadrupoles mapped on to the optimized geometry of real molecules has reinforced the importance of steric effects in the design of real molecules. The calculation of electric dipoles and quadrupoles has proved illuminating in discussing the driving mechanisms for the formation of the D phase and of the smectic C phase formed by TBBA. Linking molecular design to simulation studies through calculation of molecular properties in packages such as MOPAC has proved useful in indicating the relative importance of steric and electric effects in the formation of phases for selected real molecules.

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