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CONFORMATION ENERGY SURFACE FOR LIQUID CRYSTAL MOLECULES FROM FIRST PRINCIPLES: APPLICATION TO 5CB

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Abstract We have performed first principles molecular dynamics calculations to investigate the structure and conformation of the liquid crystal molecule 5CB which contains a pentane chain joined to two phenyl rings terminated by a cyanide group. We describe the electronic structure by using density functional theory within the generalised gradient approximation for electron exchange and correlation and expand the electronic wavefunctions in a plane wave basis set. Structural optimisation of atomic positions is performed to obtain the relaxed molecular geometry. The relative angle between the two phenyl rings and the angle of the pentane tail is allowed to vary. For each possible pair of angles we calculate the total energy of the structure from which we obtain the energy surface for these conformations. We find the optimum conformation of the molecule is non-planar with a relative angle between the phenyl rings of 31°, in excellent agreement with recent NMR data. The angle of the pentane tail has a small, but significant effect on the energetics of the molecule. We fit accurate intra-molecular potentials for biphenyl and 0CB which can be used in large empirical simulations of liquid crystals. We compare the results with similar calculations performed on liquid crystal fragments.

INTRODUCTION

Investigating the behaviour of liquid crystal phases by computer simulation has now become a common occurrence[1,2,3,4]. There is a large variation in the level of detail which is used to model liquid crystal molecules. These range from rigid rod and ellipsoid-like units to the higher detail atom-atom interactions. Real liquid crystal molecules are however highly structured, low- symmetry flexible objects with complicated intra and inter molecular interactions. The study of more realistic models is valuable for investigating what ingredients are required to reproduce observed liquid crystal behaviour and developing an intuition about liquid crystal behaviour at the microscopic level. However, the fundamental limit of the accuracy of the physical results in any of these models is the potential used to describe the interactions. There have been many successful potentials produced such as the widely used Gay-Berne potential[5] which is an anisotropic form of a the Lennard-Jones potential. These type of potentials require parameters which are fitted to experimentally determined properties.

In this paper, we calculate potential fields for liquid crystal molecules and liquid crystal fragments using large scale quantum mechanical molecular dynamics[6,7] which requirs no experimental input. This method gives very accurate potentials for interaction between atoms and molecules. Here we apply this method to the liquid crystal fragments biphenyl and cyanobiphenyl (0CB) and to the liquid crystal molecule 5CB. We calculate the energy surface from the relative rotations of the phenyl groups and for the alkyl tail of 5CB. We also discuss the change in the potential of biphenyl with the addition of a CN group (0CB) and a pentyl tail (5CB) and assess the transferability of such potentials found from liquid crystal fragments.

METHODOLOGY

We use density functional theory within the generalised gradient and pseudopotential approximations to describe the valence electrons of the molecules. This method is published elsewhere[6,7,8] therefore we only give the details relevant to calculations presented here. We place a molecule (biphenyl/0CB/5CB) in a periodically repeating cell so that we can use a plane wave basis set to describe the electrons. To fully converge the basis set we use plane waves up to an energy of 700eV which gives us about 10^7 basis functions. For each conformation of the molecule, we relax the electrons using a conjugate gradients algorithm. This gives us the total energy of the molecule for that fixed set of atomic positions. This allows us to map out the energy surface of the molecules around given rotational axes which we use to parameterise potentials. The accurate electronic structure calculations are highly computationally intensive and required use of 12000 CPU hours of a 512-node Cray-T3D.

BIPHENYL, 0CB AND 5CB

Molecular Structure

We show in Figure 1, the realxed bond lengths in each molecule. The most notable feature of this it the breaking of the 6-fold rotational symmetry of the phenyl groups in all cases. For 5CB, the C-C bonds lying adjacent to the CN and pentyl groups are shortened by 0.09Å from the relaxed benzene structure. On investigation of the valence electron charge density in these regions, it is found that electrons are moving into these shorter bonds at the expense of the other C-C bonds in the phenyl group. As the CN and pentyl groups are added, this effect becomes larger indicating that there exists charge migration along the molecule (giving $CN^{\delta-}$ and $pentyl^{\delta+}$ in 5CB).

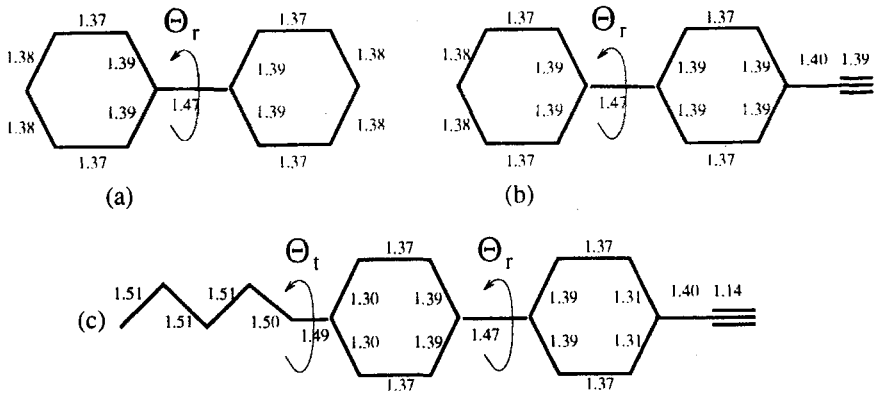

FIGURE 1 Pictures of (a) biphenyl, (b) 0CB and (c) 5CB where we define the angle in which the otherwise rigid units will be allowed to rotate. Also shown are the CC and CN bondlengths in Å. The CH bonds (unshown) are all ~1.08Å.

Using the structures calculated our *ab initio* method we rotate the rigid molecular fragments around the axes shown in Figure 1. The angles are measured relative to the flat molecule. Calculations are required only for angles in the range 0°—180° due to the symmetry of the phenyl groups. We have calculated the total energy for Θ_r in this range for biphenyl and 0CB and present these results in Figure 2(a). The optimum Θ_r for biphenyl and 0CB is 37° and 34° respectively. This is in excellent agreement with recent NMR experiments on 0CB[9]. We also show in this plot a recent calculation using an unconverged basis set[10] which overestimates Θ_r at 44° indicating the need for accurate basis sets in this type of calculation[11].

In figure 2(b) we show the full (Θ_r,Θ_t) energy plot. As can be seen there is a significant dependence on Θ_r from Θ_t indicating that the separate Θ_r/Θ_t potentials should not be decoupled. We find that the conformational energy of 5CB is most sensitive to the relative angle of the phenyl rings. A large energy barrier exists to the free rotation of the phenyl rings at 90°/270° of approximately 24.1kJ/mol. However, the equilibrium structure at Θ_r =31° and Θ_t =90° is a rather shallow minimum especially in the direction of the tail position (i.e. a line of constant Θ_r indicating that the pentyl group is relatively free to vibrate around this minimum. The height of the potential barrier to tail rotation (at the optimum relative angle of the rings) is 5.8kJ/mol which occurs at 0°/180° indicating that the flat molecule is actually an unstable equilibrium position.

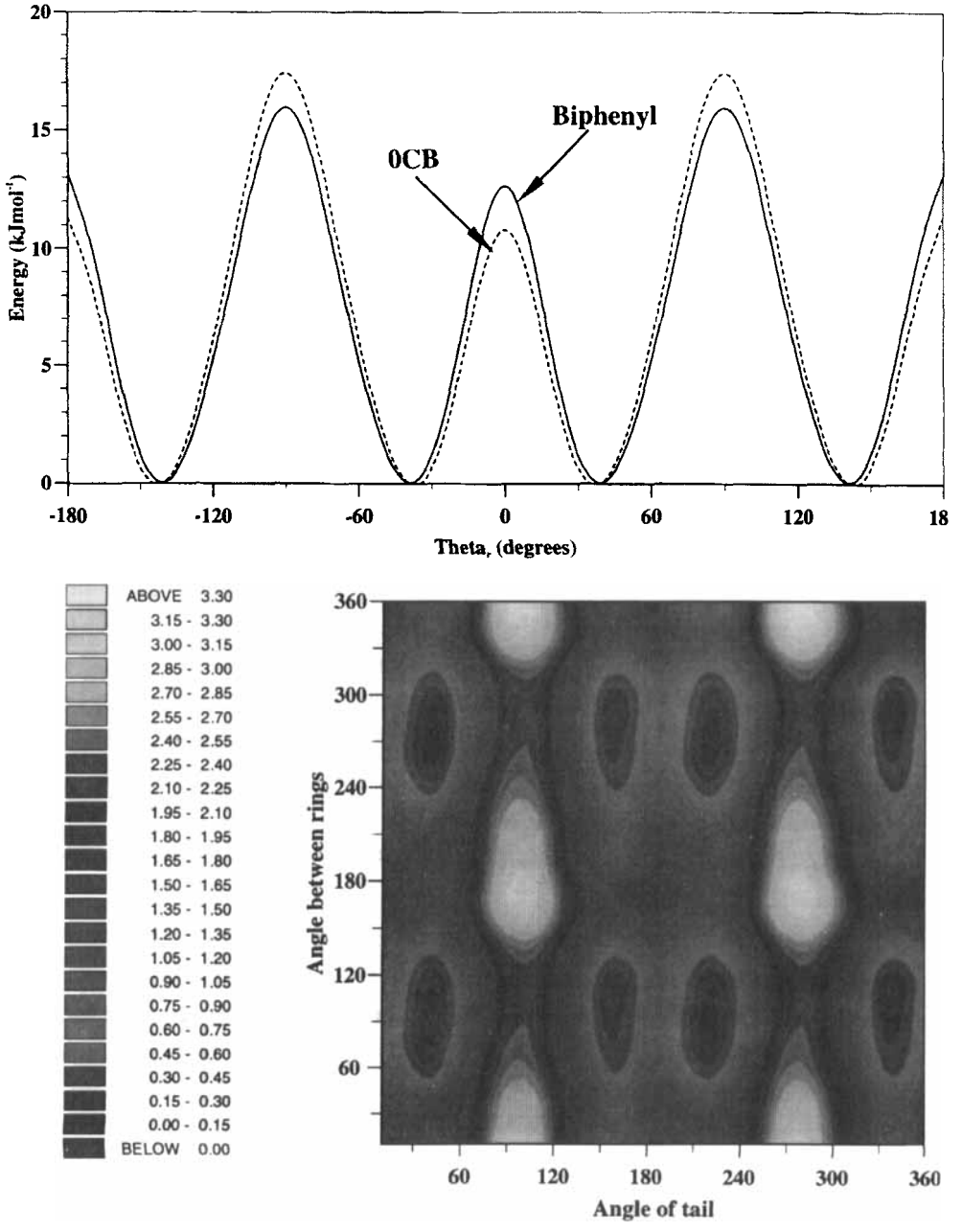

FIGURE 2 In (a) the relative energies of biphenyl and 0CB against Θ_r are shown. In (b) we show the Θ_r/Θ_t probability surface for 5CB where x on the scale indicates that the probability of finding that conformaiton is 10^{-x} times less likely that the optimum Θ_r=31° and Θ_t=90°. Fits to analytic forms of these potentials are given in Tables I and II. (See Colour Plate I).

Derivation of Intra-Molecular Potentials

In order that the *ab initio* potentials we have calculated here can be used in traditional classical molecular dynamics schemes we have parameterised each one. For the biphenyl and 0CB potentials we have fitted them to a series of cosines (there are no sine terms by symmetry) thus:

$$V(\Theta_r) = \sum_{n\in\{S\}} c_i \cos(\Theta_r) \qquad (1)$$

where the coefficients c_i are shown in Table I and {S} is the set of indices which are to be summed over. We find that about 5 terms are required to accurately fit the potential which is in contrast to an experimental attempt to fit such a potential[9] where 2 are used. We have also fitted an analytic form[12] for a $V(\Theta_r, \Theta_t)$ potential for 5CB which is

$$V(\Theta_r,\Theta_t) = \sum_{k,l\in\{S\}} a_{kl} \exp\left(\frac{-2\pi i(l\Theta_r + k\Theta_t)}{10\times 36^2}\right) \qquad (2)$$

and the coefficients are given in Table II.

TABLE I Coefficients for the potentials for biphenyl, 0CB and 5CB. These coefficients will give the energy for a given Θ_r in kJ/mol.

i	c_i for Biphenyl	c_i for 0CB
0	6.84858	6.89641
2	-2.43155	-4.00950
4	6.94367	6.74595
6	0.81483	0.74868
8	0.71154	0.71462
10	0.02516	0.02354
12	0.09522	0.08927

TABLE II Coefficients for the potential $V(\Theta_r,\Theta_t)$ describing the relative angle between the phenyl rings and the angle of the pentyl tail.

Coefficient for $V(\Theta_r,\Theta_t)$	Value (kJ/mol)
$a_{0,0}$	9.2760+0.0000i
$a_{0,2}=a^*_{0,34}$	1.6622-0.4605i
$a_{0,4}=a^*_{0,32}$	-0.0704-0.3556i
$a_{0,6}=a^*_{0,30}$	-0.2513-0.0311i
$a_{2,0}=a^*_{34,0}$	-2.9485-0.0647i
$a_{2,32}=a^*_{34,4}$	0.2169+0.0466i
$a_{2,34}=a^*_{34,2}$	0.1666+0.2258i
$a_{4,0}=a^*_{32,0}$	1.8287-0.0381i
$a_{4,32}=a^*_{32,4}$	0.1803+0.0657i
$a_{6,0}=a^*_{30,0}$	0.3344-0.0106i

CONCLUSIONS

We have applied an accurate quantum mechanical molecular dynamics method to the liquid crystal molecule 5CB and the liquid crystal fragments biphenyl and 0CB. There is subtle, but significant breaking of symmetries in each of the molecules which is associated with charge transfer in the molecules. This shortens/strengthens the C-C bonds in the phenyl groups which lie along the long axis of the molecule. Our method also allows us to calculate the total energy of each molecule for a given set of atomic positions. From this we have been able to fit accurate intra-molecular potentials which describe the relative orientation of the phenyl rings and pentyl tail.

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