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Properties of liquid crystal molecules from first principles computer simulation

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We explore the valence charge distribution, equilibrium geometry and harmonic force fields of the 4-pentyl-4'-cyanobiphenyl (5CB) molecule and the benzene (C_6H_6) molecule, which provides an important mesogenic fragment, using first principles techniques adapted from large scale electronic structure calculations of periodic solids. We present for the first time accurate structural data for the isolated 5CB molecule and observe subtle broken symmetries relative to the constituent mesogenic fragments. The dynamic properties of these molecules are determined by diagonalization of dynamical matrices, the elements of which are obtained directly from quantum mechanical Hellmann–Feynman forces. Results for both molecules are in excellent agreement with available spectroscopic data, and for benzene are comparable to the most accurate quantum chemistry calculations to date. For 5CB we also present values for the molecular dipole and quadrupole moments.

1. Introduction

For many purposes, computer simulation of thermotropic liquid crystalline phase behaviour can be performed using very simple rigid rod models for the constituent molecules [1, 2]. However, it is becoming increasingly clear that certain liquid crystalline properties are sensitive to chemical details and molecular flexibility [3]. The origins and effects of these are explicitly absent from excluded volume models. There is, therefore, growing need for efficient and accurate molecular-level simulations both as an aid to the synthesis of improved materials and as an essential step in the development of atomistic potentials for the simulation of bulk liquid crystalline phase behaviour.

The development of reliable parameter-free methods for the determination of molecular properties has been an enduring challenge in computational chemistry. There remain several distinct but related strategies aimed at addressing this problem, each of which adopts a different level of sophistication. However, nearly all of these share a number of common features and objectives. Specifically, a principal goal of quantum chemical simulations is the ability to calculate from essentially first principles (without any experimental input), the energy and electronic charge distribution in a molecule and thereby determine bond character, equilibrium geometry, energy differences between various molecular conformations and vibrational properties (harmonic and anhar-

monic force fields). Vibrational properties in particular, provide an important test of the accuracy of first principles calculations as they give direct information about bond strengths. The ability to predict the vibrational properties also supports the exploration of chemical reaction pathways, helps identify molecules and provides data for statistical thermodynamics.

A nearly universal starting point for *ab initio* calculations in computational chemistry is the expansion of the molecular electronic wavefunction in terms of localized atomic-like basis functions. When using localized basis sets, whatever the type, it is necessary to optimize the basis set for each molecular system under consideration. At the outset any calculation is inherently dependent on the effectiveness with which the basis set spans the real molecular electronic wavefunction. Also, when localized basis sets are used, the optimization of molecular geometry under the influence of quantum mechanical forces can be complicated by the need to evaluate correction terms which are due to the basis set itself. A further difficulty arises in the determination of force fields or vibrational frequencies. In conventional methods, the calculated mode frequencies are slowly convergent with respect to basis set size and therefore require extremely large numbers of basis functions. This has severely limited the size of molecules which are amenable to reliable, parameter-free force calculations.

In an attempt to avoid these basis-set-dependent difficulties, considerable efforts have been made in the field of electronic structure calculations on condensed

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matter systems as a result of the combined use of density functional molecular dynamics, plane wave basis sets and parallel computer architecture. In its most general form, density functional theory states that the total energy of a system, E , is a functional of the electron density $\rho(\mathbf{r})$ which experiences the influence of the nuclear charges which are located at coordinates R_n . The ground state electron distribution is determined by a stationary condition on E with respect to the charge density. This technique has now been demonstrated to be capable of predicting many bulk physical properties of crystalline and amorphous solids [4, 5], defects [6], liquids [7, 8] and solid–solid phase transitions [9]. It has also been applied to the study of interfaces, surface reconstruction [10–12] and chemisorption [13].

In this paper we adapt this method in order to study the physical (structural, electronic and vibrational) properties of isolated molecules of 5CB and also of benzene as an example showing the accuracy of our methods. The paper is organized as follows. Firstly we describe the general computational strategy which is used to perform the calculations. We then discuss the application of the method to these molecules to determine structural and vibrational properties.

2. Calculation method

2.1. Molecular electronic structure

The details of this method as applied to infinitely extended crystals can be found in [14, 15]. In this section we will give only those details which are relevant to the molecular case. A plausible initial molecular geometry is chosen for an isolated molecule. The molecule is then placed in the centre of a periodically repeating supercell and periodic boundary conditions are enforced. The size of the supercell must be taken to be sufficiently large so as to ensure the molecules are effectively isolated from each other. The molecular valence electron wavefunction is then expanded in a plane wave basis set up to a cut-off energy. The main approximations which enter the calculation are as follows. Firstly, in this implementation the interaction between valence electrons and ions is represented by an *ab initio* pseudo-potential [16] which for the constituent atoms in the present case is determined according to the scheme of Lin *et al.* [17]. The implicit assumption is that the atomic core electrons do not participate in molecular bonding (ie. in the case of 5CB, we assume that the $1s^2$ electrons in C and N are not involved in bonding). Secondly, the many-body effects of exchange and correlation are incorporated through the local density approximation which states that the exchange and correlation energy of an electron distribution at a given density can be treated as equivalent to that of a uniform electron gas at that density. In the present implementation, we

also incorporate gradient corrections to the local density functional. Details of this generalised gradient approximation (GGA) can be found in [18].

The use of periodic boundary conditions allows for the expansion of the molecular electronic wavefunction in terms of a delocalized plane wave basis set. Specifically, the wavefunctions of a given electron are of the form

$$\psi(\mathbf{r}) = \Omega^{1/2} \sum_j C_j \exp[i(\mathbf{k}_j + \mathbf{G}) \cdot \mathbf{r}] \quad (1)$$

where Ω is the system volume. The vector \mathbf{G} is (by analogy with the electronic structure of perfect crystals) a reciprocal lattice vector. It is well defined in this context as a result of the periodic boundary conditions. The C_j are therefore the expansion coefficients. According to this formalism, the molecular electronic wavefunction is described by a Fourier series rather than as a linear combination of atomic orbitals.

The size of the basis set (number of plane waves) required to span the molecular wavefunction is determined by the depth of the ionic pseudo-potentials which are used to represent the electron–ion interactions. The advantages of a plane wave basis set are that its convergence properties toward completeness are easily tested, it is not biased toward any particular type of chemical bond, the same basis set is used for all molecules and force calculations are simplified.

The artificial periodicity which results from the boundary conditions allows the electronic problem to be handled exactly as in the case of a periodic crystal. Specifically, the electronic energy levels are spread out to form a crystal-like band structure which must be evaluated at one or more discrete points in the Brillouin zone. The wave functions are then infinitely extended Bloch functions which are encountered in elementary treatments of the electronic structure of solids. In the present work only a single point (Brillouin zone centre) is required as the sampling point. Finer sampling is not necessary since electronic bands are dispersionless for isolated molecules. This choice of sampling point also allows for the use of real (as opposed to complex) wavefunctions which halves the computational cost of the calculation.

The coefficients of the plane waves in the expansion are then used as variational parameters until the lowest energy electronic configuration is found for a given set of ion positions. Several minimization algorithms are available which include steepest descents, simulated annealing and pre-conditioned conjugate gradients. We employ the latter method as it has been found to lead to faster convergence. The details of the algorithm can be found elsewhere [14]. In all cases, the minimization

is subject to the constraint that the electron wavefunctions be kept orthogonal to each other.

The valence electron charge distribution in the molecule $\rho(\mathbf{r})$ can then be constructed from the wavefunctions by evaluating

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2 \quad (2)$$

The charge density is computed on a discrete fast-Fourier-transform grid.

2.2. Optimization of molecular geometry

The Hellmann–Feynman force on each atom in the molecule is calculated and the atoms are moved under the influence of these forces until no force component exceeds some tolerance. If structure optimization is all that is required, a typical value of the residual forces is $0.1 \text{ eV } \text{\AA}^{-1}$. The calculation of vibrational frequencies, however, demands convergence of the forces to much greater precision, typically $0.001 \text{ eV } \text{\AA}^{-1}$. For these calculations, molecular point group symmetry is not enforced.

The wide variety of different molecular conformations correspond to local minima of the energy functional with respect to rotations of molecular segments about bond directions. The conjugate gradients minimization routine which we employ will not necessarily locate the global minimum of this functional. However, what is often even more important than the global minimum is the energy difference between competing conformations. Assuming the bond lengths do not change between different conformations, the energy of different conformations can be estimated without subsequent ionic relaxation. We will discuss the implications of this for the specific case of liquid crystals in a subsequent paper [19].

2.3. Determination of the harmonic force field

Once the equilibrium structure has been determined, the dynamical properties can be investigated by displacing each atom in the molecule and calculating the resultant forces on all atoms. The magnitude of the displacements must be chosen such that they are small enough to be within the harmonic regime but large enough to give rise to measurable restoring forces. This procedure can be used to construct a dynamical matrix of dimension $3N \times 3N$, where N is the number of atoms in the molecule. Subsequent diagonalization of this matrix gives directly all $3N-6$ normal mode vibrational frequencies and their associated eigenvector displacement patterns [20]. In principle, this approach can be used to investigate the anharmonic force field as well.

3. Results and discussion

3.1. Benzene

The motivation to study benzene prior to a mesogenic molecule is that it has been studied in considerable detail by a variety of quantum chemical methods and it is therefore an excellent test case for our simulation method. The related biphenyl group is also a constituent of many liquid crystal molecules including 5CB. Benzene exhibits regular hexagonal planar symmetry with six carbon atoms joined by σ bonds and six remaining p-orbitals which overlap to form a delocalised π bond over all six carbon atoms.

We began the calculation with a trial configuration in which the C–C and C–H bonds were 1.33 and 1.00 \AA , respectively. The molecule was placed in a periodically repeating supercell having dimensions $9 \times 9 \times 5 \text{ \AA}^3$ which gave a separation of at least 5 \AA between any pair of atoms in neighbouring cells. We test the total energy convergence with respect to unit cell size and find this cell size to be adequate to ensure the molecules are isolated. The plane wave energy cut-off was set at 700 eV for which we found energies were converged to better than 0.001 eV per atom. The structural optimization proceeded until the residual forces on the ions were below $0.001 \text{ eV } \text{\AA}^{-1}$. This gave a relaxed structure in which the C–C and C–H bond lengths were 1.396 and 1.089 \AA , respectively (as compared with experimental bond lengths of 1.393 – 1.398 \AA and 1.081 – 1.090 \AA , respectively [21]). Note that this is a 0 K calculation, therefore temperature effects such as anharmonic bond-lengthening at higher temperatures are not included. A summary of these results and those obtained by other methods is given in table 1. To within our numerical accuracy, all C–C bonds are of equal length as are all C–H bonds although no external constraint is applied to enforce this symmetry.

This relaxed structure was then used to determine the vibrational properties according to the method discussed previously. The results of this calculation for the vibrational properties are summarized in table 2.

Previous results have shown that Hartree–Fock calculations (neglecting correlation) substantially overestimate the in-plane benzene vibrational frequencies for all basis sets and that the largest discrepancies are found

Table 1. Calculated and experimental geometries for Benzene.

Method	$r(\text{CC})/\text{\AA}$	$r(\text{CH})/\text{\AA}$	Ref.
DFT-PW	1.396	1.089	Present work
CCSD	1.393	1.082	[22]
MP2	1.398	1.086	[23]
MP2	1.390	1.079	[24]
MP2	1.390	1.080	[25]
exp.	1.393–1.398	1.081–1.090	[24]

Table 2. Experimental vibrational frequencies for Benzene. The notation TZ2P+f stands for ‘triple-zeta segmented basis set with polarization functions including one of f-type’. The notation cc-VTZ stands for contracted, correlation-consistent valence triple zeta set.

Sym.	Obs. ^a / cm ⁻¹	DFT ^b PW	MP2 ^c (631G)	MP2 ^c (631G(dp))	MP2 ^d (TZ2P+f)	CCSD ^e (cc-VTZ)	DFT ^f (631G*)
A _{1g}	994	1006	1000	1015	1018	1012	1051
A _{1g}	3191	3260	3213	3240	3242	3228	3114
A _{2g}	1367	1351	1412	1367	1374	1391	1318
E _{2g}	608	597	632	610	608	613	606
E _{2g}	3174	3208	3179	3215	3217	3204	3096
E _{2g}	1607	1607	1626	1645	1637	1672	1645
E _{2g}	1178	1181	1234	1199	1195	1207	1157
B _{1u}	1010	1008	1046	1009	1039	1025	1017
B _{1u}	3174	3199	3173	3204	3218	3189	3092
B _{2u}	1309	1339	1377	1451	1461	1304	1411
B _{2u}	1150	1120	1229	1173	1178	1166	1129
E _{1u}	1038	1042	1073	1063	1074	1071	1043
E _{1u}	1494	1476	1527	1509	1515	1528	1475
E _{1u}	3181	3224	3203	3231	3238	3221	3108
B _{2g}	990	993	—	—	—	—	—
E _{2u}	967	962	—	—	—	—	—
B _{2g}	707	722	—	—	—	—	—
E _{2u}	398	399	—	—	—	—	—
A _{2u}	674	667	—	—	—	—	—
E _{1g}	847	833	—	—	—	—	—

^a [23]. ^b Present work. ^c [26]. ^d [25]. ^e [22]. ^f [27].

for the CH stretch modes [23, 26]. Second-order Moller–Plesset theory (incorporating correlation as a perturbation) improves the agreement with experiment, but the results evidently depend strongly on the basis set used. Also MP2 methods are known to have difficulty in handling multiple bonds which occur in the carbon frame of benzene [22]. Notably, the MP2 method fails particularly badly for the B_{2u} mode when large (TZ2P+f) basis sets are used. A more accurate treatment of electron correlation using coupled-cluster single and double excitations (CCSD) is very computationally demanding but has been performed for benzene using valence triple-zeta basis sets [22] and the results are also shown.

Comparing DFT with correlation-corrected HF methods using localized basis functions, we note that the results are broadly similar. However, the sources of error in both cases are different: in our DFT implementation, the GGA neglects non-local effects in exchange and correlation, while in the HF methods the non-self-consistent treatment of energy and forces is likely to be a significant source of error. In comparison with MP2 calculations, it is clear that our DFT-PW calculations give results significantly closer to experiment. This is probably related to convergence of the basis set as the choice of basis is clearly important for the MP2 studies. In what follows we will treat a liquid crystal molecule in which carbon adopts many different bonding config-

urations—a system for which the choice of basis function would be extremely difficult.

3.2. 5CB

3.2.1. Molecular structure

We have shown that our *ab initio* method for calculating molecular structure and harmonic force fields gives excellent agreement with experiment for benzene which gives us confidence to apply them to the more complicated 5CB molecule where experimental measurements are more difficult to obtain. Convergence of energy and forces for the 5CB calculation was similar to that obtained for benzene. The plane wave energy cut-off was also the same as was the minimum distance between atoms in adjacent cells. The calculated equilibrium bond lengths and angles for 5CB are shown in figure 1. We note that the six-fold rotational symmetry of the phenyl groups has been broken by a contraction along the axis of the molecule. The C–C bonds parallel to the long axis of the molecule shorten to approximately 1.37 Å while the rest are in the range of 1.38 to 1.39 Å. This differs from the standard model of aromatic compounds where phenyl groups are expected to preserve ideal sixfold symmetry. It is also interesting to note that the C–C–N bond angle differs from 180° by bending towards the tail by nearly 2°. This is well outside our numerical noise (which is less than 0.1° based on our convergence tests) and we believe that this departure from linearity

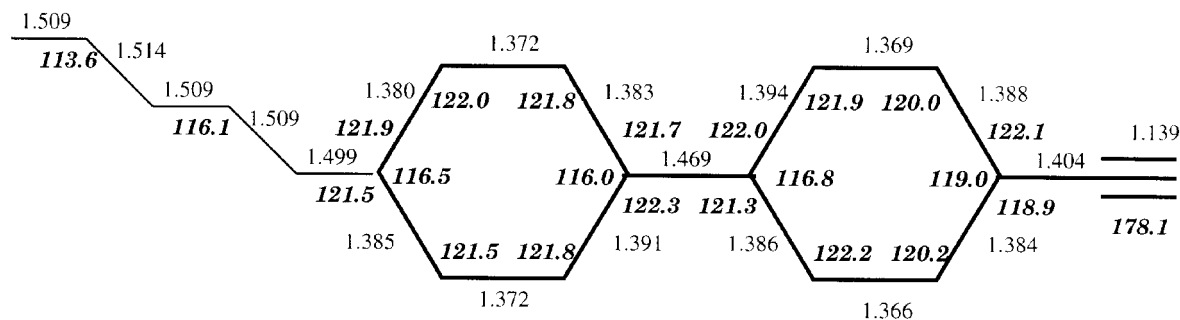


Figure 1. Bond distances and selected bond angles as calculated by relaxation under the influence of Hellmann–Feynman forces for the planar conformation of 5CB. Note that the six-fold symmetry of the constituent phenyl rings is broken in the molecular environment. This relaxed structure was used as the starting point for the normal mode calculations which are described later.

is a consequence of the intramolecular charge distribution as evident from the high dipole moment (discussed in the following section).

3.2.2. Electronic properties

To explore the electronic structure in more detail, we have examined the valence electron charge density which is shown in figure 2. From this electronic charge distribution and the relaxed atomic positions we have determined the molecular dipole moment and find it to be 7.1 D and directed along the major molecular axis.

We have also performed a multipole expansion to extract the molecular quadrupole. There is no unique definition of the quadrupole which essentially measures deviation from spherical symmetry. We define a quadru-

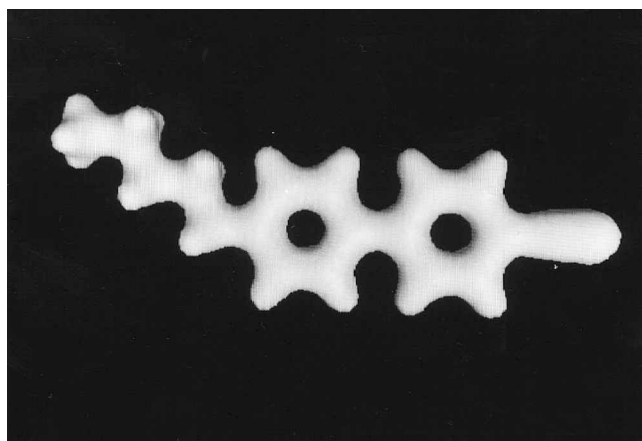


Figure 2. Calculated valence charge distribution for a 5CB liquid crystal molecule as reconstructed from the electron wavefunctions corresponding to occupied bands. The two phenyl groups, hydrocarbon chain and cyano end group are clearly visible. The charge density is evaluated on a discrete grid. A 700 eV cut-off was used for this calculation which results in a basis set containing 2.5 million plane waves. The entire calculation (including structural relaxation) took six hours on a 256 node CRAY-T3D.

pole tensor to be

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

where q_i is the electronic or ionic charge and x_i , y_i and z_i are Cartesian coordinates and r is the position relative to some origin. Diagonalization yields the quadrupole moments relative to the principle axis of the molecule. These are $-0.657 \ -0.271 \ 0.928 \ ea_0^2$.

3.2.3. Molecular vibrations

In figure 3 we show the frequencies of all normal modes as calculated by our *ab initio* method. The calculated frequencies are shown as tick marks along the bottom of the graph. On the plot we also show the results of room temperature Raman scattering measurements. To collect the Raman spectrum we used the 6764 Å line of a Kr^+ laser as the excitation source which gives a power of approximately 90 mW at the sample. A Coderg T-800 triple grating spectrometer was used in 90° scattering geometry. A count time of 5 s per data point was used. We have not performed a full symmetry analysis of all the modes and we therefore only compare frequencies. In general we find a large number of modes with frequencies up to about 1630 cm^{-1} . On examination of the eigenvectors for these vibrational modes, we find that these correspond to molecular bond bending and torsional modes. The calculation also shows good agreement at the higher frequencies near 3000 cm^{-1} which is dominated by C–H stretching modes. In between these two regions we calculate two more modes having frequencies of 2054 and 2255 cm^{-1} . Upon examination of the calculated eigenvectors, the former of these modes is associated with a pure C≡N stretch. The latter mode is not observed in our spectrum and we conclude that it is Raman silent. Since our calculation does not include

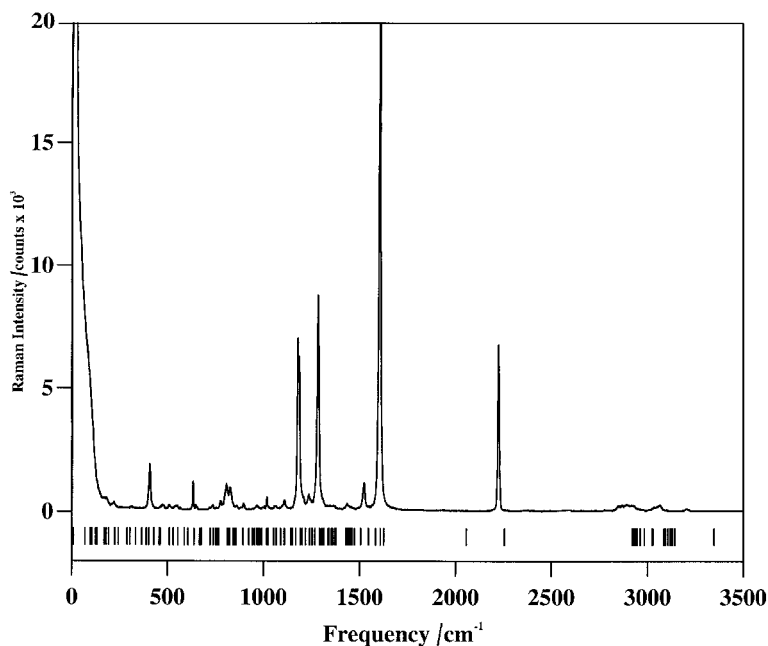


Figure 3. The calculated vibrational frequencies for an isolated molecule of 5CB are shown as vertical tick marks running along the bottom of the figure. Also shown for comparison is the room temperature Raman spectrum of 5CB.

temperature effects, we would expect the theoretical frequencies to overestimate the experimental values. This effect is most pronounced in the high frequency regime. We have not attempted to calculate the Raman line intensity here as this requires the molecular polarizability which, in principle, can be calculated using our quantum mechanical technique, but is not trivial for such a large molecule.

4. Summary and conclusions

In this paper we have applied algorithms which are normally used in first principles electronic structure calculations on perfect infinite crystals in order to study the properties isolated benzene and 5CB molecules.

We have shown that the DFT-PW method is capable of determining electronic, structural and dynamic properties of liquid crystal molecules and mesogenic fragments to a level of accuracy previously attainable only for very small molecules. Since no experimental input is required, the technique can be applied to as yet unsynthesized molecules with the same level of reliability and can thereby contribute to the exploration of structure-property relationships in liquid crystals.

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