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Structure and properties of isolated liquid crystal molecules: jet spectroscopy and *ab initio* calculations of 4-cyanobiphenyl

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We explore the structure, torsional frequencies and electronic properties of the gas phase 4-cyanobiphenyl molecule, a prototypical liquid crystal core fragment, in its ground and first excited singlet electronic states. We employ a methodology which combines *ab initio* quantum mechanical calculations and fluorescence spectroscopy of laser-desorbed, jet-cooled molecules. The aim is to test the predictive power of parameter-free calculations of structure and dynamics in an experimental environment which is similar to the computational conditions of low thermal activation and negligible intermolecular interaction. Both spectroscopic and computational results indicate that very large molecular conformational changes accompany the optical $\pi \rightarrow \pi^*$ transition. These are found to have a significant influence on the molecular flexibility and electronic polarity.

1. Introduction

Elucidating the relationship between molecular structure and macroscopic material properties of liquid crystals has been a longstanding but, as yet, unrealized objective. Over several decades, a number of empirical trends, which relate molecular and macroscopic properties, have been established. In general, however, these are unable to predict quantitatively condensed phase properties from known molecular constituents. Computer simulation is therefore finding an increasingly influential role in placing empirical structure–property relationships on firm theoretical foundations. For example, it has been recognized for some time that computer simulation, using very simple molecular models of liquid crystals [1], is capable of accounting for various types of orientational order [2], and aspects of anisotropic diffusion [2], elastic response [3], viscosity [4] and even pretransitional phenomena [5]. It is equally well known, however, that chemical alterations in molecular structure can lead to large differences in macroscopic properties [6] and that the condensed phase environment has a large influence on molecular structure [7]. As a result, there has been a major recent effort aimed at incorporating greater chemical detail into computer models of liquid crystals [8]. One of the most promising routes to emerge has been the application of *ab initio* methods to derive properties (intramolecular potentials) that can then be used in consequent condensed phase simulations [9–11]. A difficulty with this approach is that the most reliable *ab initio* simulations are performed on isolated molecules at effectively zero temperature. These conditions, while natural for the derivation of intramolecular potentials, are far from those normally encountered in experimental measurements. Moreover, condensed and vapour phase spectroscopies, while very informative in principle, have serious limitations when applied to large, relatively flexible molecules. In the condensed phase, the structure, and hence vibrational properties, of the molecule are perturbed, relative to the gas phase, by intermolecular interactions. In the vapour phase, the large populations of low frequency modes result in the spectrum being congested and analytically intractable due to the overlap of numerous hot band transitions. As a result, direct comparison between *ab initio*-derived results and experiment has so far been lacking.

In this paper we explore the molecular structure, flexibility and electronic properties of 4-cyanobiphenyl, using a methodology which combines *ab initio* computation and fluorescence spectroscopy of laser-desorbed molecules cooled in a supersonic jet. The experimental

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molecular environment is similar to the corresponding conditions of the calculation. A fairly large molecule, of say twenty or more atoms can be cooled in a supersonic expansion to around 50 K vibrationally and 10 K rotationally, while remaining in the gas phase.

The choice of 4-cyanobiphenyl is motivated by several considerations: (i) It is a fragment of some of the most well-studied liquid crystal molecules including 4′-pentyl-4-cyanobiphenyl (5CB, a room temperature nematic) and 4′-octyl-4-cyanobiphenyl (forming both nematic and smectic phases); (ii) it is flexible, having a single torsional degree of freedom about the central ring–ring bond and (iii) the cyano terminal group introduces a strongly dipolar segment which influences the condensed phase behaviour. The unsubstituted biphenyl molecule has been the subject of a number of previous studies: in the gas phase, in solution and in the solid state. The introduction of the cyano substituent is expected to perturb the electron distribution in the ring system and may consequently perturb the torsional behaviour.

The torsional structure of biphenyl is determined primarily by its molecular environment. In the crystal the molecule is known to be planar [12], while in the vapour phase it is twisted with a dihedral angle of 42° [13]. The equilibrium structure in solution is known to have an intermediate twisted form, with a dihedral angle of 20°–35° depending on the solvent. Though the gas phase dihedral angle is well known, the exact form of the ground state torsional potential has yet to be determined unambiguously. Several techniques have been employed to this end. An analysis of overtone stretching frequencies in the Raman spectrum has led to a value of $25.25\,\mathrm{cm}^{-1}$ for the torsional frequency [14]. Fluorescence emission experiments on deuteriated biphenyl return $58\,\mathrm{cm}^{-1}$ [15] for this quantity, while an analysis of sequence and hot bands in the mass-resolved multiphoton ionization spectra give $50\,\mathrm{cm}^{-1}$ [16]. These results do, however, require a certain optimistic interpretation of the data. Barriers to internal rotation have been reported in the range 2–$3\,\mathrm{kJ\,mol}^{-1}$ to tens of $\mathrm{kJ\,mol}^{-1}$, from parameterization of experimental data. But in the absence of the torsional spacings in the ground state, there is nothing to support any claim.

Similar problems are encountered in the elucidation of the first excited singlet (S_1) state potential. The torsional frequency is known from multi-photon ionization experiments (MPI) [15, 17]. The long progressions in the torsional mode imply a large change in the torsional coordinate between the S_0 and S_1 states. Gas phase Raman experiments show a positive shift in the inter-ring stretching frequency in both the S_1 and T_1 states relative to the S_0 state [18], and this has been explained by a strengthening of the inter-ring bond on electronic excitation. Indeed simple molecular orbital schemes considering the HOMO and LUMO predict that biphenyl undergoes a quinoidal type distortion to both rings on excitation, and that the central C–C bond does indeed acquire more double bond character [19].

The aim of this work is to introduce the combination of *ab initio* electronic structure calculations and jet fluorescence spectroscopy as a viable method by which to determine and test intramolecular potentials for liquid crystals. Specifically, we explore the ground and excited state structures, torsional frequencies (flexibility) and electric dipole moments for 4-cyanobiphenyl and thereby examine how these properties are influenced by optical transitions in the molecule.

2. Experimental

In a conventional supersonic expansion, the molecule of interest is seeded in a monatomic carrier gas and expanded through a small nozzle. The expansion cools the translational degrees of freedom of the gas mixture, and, in the post-nozzle region of the expansion, collisions between molecules result in the energy stored internally as vibrations and rotations being partitioned into translation. Thus the translational bath acts as a refrigerant for the other degrees of freedom. As the expansion continues the density of the gas drops until eventually the number of collisions tends to zero and the internal degrees of freedom are fixed. This is called the free jet region and it is in this portion of the expansion that high resolution spectroscopy is carried out [20, 21].

The technique we employ differs slightly from the conventional method in that we use laser desorption to seed the molecular beam. The experimental arrangement has been described previously [22]. The 4-cyanobiphenyl sample was obtained from Merck Ltd and used without further purification. The solid sample was vapourized using a pulsed TEA CO_2 laser (Alltec 854MS) and the resulting vapour entrained in the jet via an extension block fitted to the pulsed supersonic valve (General Valve Corporation Series 9). The main advantage of laser desorption over thermal vapourization is that it allows thermally labile compounds to be investigated, as desorption occurs without molecular decomposition [23].

The jet-cooled molecules were investigated by laser-induced fluorescence (LIF) spectroscopy. The fluorescence is excited by a tunable Nd:YAG-pumped dye laser; the laser beam intersects the molecular beam in the free jet region, about 8 mm downstream of the nozzle. The wavelength of the dye laser is tuned and the undispersed fluorescence collected by a photomultiplier tube (Hamamatsu R928) and processed by a gated integrator (SRS 345). A plot of fluorescence intensity versus excitation wavelength gives the fluorescence excitation spectrum.

3. Computational method

For the *ab initio* calculations, we have used Amsterdam Density Functional (ADF) code [24, 25] which is a general purpose code based on density functional theory (DFT) [26] for the calculation of the electronic structure of polyatomic systems. The program uses a basis set comprising Slater-type orbitals. We have used a basis set of double-zeta quality, which includes polarization functions on the C and N atoms. Comparative calculations using larger basis sets were also performed, and we found the differences in optimized geometry and relative energy to be minimal. The core 1s electrons of C and N atoms were frozen in the calculations. The Vosko–Wilk–Nusair form of the Local Density Approximation (LDA) [27] was used. Non-local (gradient) corrections to account for the over-binding of the LDA were those of Perdew and Wang [28]. We found that optimized parameters, particularly the dihedral angle between the two phenyl rings, were particularly sensitive to optimization criteria. As a result of this, the optimizations were continued until the changes in energy and Cartesian coordinates were less than 0.0001 Hartrees Å^{-1} and 0.001 Å, respectively.

The calculation procedure involved geometry optimization at successive constrained dihedral angles; that is, the angle between the two phenyl rings. The overall dihedral angle was the only constraint; all bonds and angles comprising the dihedral were free to relax. The dihedral angle was stepped at intervals of 4°, close to the potential minima, and 10° over the remainder of the potential surface.

4. Results and discussion

4.1. *Laser-induced fluorescence excitation spectrum*

The LIF excitation spectrum shows transitions between the ground electronic state, S_0 (a singlet state in which all the orbitals are doubly occupied) and the first excited singlet state, S_1 (where the two highest orbitals are both singly occupied by electrons with antiparallel spins). The excitation spectrum of jet-cooled laser-desorbed 4-cyanobiphenyl is shown in figure 1. The spectrum is dominated by a progression of vibronic bands which correspond to transitions between the $v''=0$ level of the ground electronic state and progressively higher vibrational levels, v', in the S_1 state. The progression is essentially harmonic with a fundamental frequency of 56 cm^{-1}. Such a low frequency leads us to assign the progression-forming mode as the inter-ring torsion, the lowest frequency mode in the molecule. Similar motion is observed in the supersonic jet spectrum of biphenyl [17], the parent molecule, which has a torsional frequency of 66 cm^{-1} in the S_1 state.

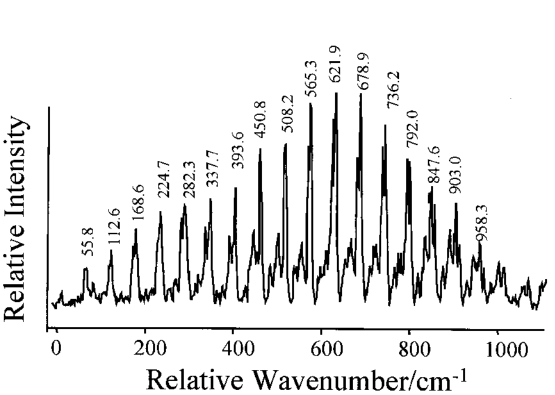

Figure 1. The LIF excitation spectrum of jet-cooled, laser-desorbed 4-cyanobiphenyl.

The appearance of this long progression in the spectrum is strongly indicative of an appreciable change in geometry of the molecule, with respect to the torsional coordinate, on electronic excitation. A harmonic progression implies that the excited state potential from which it originates is also harmonic in form, and the length of the progression observed suggests significant torsional barriers. Since 18 members are observed with unperturbed harmonic spacing, we can say that the torsional barriers must be at least 12.1 kJ mol^{-1}. There is no evidence that the first observable feature is the 0-0 transition, and therefore the barriers may be significantly higher.

A Franck–Condon analysis of the experimental data has been carried out using the method of Lewis *et al.* [29]. The torsional wave equation is shown in equation (1).

$$\left[-B\frac{\partial^2}{\partial\phi^2}+\frac{1}{2}\sum V_n(1-\cos n\phi)\right]\Psi(\phi)=E(\phi)\Psi(\phi) \qquad (1)$$

where ϕ is the torsional angle, B is the rotational constant of the rotor ($=h/8\pi^2 cI$) and I is the reduced moment of inertia. B was determined to be 0.3715 cm^{-1} using the method of Pitzer and Gwinn [30]; the value of B was found to be independent of the torsional angle. The expansion of the torsional potential as a cosine Fourier series is a standard technique [14, 16, 29]. The Hamiltonian matrix was constructed and diagonalized, in a basis of 200 free-rotor functions, to obtain the torsional frequencies.

The Franck–Condon factors, which are proportional to the intensity of each vibronic transition, are given by the square of the overlap integral of the wave functions in the initial and final states for each vibronic transition. Hence the potential parameters for each state can be varied until the spectral intensity distribution in the fluorescence excitation spectrum is reproduced. In the absence of any ground state experimental data, the ground state potential obtained from the DFT calculations was used and the excited state torsional parameters were varied until the experimentally obtained spectral features were reproduced. The best fit to the spectral intensity distribution was obtained with an excited state equilibrium dihedral angle of 0°, and a barrier to internal rotation of 39.6 kJ mol^{-1}. However, as a cautionary note, we add that the value of the barrier height can be attributed little significance, since the fitted torsional levels do not approach the barrier energy. From this analysis, the first observable feature in the spectrum is predicted to correspond to the $v'' = 0 \rightarrow v' = 6$ transition.

4.2. *Molecular electronic structure calculations*

A series of *ab initio* calculations for the ground and first excited singlet electronic states of the 4-cyanobiphenyl molecule were performed. We proceed with a description of structural differences between these two electronic states, before discussing the calculated torsional potentials. The most striking structural difference between the ground and singlet excited state optimized geometries (shown as insets on figures 2 and 3, respectively) is the dihedral angle between the two phenyl rings. In the ground state it is found to be 44°, while in the first singlet state, the molecule is effectively planar (dihedral of 1°). The bonding pattern of the S_1 state is also different from that of the ground state. The inter-ring carbon–carbon bond contracts, becoming essentially of double bond character. The bonding pattern becomes similar to that of α,β unsaturated ketones (quinones). The dramatic structural changes are reflected in the torsional potentials of the respective states, as described below. The dipole moment of the molecule changes from 5.36 D in the ground state to 6.27 D in the S_1 state. We find, however, that the molecular electric dipole is relatively insensitive to ring angle in the ground electronic state. We therefore conclude that the observed alteration of the dipole is due almost entirely to the redistribution of electronic charge in the excited state.

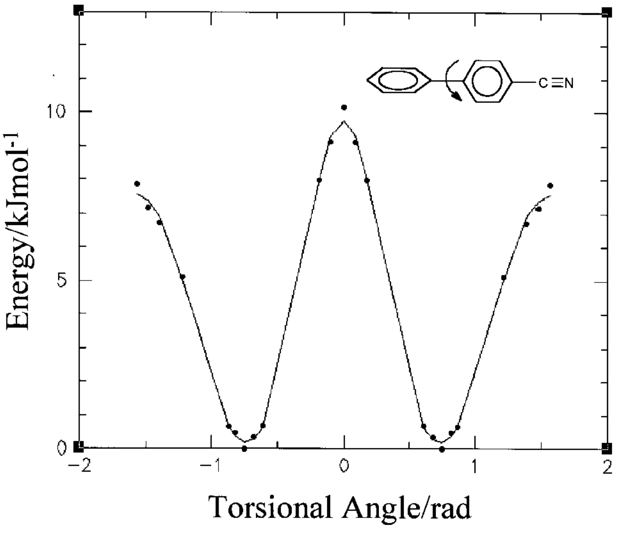

Figure 2. The ground state torsional potential of 4-cyanobiphenyl, calculated using the ADF density functional method. The points correspond to individual calculations at constrained torsional angles. The solid curve corresponds to a fit of equation (2) to the data.

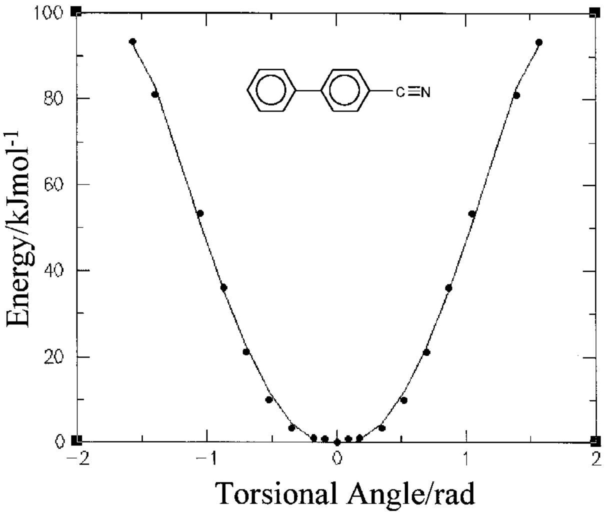

Figure 3. The excited state torsional potential of 4-cyanobiphenyl, calculated using the ADF density functional method. The points correspond to individual calculations at constrained torsional angles. The solid curve corresponds to a fit of equation (3) to the data.

The torsional potential of the ground state of 4-cyanobiphenyl is shown in figure 2. This was calculated by incrementally fixing the torsional angle between the two rings and relaxing all other structural parameters. The curve on figure 2 corresponds to a fit of the data to equation (2). The values of the fitted parameters are given in the table.

$$V = a_0 + \sum_{n=1}^{6} a_n \cos(2n\phi). \tag{2}$$

Table. Values of the best-fit parameters to describe the torsional potentials of the ground and first singlet excited states of 4-cyanobiphenyl by equations (2) and (3), respectively.

Parameter	S_0 value/kJ mol^{-1}	S_1 value/kJ mol^{-1}
a_0	4.25268	− 2.78033
a_1	0.181469	59.1739
a_2	4.114000	− 9.01537
a_3	0.798055	
a_4	0.262846	
a_5	0.0904759	
a_6	0.147322	

The potential surface is symmetric around 0°, having two equivalent minima at 44° ± 2°. The barrier at 0° reflects the steric repulsion between the hydrogens on either side of the inter-ring bond when the molecule is in a planar configuration. The barrier at 90° arises from the loss of π-conjugation between the rings. The equilibrium dihedral angle is the result of a subtle balance between these two opposing effects in the molecule: the π-interaction, maximized when the molecule is planar, and the steric hindrance of the ring hydrogens, seeking to force the molecule into a perpendicular conformation. The energies associated with these two barriers are relatively small, the steric interaction having a slightly higher barrier of 9.8 kJ mol^{-1}, while the barrier to loss of π-conjugation is 7.8 kJ mol^{-1}. These values compare favourably to recent estimates for the S_0 torsional barriers in biphenyl [31].

Previous theoretical studies employing a plane-wave (PW) basis set [9–11] have predicted slightly different potential surfaces for the ground state of 0CB. We have found that the equilibrium torsional angle predicted using an atom-centred basis set is particularly sensitive to the convergence criteria for the calculation. Default convergence criteria yielded a value of 35°, almost identical to that from the PW calculations, whereas criteria tighter by a factor of 10 yielded a value of 44°. It is also interesting to note that other calculations employing atom-centred Gaussian-type basis sets [31, 32] predict an equilibrium torsional angle of 47°, greater than the value of 38° obtained using a PW basis set. The atom-centred basis sets [31, 32, this work] predict a similar shape for the torsional potential, having the greater barrier at an angle of 0° and a lesser barrier at 90°. The PW calculations invert this pattern. However, it is probably unwise to read too much into this, since the absolute energy differences are very small, of the order of 5 kJ mol^{-1}.

The S_1 potential is significantly different in form to that of the S_0 state, as shown in figure 3. The potential is now harmonic in form due to the increase in bonding order of the inter-ring carbon–carbon bond. That is, we are now dealing with torsional motion around an essentially double bond, compared with motion around a single bond in the ground state. The result of this change in bond order means that the π-interaction is now the dominant process which determines the equilibrium geometry, with steric barriers being completely absent from the potential. A closer examination of the excited state structure reveals that the quinoidal type distortion in the ring systems has the effect of increasing the distance between opposing hydrogens, and this may have a significant effect on alleviating the steric repulsion.

$$V = a_0 + a_1\phi^2 + a\phi^4. \qquad (3)$$

The potential is well fitted to a harmonic series, given by equation (3), as shown by the solid curve on figure 3. The fit parameters are listed in the table. The barriers at $\pm\pi/2$ radians, which correspond to total loss of conjugation, are around 100 kJ mol^{-1}. This is a significantly higher barrier energy than that predicted by the Franck–Condon analysis. However, it must again be emphasized that the experimentally probed section of the potential surface is small, allowing neither confirmation nor repudiation of this value.

The torsional frequency for the S_1 state was determined from the fitted function by treating the molecule as a harmonic torsional oscillator, as described by equation (4).

$$\nu = \frac{1}{2\pi}\left(\frac{\kappa}{I}\right)^{1/2} \qquad (4)$$

where κ is the torsion constant for the motion, and I is the reduced moment of inertia of the molecule.

Using this equation the torsional frequency was determined to be 78 cm^{-1}. This is slightly higher than the experimental value of 56 cm^{-1}, implying an overestimation of the magnitude of the π interaction in the S_1 state. A previous investigation of the predictions of DFT versus *ab initio* methods [33] noted that DFT calculations tend to overestimate torsional barriers with a significant π contribution by a similar amount to that underestimated by conventional Møller–Plesset second order, and *ab initio* Self Consistent Field methods in ground state torsional potential calculations. The DFT calculations, however, were more accurate in their predictions of molecular geometry for all the molecules for which experimental geometric parameters were available. This conclusion appears to be borne out in our study.

5. Conclusions

The combination of supersonic jet spectroscopy and first-principles calculations shows excellent promise as a powerful probe of structural and electronic properties of complex mesogenic molecules and their fragments. For 4-cyanobiphenyl, the calculated potential surfaces compare well with the spectroscopic observations. Specifically, the large change in geometry on electronic excitation is predicted computationally and the form of the excited state torsional potential surface fits experimental observations.

It is apparent that major structural and electronic changes accompany the ground to excited state transition in 4-cyanobiphenyl. The implications of these changes for condensed phase behaviour clearly require further consideration, though it is well known that both molecular shape and the magnitude of the electrostatic dipole have a profound influence on mesomorphic phase diagrams [34]. The generality of these results for other mesogenic systems also remains to be explored though we expect that these conclusions apply at least to the large number of biphenyl-containing mesogens.

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