Theoretical study of the experimental behavior of two homologous series of liquid crystals

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Abstract

In this paper we present a theoretical approach to the study of the observed liquid crystal behavior of a 4´-alkyl-biphenyl-4-carbonitrile and 4´-alkoxy-biphenyl-4-carbonitrile homologous-series. We employ an electronic structure method at the *Abinitio* HF/3-21G//PM3 level of theory/numerical precision. We have used this quantum-mechanical methodology to compute a number of molecular properties that we correlate to the mesomorphic behavior of the chosen molecules. These properties are: ovality, the trace of the electric quadrupolar moment and the anisotropy. Our study allows us to correlate them with the experimentally observed even-odd effect.

Absolute values of these properties are shown to depend linearly with the number (**n**) of methylenic units in the side chain, ($1 \leq \mathbf{n} \leq 12$). The linear fits provide excellent correlation-regression coefficients, R^2=(0.9915, 0.9999). Therefore we suggest that these properties may be employed to study and characterize homologous series of molecules that show different mesophases, since we can distinguish mesomorphic behavior zones and predict molecular properties. Our electronic structure methodology is found to be appropriate for the study of the chosen thermotropic liquid crystals homologous-series, and may be applied to other homologous series.

Keywords: 4´-Alkyl-biphenyl-4-carbonitrile, 4´-alkoxy-biphenyl-4-carbonitrile, liquid crystals, quadrupole moment, *ab initio*, electronic structure calculations

Introduction

The liquid crystal (LC) concept[1-3] is used to describe an aggregation state whose properties are intermediate between a crystalline solid and an amorphous liquid. A substance in this state is highly anisotropic in some of its properties but may show certain degree of fluidity and viscosity, in many situations comparable to an ordinary liquid.

Liquid-crystalline phases are also known as mesophases (meaning *intermediate* phase) or mesomorphic phases, and molecules that compose them are known as mesogens. Transitions to these intermediate states may be induced by merely thermal processes (thermotropic mesomorphism) or by the action of some solvents (lyotropic mesomorphism)[4-6]. From this point of view, liquid crystals may be classified into two distinct categories: lyotropic and thermotropic. The former behave mesomorphically as a function of concentration while the latter has a definite mesomorphic behavior within a specific temperature range and may show different mesophases depending on temperature.

Many liquid crystal molecules possess geometrical forms such as disks or rods. Therefore the main thermotropic liquid crystals are either (a) *discotic* (whose molecules are of a planar disk-like form such as a core of linked aromatic rings) and (b) *calamitic* (whose molecules are cylinder-shaped). Most of the thermotropic liquid crystals are of the latter kind. Their mesophases display several degrees of orientational and positional order. Based on the observed degree of molecular ordering, liquid crystals may be further classified into *nematic* or *smectic*[3]. Nematic phases involve the domain of orientational order; hereby are represented by **N**, whereas **S** is used for smectic phases (where positional order is additionally observed); and **I** is used to indicate the isotropic phase.

Many factors influence the actual liquid crystal phase exhibited. It is usually believed that the observed phase is mainly determined by the molecule geometrical shape. However, other properties such as intermolecular repulsions, attractive interactions and hydrogen bonds may play an important role. Interaction between molecular electric dipoles generates important attractive forces among molecules. Furthermore, in molecules that contain aromatic ring systems quadrupole-quadrupole interactions are very important.

A typical thermotropic liquid crystal molecule contains two or more aromatic rings, either directly fused or connected through other more or less rigid functional groups, plus terminal lateral hydrocarbon chains. The 4´-pentyl-biphenyl-4-carbonitrile and 4´-pentoxy-biphenyl-4-carbonitrile homologous series are an example of this kind of liquid crystals. These molecules show both nematic and smectic mesophases, that depend on the length of the side chains[7]. The stability of the nematic phase refers to the upper limit of the range of temperature ($T_{N\text{-}I}$) at which the nematic phase exists.

The purpose of this work is to theoretically calculate molecular properties of the chosen model liquid crystal molecules and correlate them with experimentally measured properties[7]. Model molecules used in this study involve 4´-alkyl-biphenyl-4-carbonitrile and 4´-alkoxy-biphenyl-4-carbonitrile homologous series. Molecular properties are derived using quantum-mechanical electronic structure methods. In this way, a novel first-principles approach is carried out in order to understand the mesomorphic behavior of LC´s.

Experimental Section

We compare our theoretical results with experimental data of thermotropic liquid crystals that possess nematic or smectic phases or even both, as a function of the number **n** of methylenic units in the side chain. Experimental data for two different thermotropic liquid crystals homologous series have been obtained from the *Liquid Crystals Databases Version*[8].

The chosen series are hereby denoted as *SERIES I* and *SERIES II*. These series contain a biphenyl-4-carbonitrile group and the data base provides observed phases and the transition temperatures: isotropic → nematic ($T_{N\text{-}I}$), and isotropic → smectic ($T_{S\text{-}I}$). In Figure 1, the general patterns of structures for all molecules in each series are shown. In Tables 1 and 2 their liquid crystal properties are displayed.

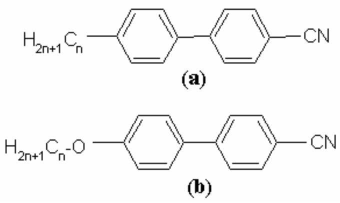

Figure 1. (a) General structure for *SERIES I* molecules (b) General structure for *SERIES II* molecules.

Table 1. The phase transition temperatures, $T_{N\text{-}I}$ and $T_{S\text{-}I}$, in ^{0}C, and observed mesophases, for molecules in *SERIES I*. The asterisk denotes the molecule identifier in the data base[8]. Cr and Cr' denote crystalline phases, N, A and I indicate nematic, smectic an isotropic phases respectively

Molecule Identifier*	Methylenic units	Experimental Mesophase	The phase transition temperature, $T_{N\text{-}I}$ and $T_{S\text{-}I}$, ^{0}C.
1260	**1**	NEMATIC	Cr109.0 (N45.0)
1261	**2**	NEMATIC	Cr75.0 (N22.0)
1262	**3**	NEMATIC	Cr67.3 (N30.3) I
1263	**4**	NEMATIC	Cr48.0 (N16.5) I
1264	**5**	NEMATIC	Cr24.0 N35.3 I
1265	**6**	NEMATIC	Cr14.3 N30.1 I
1266	**7**	NEMATIC	Cr'15.0 Cr30.0 N42.8 I
1267	**8**	NEMATIC and SMECTIC	Cr21.5 A33.5 N40.5 I
1268	**9**	NEMATIC and SMECTIC	Cr'29.5 Cr42.0 A48.0 N49.5 I
1269	**10**	NEMATIC and SMECTIC	Cr44.0 A54.5 I
1270	**11**	NEMATIC and SMECTIC	Cr53.0 A57.5 I
1271	**12**	NEMATIC and SMECTIC	Cr48.0 A58.5 I

Table 2. The phase transition temperatures**,** T_{N-I} and T_{S-I} , in ^{0}C, and observed mesophases, for molecules in *SERIES II*. The asterisk denotes the molecule identifier in the data base[8]. Cr and Cr’ denotes crystalline phases, N, A and I indicate nematic, smectic an isotropic phases respectively

Molecule Identifier*	Methylenic units	Experimental Mesophase	The phase transition temperature, T_{N-I} and T_{S-I}, ^{0}C.
1272	**1**	NEMATIC	Cr104.0 (N85.5) I
1273	**2**	NEMATIC	Cr’100.0 Cr102.0 (N90.5) I
1274	**3**	NEMATIC	Cr74.5 (N64.0) I
1275	**4**	NEMATIC	Cr78.0 (N75.5) I
1276	**5**	NEMATIC	Cr48.0 Cr53.0 N68.0 I
1277	**6**	NEMATIC	Cr’44.0 Cr57.0 N75.5 I
1278	**7**	NEMATIC	Cr’47.5 Cr53.5 N75.0 I
1279	**8**	NEMATIC and SMECTIC	Cr’46.0 Cr’51.0 Cr54.5 A67.0 N80.0 I
1280	**9**	NEMATIC and SMECTIC	Cr64.0 A77.5 N80.0 I
1281	**10**	NEMATIC and SMECTIC	Cr59.5 A84.0 I
1282	**11**	NEMATIC and SMECTIC	Cr71.5 A87.5 I
1283	**12**	NEMATIC and SMECTIC	Cr70.0 A90.0 I

Molecules in *SERIES I* are similar in chemical structure to molecules in *SERIES II*. The only difference between them is the ether functionality present in the lateral hydrocarbon chain for *SERIES II*. In both series, lateral chains increase by one methylenic unit, and the observation of the different liquid crystal phases is a function of the number of methylene units **n** present in the molecule.

In Figure 2, a plot of the experimental T_{N-I} versus **n** is shown. It is important to note that in both series, the ***even-odd effect*** (oscillations according to chain size when **n** takes even or odd values between **n**=1 to **n**=8) is present. The range of **n** values actually conforms to a *nematic behavior region*, and above **n**=8 there is no apparent ***even-odd effect*** in T_{N-I}**.** For **n**=8 to **n**=12 a *smectic behavior region* is observed, and T_{N-I} shows an almost linear dependence on **n**. In both series the actual values of T_{N-I} for the boundary between regions is different.

One can also observe in this Figure that there is no crossing between the series at any point. For molecules of *SERIES II* the transition temperatures are always higher than the corresponding ones in *SERIES I*, indicating a wider range for phase stability.

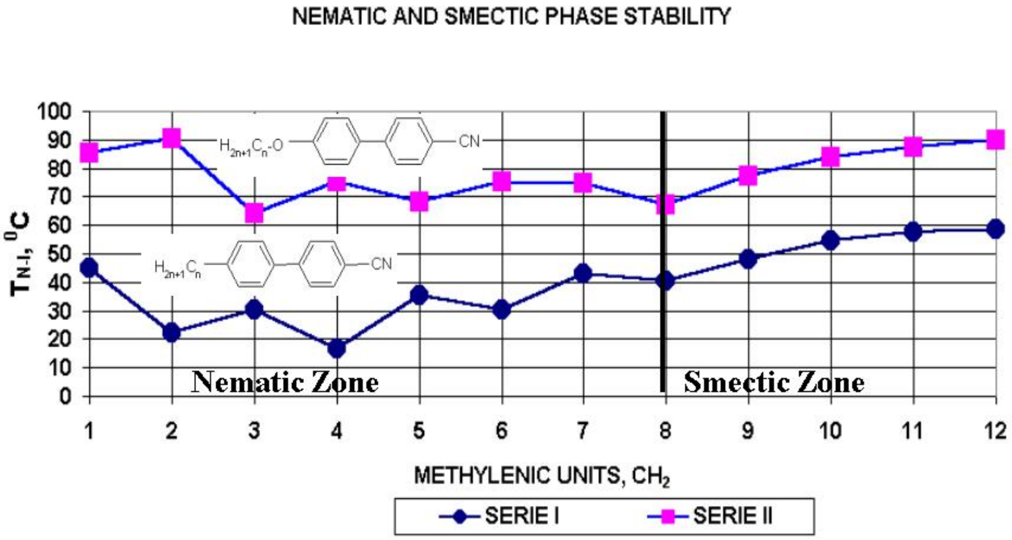

Figure 2. Experimental $T_{N\text{-}I}$ versus **n** is shown.

Computational methodology

Electronic structure methods provide useful information on the molecular structure and charge distribution, so they are useful to understand and describe systems where electronic effects and molecular orbital interactions are dominant. Depending on the theoretical assumptions used for calculations, electronic structural methods belong to one of two fundamental groups: *abinitio* and semi-empirical.

Semi-empirical methods use parameters derived from experimental values that simplify theoretical calculations. These methods usually do not require long computation times, and lead to qualitative descriptions of molecular systems. In particular, the semi-empirical PM3 method makes uses of an accurate procedure to predict chemical properties, through a simplified Hartree-Fock (HF) Hamiltonian [9].

Abinitio methods do not rely on experimental parameters; calculations are solely based in the quantum mechanics laws and in the values of a small number of universal physical constants. These methods provide moderate to high-quality predictions for a wide variety of systems[10] but are more computer-power-demanding, depending on the level of theory and on the type of basis set used for the calculation.

Based on the above considerations, the following methodology was chosen for our computer simulations. A full quantum mechanical geometry optimization with no symmetry restrictions was performed at the Semiempirical PM3 level of theory[9]. Once the lowest energy structures were obtained for all species, vibrational frequencies were computed in each one to make sure that global minima on the potential energy surfaces (PES) were obtained[10].

Henceforth, the quality of the final wave functions, energies and electron properties were improved through a single point *Abinitio* Hartree-Fock (basis set 3-21G) calculation on each species so the final level of calculation is denoted hereby as HF/3-21G//PM3. The 3-21G basis set is of low-to-moderate quality but has been reported[10,15] to yield acceptable geometries and charge distributions in simple organic molecules, in general improving the latter over the PM3 results and not too far from more costly correlated theories such as MP2 or DFT-based ones. An excellent way to assess the charge distribution in a molecule is through the dipole moment which can be both calculated and measured experimentally. In order to support our election of level of theory/precision, different molecules with different levels of calculation are compared to the experimental dipole moment to In Table 3.

Table 3. Computed and Experimental Dipole Moments (Debyes) for several molecules[15]

Molecule	PM3	HF/3-21G	MP2/6-31G	Expt.
NH_3	1.55	1.75	1.97	1.47
NMe_3	1.15	0.89	0.74	0.61
H_2O	1.74	2.39	2.20	1.85
PH_3	1.18	0.87	1.00	0.58
PMe_3	1.08	1.28	1.41	1.19
H_2S	1.78	1.41	1.48	0.97
Me_2S	1.96	1.75	1.75	1.50

As can be seen in the above Table, Hartree-Fock methods are moderately successful to reproduce dipole moments (overall charge distributions) if one employs a split-valence basis set such as 3-21G. In many of the molecules displayed, HF/3-21G results are better than PM3 when compared to experiment and not to far from the more costly correlated MP2 with a much larger basis set such as 6-31G. Since the aim of this work is to **compare trends** in a series of many molecules of much bigger sizes, we believe that for a qualitative and semi-quantitative study the chosen level of calculation is appropriate.

We chose to compute a set of molecular properties for our two series of LC molecules at the level discussed above. Our aim is to study possible correlations with the phenomenological measures of transition temperatures. We chose properties that are more likely to depend on geometry, electronic structure and charge distribution. We found that better correlations are obtained for surface area, (A), molecular volume, (V); energy and the magnitudes of electrical dipole and quadrupole moments, and for the latter also magnitudes of individual diagonal components.

Furthermore, from the above basic molecular properties we computed a number of derived properties such as:

- **Ovality**, (O), defined by $O= (A/4\pi)(3V/4\pi)^{2/3}$. This property is an indicator of how close is the molecule geometry to a sphere, a cylinder or a disk. If O=1.0 it is a perfect sphere, if O>1.0 it is a cylinder and if O<1.0 it is closer to a disk. Although it is directly related to the molecular geometry (PM3) it also depends on the single-point level of calculation of the Wavefunction (*abinitio* HF/3-21G), since the density derived from it is used to compute the molecular volume employed in the ovality formula.
- The electric **quadrupole moment trace**, defined as the absolute value of the sum of its diagonal components, $\text{Trace}= Q_{xx}+Q_{yy} +Q_{zz}$
- Molecular **anisotropy**, defined from the electric quadrupole moment diagonal components, $\text{Anisotropy}=Q_{zz} - 0.5(Q_{xx}+Q_{YY})$.

For the electronic calculations, we used the *Gaussian 94* program[12] and prepared molecular coordinates inputs and visualized results with the *Spartan 5.1.1* graphical interface[13].

Results and Discussion

Tables with detailed numerical results are presented in the **Supplementary Section on page 227**. Here we provide a more visual display of results through use of several plots and figures. In Figure 3, the optimized geometries for one molecule of *SERIES I* and one molecule of *SERIES II* are shown. In both, the number **n** of methylene units is 7.

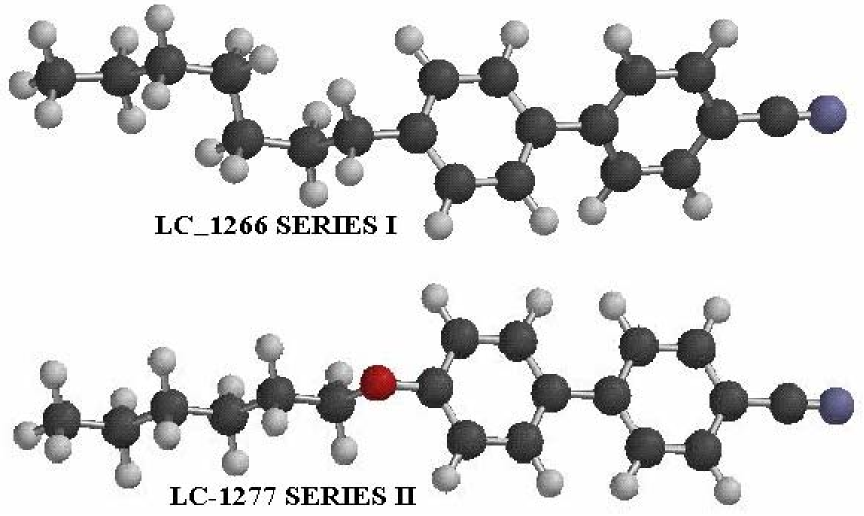

Figure 3. PM3 Optimized geometries for molecules with seven methylene units of SERIES I and SERIES II.

Dipole moments calculated for these molecules are very similar, which indicate that differences in dipolar interactions between the two series are not significant.

In Figures 4, 5, and 6, transition temperatures have been plotted versus the computed ovality, the absolute value of the quadrupolar moment trace and the anisotropy, respectively. In each plot the even-odd behavior is evident. Note that the properties that present this behavior are related with the molecular geometrical shape and charge distribution; thus, it is expected that they have an important influence in the mesomorphic behavior. The same behavior is also observed for each individual diagonal component of the quadrupolar moment tensor (see Figures 10, 11 and 12 in **Supplementary Section on page 230**.

In Figure 4, it can be observed that the *smectic* behavior is present when ovality values are greater that 1.6. This fact indicates that the corresponding geometry is related to more-ordered mesophases through intermolecular interactions where the aliphatic side chains are involved.

The smectic zone is observed for larger values of ovalities for ***SERIES II***, compared with those for *SERIES I*. This observation suggests that molecules should attain a sufficient degree of anisotropy in order to entropically favor the formation of more-ordered phases.

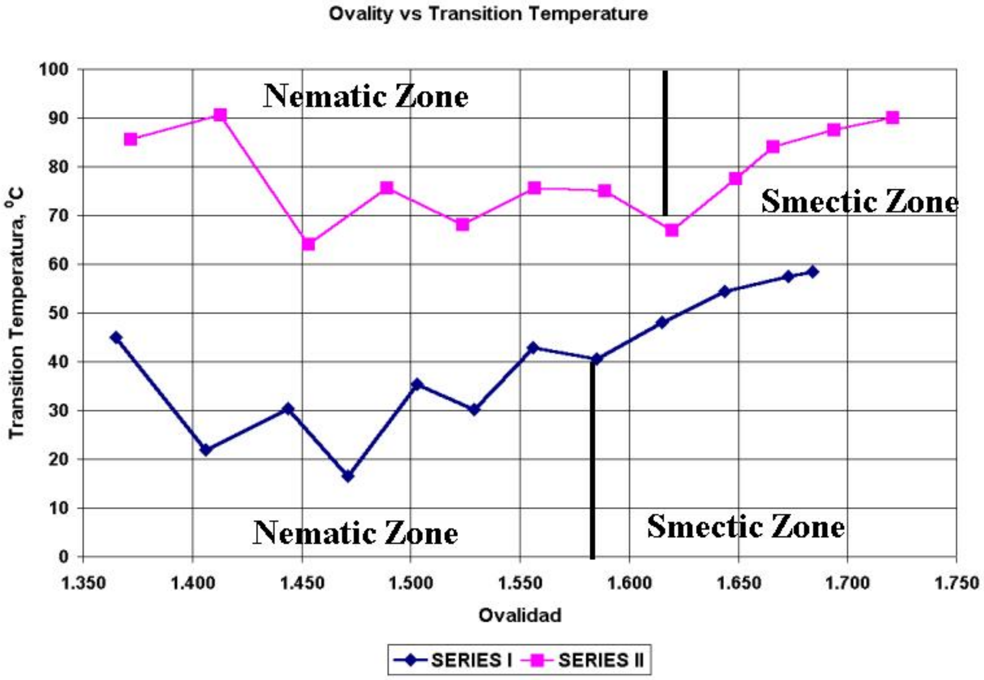

Figure 4. Transition temperature versus computed ovality at HF/6-31G//PM3 level.

In Figure 5, it can be observed that the range of the absolute value of the trace of the quadrupolar electric moment tensor where the smectic phase is stable is similar for both series. Besides, from values in Tables 6 and 9 in the **Supplementary Section on page 228 and 230** it is observed that the magnitude of the Q_{XX} and Q_{ZZ} components of the quadrupolar electric moment tensor of molecules in SERIES II is in the average 27% and 11% smaller than the corresponding ones in molecules of SERIES I. However, for the Q_{YY} component of these molecules the situation is reversed since in the average those in SERIES II are 60% **larger** in its absolute value than those of molecules in SERIES I. This is the reason for the fact that anisotropy in SERIES II is the only property studied that has a distinct larger value than in SERIES I molecules, as can be seen in Figure 6 and Tables 6 and 9. These anisotropy different values between both series of molecules may also be responsible for the increased thermal stability of SERIES II molecules phases.

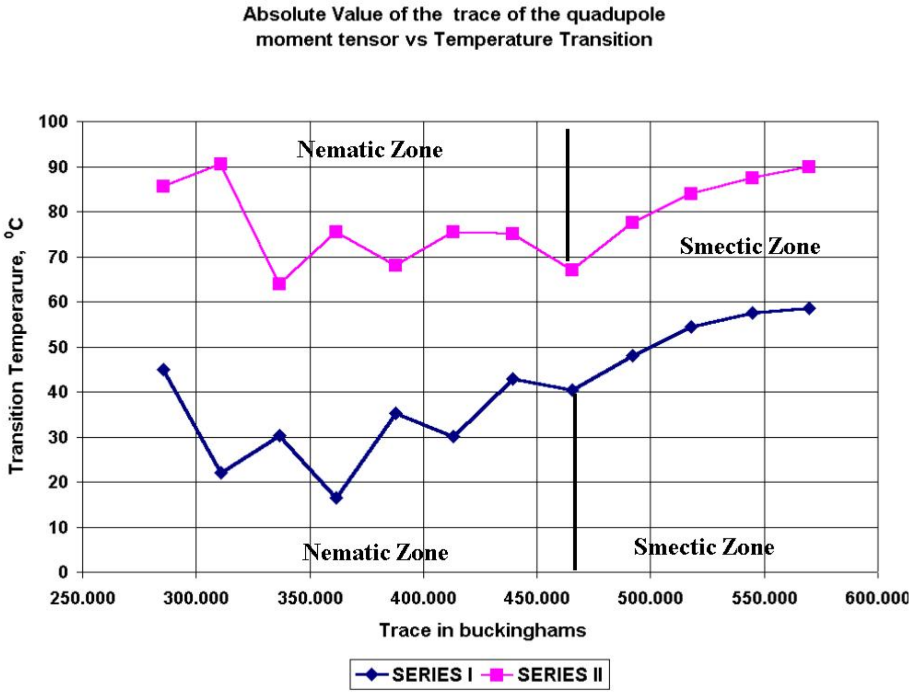

Figure 5. Transition temperature versus computed absolute value of the quadrupolar moment trace at HF/6-31G//PM3 level.

From all molecular properties analyzed for both series, the most important differences are observed for those related to forces of quadrupolar nature. This means that quadrupolar forces play an important role in the observation of liquid crystallinity of the studied molecules. These results are in agreement with those obtained for other series of Liquid crystals in our group[14]. Effect of anisotropy is also evident in Figure 6, where transition temperatures are plotted against this variable. To calculate anisotropy, diagonal components of the quadrupolar moment matrix are involved.

It is evident from Figure 6 that an increment in the number of methylene units (from 1 to 8) yields an alternation of the stability of the nematic phase for both series. For **n** >8, stability of the nematic phase shows an almost-linear dependence with *n*. Anisotropies for *SERIES II* are higher than those for *SERIES I*. This indicates that more stable mesophases are observed for the molecules of *SERIES II*.

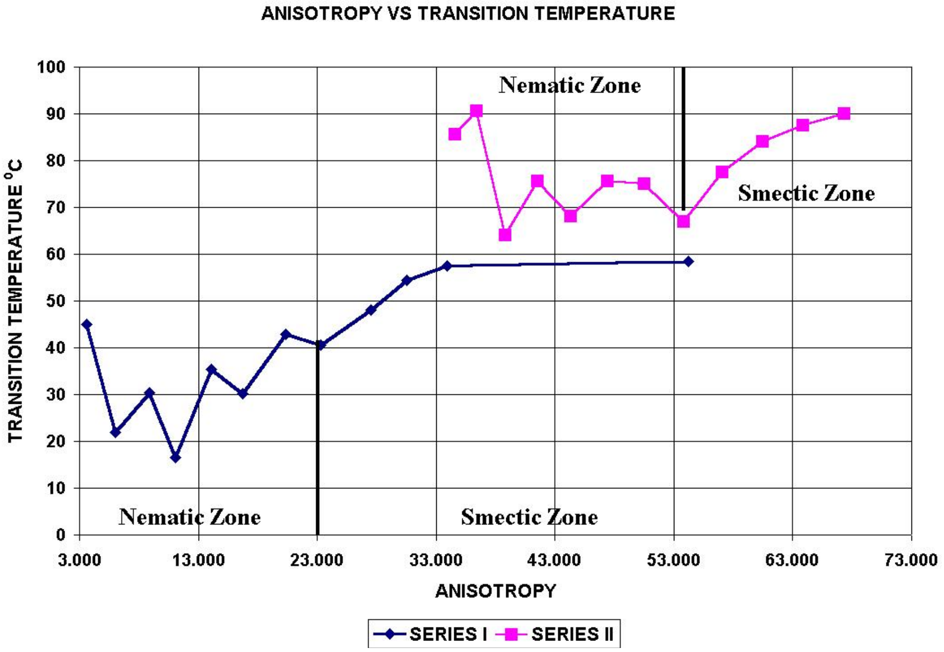

Figure 6. Transition temperature versus computed anisotropy at HF/6-31G//PM3 level.

Ovality, quadrupolar electric moment trace and anisotropy were plotted against side chain length for both series (see Figures 7, 8 and 9). In most cases, a linear dependence with good correlation coefficients, R^2=(0.9915-0.9999) were observed. For anisotropy, the correlation coefficient (R^2=0.8954) for *SERIES I* indicates a non-linear dependence.

The even-odd effect is observed when typical liquid crystal experimental variables are plotted against variables related with molecular shape and charge distribution. This feature indicates that mesomorphic behavior is closely related with these variables. Therefore, properties such as ovality, quadrupolar electric moment trace and anisotropy apparently may be used to predict liquid crystal behavior and applied to study similar systems.

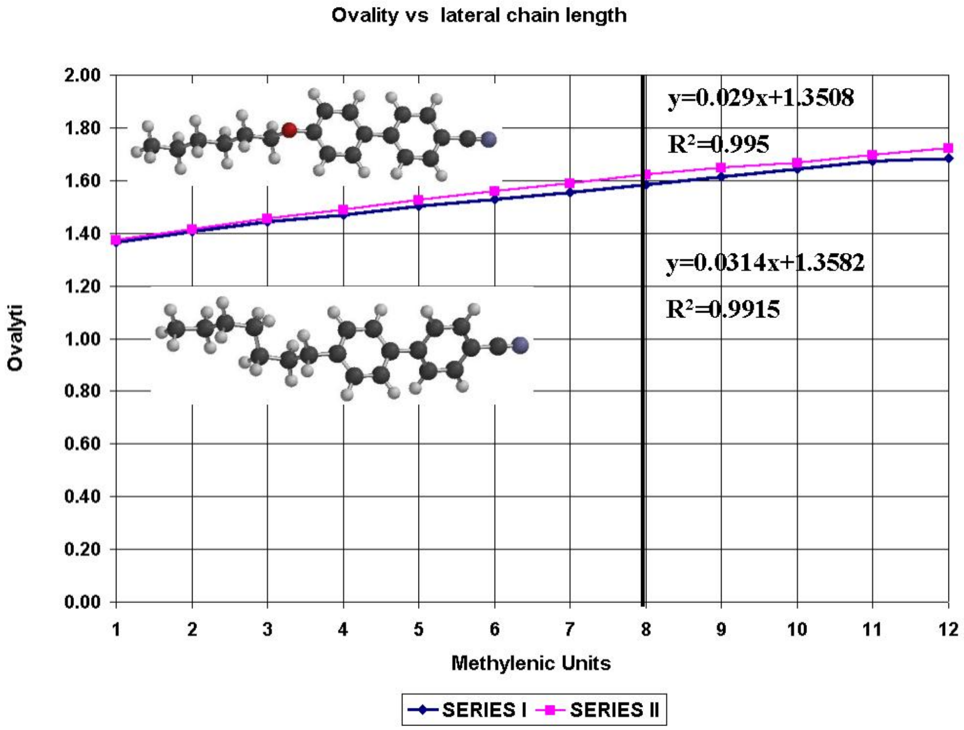

Figure 7. Ovality plotted against side chain length for both series at HF/6-31G//PM3 level.

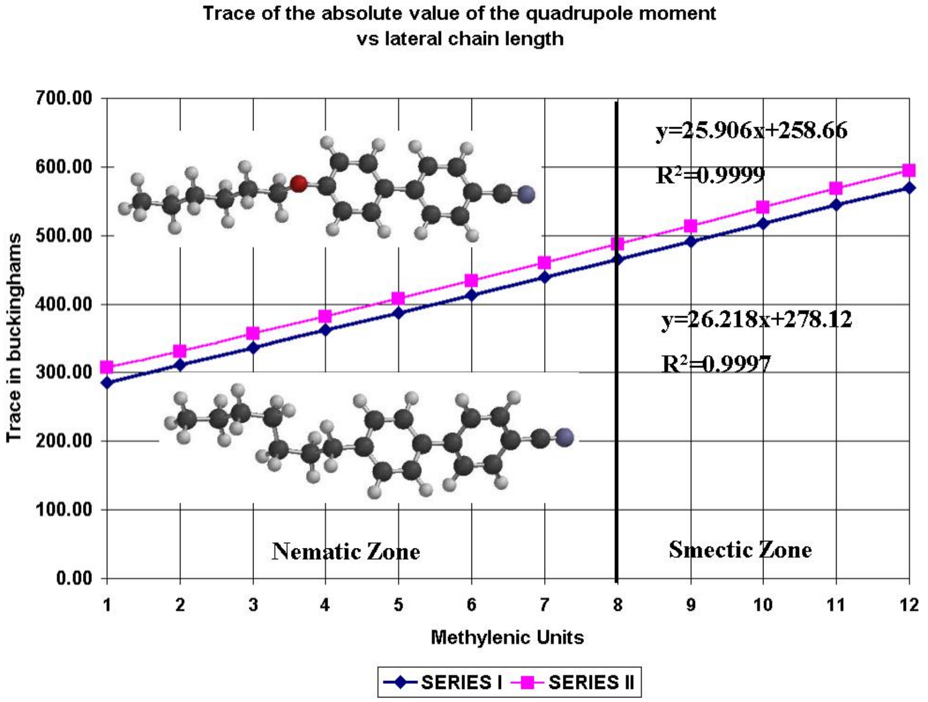

Figure 8. Absolute value of the quadrupolar moment trace plotted against side chain length for both series at HF/6-31G//PM3 level.

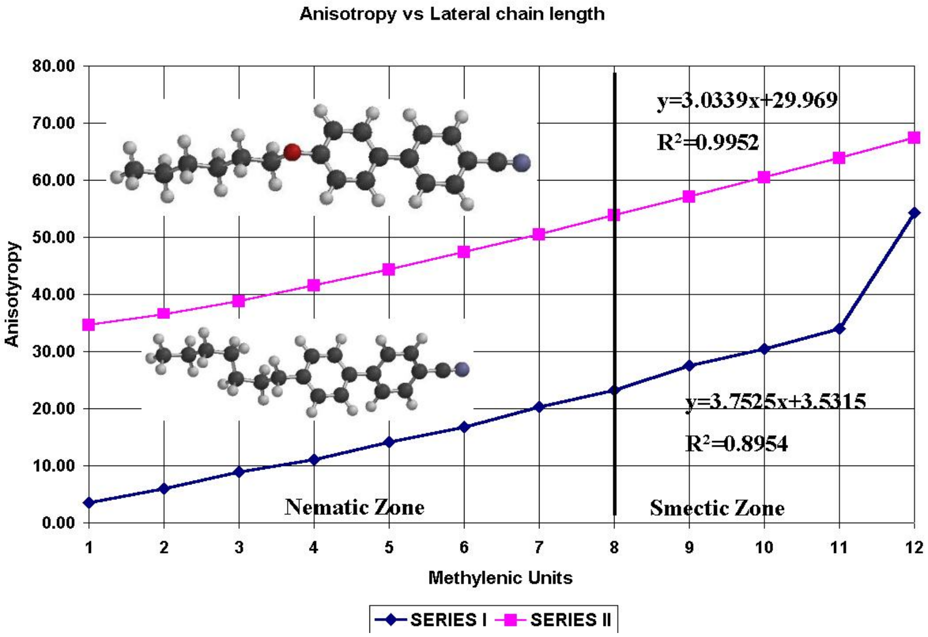

Figure 9. Absolute value of the anisotropy plotted against side chain length for both series at HF/6-31G//PM3 level.

Conclusions

In this work, electronic structure properties for homologous 4´-alkyl-biphenyl-4-carbonitrile and 4´-pentoxy-biphenyl-4-carbonitrile (1≤ n ≤12) series have been calculated using electronic structure methods. Relationships between these properties and experimental measurements related with liquid crystal behavior were established.

In the homologous-series molecules studied here, molecular geometry and quadrupolar electric moment are found to apparently be related with their mesomorphic behavior. The molecular properties related with this behavior are ovality, quadrupolar electric moment trace and anisotropy.

Plots of transition temperature against ovality, quadrupolar electric moment trace and anisotropy show an even-odd behavior. This fact indicates that molecular shape and charge distribution are factors that have a profound influence in the formation of experimentally observed mesophases.

The only computed property that exhibits larger values for *SERIES II* molecules than for molecules in *SERIES I* is the anisotropy. This correlates with the fact that molecules in *SERIES II* possess much higher stabilities and transition temperatures. Calculated dipole moments are similar for the two series studied here. More important differences are observed for calculated quadrupole-quadrupole interactions, and they can be related with thermal stability and appearance of smectic phases.

We have demonstrated that an increment in ovality (a concept that had not been used in the liquid crystal literature yet) favors molecular interactions (due to effects of the lateral chains), and an increment in anisotropy, inducing the formation of smectic phases and increasing mesophase stability.

There is a linear relationship between ovality, quadrupolar electric moment trace and anisotropy with respect to the number of methylene units present in the lateral chain with good regression coefficients, R^2=(0.9915,0.9999). These molecular properties can be calculated for other homologous series and linked to the mesomorphic behavior. They are also useful to establish boundaries in phase-like diagrams where mesophases are stable.

Supplementary Information is available on page 227

In this section, several Tables compiling geometrical properties, electronic structure data and charge distribution calculated for the molecules of the two series studied at the *Abinitio* HF/3-21G//PM3 level are shown. Also included are the plots for the diagonal components of the quadrupolar electric moment against phase transition temperatures.

Acknowledgements

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