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4′-Methyl-biphenyl-4-carbonitrile and the 4′-Methoxy-biphenyl-4-carbonitrile homologous series are known to exhibit calamitic (nematic and/or smectic) liquid crystal phases. In this work, aspect ratios x (length/diameter) for these molecules are computed from electronic structure calculations using ab initio HF/3-21G//PM3 level of theory/numerical precision. Aspect ratios were calculated from ***ovality*** *O_v, defined as $O_v = (A/4\pi)/(3V/4\pi)^{2/3}$, where V is the molecular volume and A the surface area. Derivations of thermotropic liquid crystal aspect ratios as a function of O_v, by this model are in agreement with observed values and permit an adequate description of the liquid crystal molecular geometry.*

Keywords: 4′-alkyl-biphenyl-4-carbonitrile; 4′-alkoxy-biphenyl-4-carbonitrile; aspect ratios; electronic structure calculations; homologous series; liquid crystals; ovality

INTRODUCTION

Liquid crystal (LC) molecules possess a certain degree of anisotropy, which promote orientational and sometimes positional order. From the geometrical point of view, this means that one molecular axis is very different from the other two. Based on their geometrical features, thermotropic LC can be classified into two different categories: (a) *discotic* (molecules whose molecular shape are planar disk-like,

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such as that observed in molecules with a core of linked aromatic rings) and (b) *calamitic* (rod-shaped molecules). Most of the thermotropic LC are of the latter kind [1,2]. The different mesophases determined experimentally 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 hereby represented by **N**, involve the domain of orientational order, whereas **S** is used for smectic phases (where positional order is additionally observed). **I** is used to indicate the non-ordered isotropic phase. Many factors influence the actual LC 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 [4]. 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 [5,6]

A calamitic LC molecule can be represented by a hard spherocylinder core with cylinder length L, diameter D and aspect ratio $x = L/D$. When $x < 3$, only isotropic phases are experimentally observed, whereas for x values higher than 3, nematic phases are detected. For highly elongated geometries, smectic phases are exhibited [7–13]. The 4′-alkyl-biphenyl-4-carbonitrile and 4′-alkoxy-biphenyl-4-carbonitrile homologous series (see Figure 1) are an example of this kind of LC. It has been reported that molecules of the 4′-Methyl-biphenyl-4-carbonitrile and the 4′-Methoxy-biphenyl-4-carbonitrile homologous series exhibit the calamitic (nematic and/or smectic) LC phases depending on the number of methylene units n of the lateral substituents. Observation of smectic phases is favored for higher n values [14].

The purpose of this work is (1) theoretically compute the aspect ratios of the chosen LC's molecules from quantum-mechanical

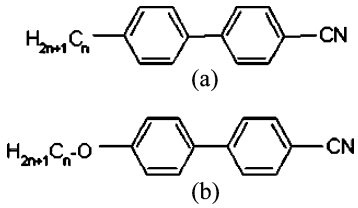

FIGURE 1 Chemical structure for (a) SERIES I molecules and (b) SERIES II molecules.

electronic structure methods calculations and (2) correlate these values with experimentally observed LC phases. In this way, a novel first-principles approach is carried out in order to determine aspect ratios and to understand the mesomorphic behavior of LC's.

EXPERIMENTAL SECTION

Experimental data for two different thermotropic LC homologous series have been obtained from the *Liquid Crystals Database Version* 3.4 [14]. 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 chemical structures for molecules in each series are shown. In Tables 1 and 2 their LC properties are displayed. Molecules in *SERIES I* are similar in chemical structure to molecules in *SERIES II*. The only difference between them is the presence of an ether functionality in the lateral hydrocarbon chain for *SERIES II*. In both series, lateral chains increase by one methylenic unit, and the observation of the different LC phases is a function of the number of methylene units n present in the molecule.

TABLE 1 The Phase Transition Temperatures, $T_{N\text{-}I}$ and $T_{S\text{-}I}$, in °C, and Observed Mesophases, for Molecules in *SERIES I*. The * Denotes the Molecule Identifier in the Data Base[14]. Cr and Cr′ denote crystalline phases, N, A and I indicate nematic, smectic and isotropic phases respectively

Molecule identifier*	Methylenic units	Experimental mesophase	The phase transition temperature, $T_{N\text{-}I}$ and $T_{S\text{-}I}$, °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 N30.1I
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	SMECTIC	Cr44.0 A54.5 I
1270	11	SMECTIC	Cr53.0 A57.5 I
1271	12	SMECTIC	Cr48.0 A58.5 I

TABLE 2 The Phase Transition Temperatures, $T_{N\text{-}I}$ and $T_{S\text{-}I}$, in °C, and Observed Mesophases, for Molecules in *SERIES II*. The * Denotes the Molecule Identifier in the Data Base[14]. Cr and Cr′ denote Crystalline Phases, N, A and I Indicate Nematic, Smectic and Isotropic Phases Respectively

Molecule identifier*	Methylenic units	Experimental mesophase	The phase transition temperature, $T_{N\text{-}I}$ and $T_{S\text{-}I}$, °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	SMECTIC	Cr59.5 A84.0 I
1282	11	SMECTIC	Cr71.5 A87.5 I
1283	12	SMECTIC	Cr70.0 A90.0 I

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: *ab initio* or 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 use of an accurate procedure to predict chemical properties, through a simplified Hartree-Fock (HF) Hamiltonian [15]. *Ab initio* 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 [16] 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 calculations. A full quantum mechanical geometry optimization with no symmetry restrictions was performed at the Semiempirical PM3 level of theory [15]. This method provide quite good geometries for a simple organic molecules. 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 [16].

Henceforth, the quality of the final wave functions, energies and electron properties were improved through a single point *Ab initio* 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 [16,17] 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.

For the electronic calculations, we used the *Gaussian 94* program [18] and prepared molecular coordinates inputs and visualized results with the *Spartan 5.1.1* graphical interface [19].

We have chosen properties that more likely depend upon geometrical shape: surface area, (A) and molecular volume, (V). Furthermore, from the above basic molecular properties we computed the *Ovality*, (O_v), a derived property [5,6], defined by

$$O_v = (A/4\pi)(3V/4\pi)^{-\frac{2}{3}} \tag{1}$$

This property is an indicator of how close is the molecule geometry to a sphere, a prolate spheroid or an oblate spheroid. If O = 1.0 a perfect sphere is observed. For O > 1.0, prolate spheroid geometry is present, and for O $\ll$ 1.0, the geometrical shape is closer to an oblate spheroid. Although *ovality* is directly related to the molecular geometry (PM3), it also depends on the single-point level of calculation of the wave function (*ab initio* HF/3-21G), since the density derived from it is used to compute the molecular volume employed in the ovality formula.

For cylinder-shape molecules, *ovality* and aspect ratio (x = L/D) are related by equation

$$O_v = \left(\frac{3}{54}\right)^{\frac{1}{3}} \frac{2x+1}{(\sqrt[3]{x})^2} \tag{2}$$

where x represents the aspect ratio (length/diameter) for the molecules of the two homologous series of calamitic liquid crystals.

RESULTS AND DISCUSSION

In Figure 2, the optimized geometries for one molecule of *SERIES I* and one molecule of *SERIES II* are shown. In both cases, the number of methylene units *n* is 7. Observe the elongated shapes in both structures.

In Tables 3 and 4, computed *ovalities* for molecules of both series are shown.

One can see that *Ovalities* for molecules of both homologous series (calculated at HF/3-21G//PM3 level) are in the range $(1.365 \leq O_v \leq 1.724)$.

In Figure 3, the theoretical curve for equation (2) is shown. It is evident that a linear relationship between *ovality* and x can be established within certain range. For the range of *ovality* values obtained at HF/3-21G//PM3 level of calculation for molecules of both homologous series, the obtained aspect ratios for cylinder-shaped molecules are found in the range of 3.5 to 10.

For the molecules of the homologous series studied here, the relationship between ovality and x can be fitted to a straight line with

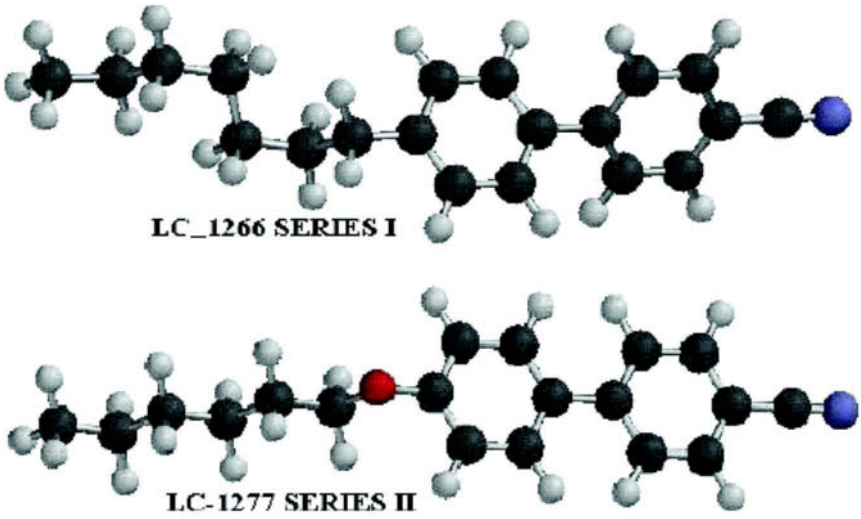

FIGURE 2 PM3 optimized geometries for molecules with seven methylene units of SERIES I and SERIES II.

TABLE 3 Molecular Properties of the Series I, at the HF/3-21 G//PM3 Level of Calculation. The * Denotes the Molecule Identifier in the Data Base[14]

Molecule identifier*	Molecular volume (Å^3)	Molecular surface (Å^2)	Ovality
LC_1260	237.99	253.47	1.365
LC_1261	258.49	275.79	1.406
LC_1262	278.98	298.10	1.444
LC_1263	299.20	318.15	1.471
LC_1264	319.00	339.35	1.503
LC_1265	339.26	359.52	1.529
LC_1266	358.99	379.97	1.556
LC_1267	380.00	401.99	1.585
LC_1268	400.46	424.23	1.615
LC_1269	420.94	446.56	1.644
LC_1270	441.44	468.98	1.673
LC_1271	460.78	485.75	1.684

a good regression coefficient, $R^2 = 0.9944$

$$O_v = 0.0626x + 1.116 \tag{3}$$

Equation (3) allows the calculation of aspect ratios from *ovalities* derived by quantum mechanical calculations, and much better than from a crude geometrical model as is usually done.

In Tables 5 and 6, the experimentally observed mesophases and aspect ratios calculated for the molecules of the two homologous series are shown. It can be observed that higher values for *ovalities* (and

TABLE 4 Molecular Properties of the Series II, at the HF/3-21G//PM3 Level of Calculation. The * Denotes the Molecule Identifier in the Data Base[14]

Molecule identifier*	Molecular volume (Å^3)	Molecular surface (Å^2)	Ovality
LC_1272	248.02	261.91	1.372
LC_1273	268.66	284.57	1.413
LC_1274	289.15	307.19	1.453
LC_1275	309.65	329.60	1.489
LC_1276	330.15	352.01	1.524
LC_1277	350.66	374.42	1.557
LC_1278	371.16	396.83	1.589
LC_1279	391.67	419.24	1.620
LC_1280	412.16	441.64	1.649
LC_1281	441.09	466.86	1.666
LC_1282	461.60	489.27	1.694
LC_1283	482.10	511.67	1.721

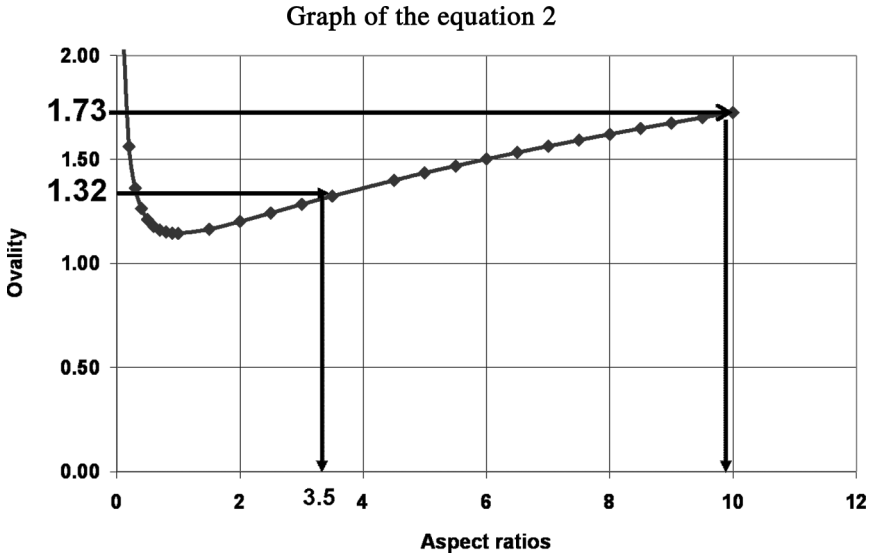

FIGURE 3 Graph of *ovality* versus aspect ratios for molecules with cylinder-shape geometry.

TABLE 5 Observed Mesophases and Calculated Aspect Ratios for 4′-Methyl-biphenyl-4-carbonitrile Homologous Series

Methylene units in the lateral chain	Observed experimental mesophase	Ovality[a]	Calculated[b] aspect ratio x
1	N*	1.37	3.98
2	N	1.41	4.63
3	N	1.44	5.24
4	N	1.47	5.67
5	N	1.50	6.18
6	N	1.53	6.60
7	N	1.56	7.03
8	S*	1.59	7.49
9	S	1.62	7.97
10	S	1.64	8.43
11	S	1.67	8.90
12	S	1.68	9.07

*N = Nematic phase; S = smectic phase; [a]at the HF/3-21G//PM3 level of calculation; [b]calculated with equation (3).

TABLE 6 Observed Mesophases and Calculated Aspect Ratios for 4′-Methoxy-biphenyl-4-carbonitrile Homologous Series

Methylene units in the lateral chain	Observed experimental mesophase	Ovality[a]	Calculated[b] aspect ratio x
1	N*	1.37	4.09
2	N	1.41	4.74
3	N	1.45	5.38
4	N	1.49	5.96
5	N	1.52	6.52
6	N	1.56	7.04
7	N	1.59	7.56
8	S*	1.62	8.05
9	S	1.65	8.51
10	S	1.67	8.79
11	S	1.69	9.23
12	S	1.72	9.66

*N = Nematic phase; S = smectic phase; [a]at the HF/3-21G//PM3 level of calculation; [b]calculated with equation (3).

their corresponding aspect ratios) correspond to molecules that exhibit smectic behavior.

CONCLUSIONS

In this work, aspect ratios x for two homologous series are rationalized and derived by an electronic structure method at the HF/3-21G//PM3 level of calculation. These values were correlated with the mesomorphic behavior. Aspect ratios were obtained from *ovality* O_v, defined as $O_v = (A/4\pi)(3V/4\pi)^{-2/3}$, where V is the molecular volume and A the surface area. V and A are calculated from the quantum electronic density. Derivations of thermotropic liquid crystal aspect ratios by this model are in agreement with observed values and permit an adequate description of the liquid crystal molecular geometry. 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 similar systems.

REFERENCES

[1] de Gennes, P. G. & Prost, J. (1995). *The Physics of Liquid Crystals*, 2nd ed. Oxford University Press: Oxford.

[2] Chandrasekhar, S. (1992). *Liquid Crystals*, 2nd ed. Cambridge University Press: London.

[3] Collings, P. J. & Hird, M. (1997). *Introduction to Liquid Crystals – Chemistry and Physics*, Taylor and Francis: London.
[4] Luckhurst, G. R. & Gray, G. W. (1979). *The Molecular Physics of Liquid Crystals*, Academic Press: London.
[5] Villanueva-García, M., Robles, J., & Martínez-Richa A. (2001). *Computational Materials Science*, *22*, 300.
[6] Villanueva-García, M., Huerta-Salazar, N., Martínez-Richa, A., & Robles, J. (2003). Regional Issue *"Organic Chemistry in Mexico" ARKIVOC*, (*xi*), 149–162.
[7] Frenkel, D., Mulder, B. M., & McTague, J. P. (1984). *Phys. Rev. Lett.*, *52*, 287.
[8] Stroobants, A., Lekkerkerker, H. N. W., & Frenkel, D. (1986). *Phys. Rev. Lett*, *57*, 1452.
[9] Stroobants, A., Lekkerkerker, H. N. W., & Frenkel, D. (1987). *Phys. Rev. A.*, *36*, 2929.
[10] Frenkel, D. (1988). *J. Chem. Phys.*, *92*, 11.
[11] Veerman, J. A. C. & Frenkel, D. (1990). *Phys. Rev. A.*, *41*, 3237.
[12] Poniewierski, A. (1992). *Phys. Rev. A.*, *45*, 5605.
[13] García, E., Williamson, D. C., & Martínez-Richa, A. (2000). *Molec. Phys.*, *98*, 179.
[14] (1998). *Liquid Crystals Database Version 3.4*, LCI Publisher GmbH, Eichenstr. 3, D-20259, Hamburg, Germany. http://www.lci-publisher.com/liqcryst.html
[15] Stewart, J. J. P. (1989). *J. Computational Chem.*, 10, 209.
[16] Hehre, W. J., Radom, L., Schleyer, P. V. R., & Pople, J. A. (1986). *Ab Initio Molecular Orbital Theory*, Wiley: New York.
[17] Hehre, W. J., Yu, J., & Klunzinger, P. E. (1997). *A Guide to Molecular Mechanics and Molecular Orbital Calculations in SPARTAN*, Wavefunction, Inc.: USA.
[18] Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T., Petersson, G. A., Montgomery, J. A., Raghavachari, K., Al-Laham, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Cioslowski, J., Stefanov, B. B., Nanayakkara, A., Challacombe, M., Peng, C. Y., Ayala, P. Y., Chen, W., Wong, M. W., Andres, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. J., Binkley, J. S., Defrees, D. J., Baker, J., Stewart, J. P., Head-Gordon, M., Gonzalez, C., & Pople, J. A. (1995). *Gaussian 94*, Revision E.2, Gaussian, Inc.: Pittsburgh, PA.
[19] *Spartan*, version 5.1.1., Wavefunction Inc., 18401 Von Karman Ave., Suite 370, Irvine, CA, USA, 1999.