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# Steric and Electronic Situation in the 4-X-4'-[(4''-Y-Phenyl)ethynyl]biphenyl Homologous Series: A Joint Theoretical and Spectroscopic Study

Pedro D. Ortiz,<sup>†,||</sup> Reynier Suardíaz,<sup>‡,§</sup> Laura de Vega,<sup>†</sup> Gunther Hennrich,<sup>\*,†</sup> and Pedro J. Ortiz<sup>\*,‡</sup>

Departamento de Química Orgánica y Departamento de Química-Física Aplicada, Universidad Autónoma de Madrid, Madrid, 28049, Spain, and Departamento de Química-Física, Universidad de La Habana, La Habana 10400, Cuba

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In this work we have studied the rotational barriers, the polarization of the acetylenic triple bond, and the molecular dipole moments in the 4-X-4'-[(4''-Y-phenyl)ethynyl]biphenyl homologous series using the density functional theory (DFT) and 1D/2D NMR spectroscopy. This series of compounds constitutes an effective base for the acquisition of liquid crystals. The equilibrium angle ( $\theta_{eq}$ ) and the torsional barriers  $\Delta E(0^\circ)$  and  $\Delta E(90^\circ)$  are not very sensitive to the substituent effects. We have found evidence for the similarity in the  $\pi$ -conjugation of the Y-substituted and X,Y-disubstituted compounds, the latter with mesomorphic properties, by means of the graphic analysis of the relationship between the molecular dipolar moment  $\mu(D)$  and the difference between the  $^{13}C$  NMR chemical shifts of the acetylenic carbon atoms ( $\Delta\delta_{C\equiv CII}$  [ppm]). The obtained results contribute to a better understanding of the structure–activity relationship for potential liquid crystalline systems.

## 1. Introduction

Liquid crystals are substances that show anisotropic properties as solids, combined with a degree of fluidity characteristic of liquids.<sup>1,2</sup> For this singular behavior, liquid crystals are of great importance for high quality displays and other modern device manufacture.<sup>3–7</sup>

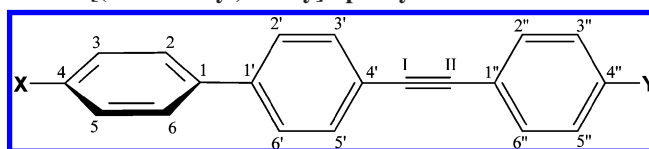
Thermal and dynamic properties of mesogenic compounds are strongly influenced by both electronic and molecular structure of individual building units, as well as the intermolecular interactions operative in the bulk.<sup>8–11</sup> The mesomorphic behavior of an organic compound can be varied by modifying its molecular structure.<sup>12</sup> For example, the molecular order in the liquid crystal phase depends on the mesogenic core structure and its geometry, polarizability, molecular conformation, and permanent dipole moment.

In this work we have studied molecules of the 4-X-4'-[(4''-Y-phenyl)ethynyl]biphenyl homologous series, with the biphenyl fragment being a common structural motif for thermotropic calamitic liquid crystals<sup>13</sup> (Scheme 1).

It is important to obtain information about the effect of the terminal substituents (X, Y) on the biphenyl fragment and the carbon–carbon triple bond. For biphenyl systems, Johansson and Olsen reported values very close to the experimentally obtained equilibrium angle and torsion barriers using a combination of coupled cluster, density functional theory, and thermal corrections.<sup>14–16</sup>

In order to obtain geometrical and spectroscopic data, keeping the computational effort within reasonable limits, we explore

SCHEME 1: Molecular Structure of 4-X-4'-[(4''-Y-Phenyl)ethynyl]biphenyl



the possibility whether useful results can be achieved using the density functional theory (DFT) approach as a theoretical method. DFT calculations have proved to be an accurate method for the evaluation of different properties for a plethora of molecular systems including biphenyl systems.<sup>14,17,18</sup>

## 2. Methods

**2.1. Theoretical Calculations.** The geometry optimizations and the calculation of frequencies were performed at the DFT<sup>19,20</sup> level using the B3LYP functional and 6-311G(d,p) basis set.<sup>21,22</sup>

The  $^{13}C$  NMR nuclear chemical shielding tensors were calculated by the gauge-including atomic orbital (GIAO) method.<sup>23,24</sup> In our case, it can be assumed that the length of side chains does not play a significant role in the electronic properties of the target molecules. Therefore, all alkyl side chains have been replaced by  $CH_3$  groups in the corresponding theoretical models, in order to reduce calculation complexity.

For comparison with experimental NMR data, the  $\delta(ppm)$  relative chemical shifts were calculated by referring the absolute shielding tensor obtained by DFT to the absolute shielding tensor of tetramethylsilane (TMS), 184.5 ppm, which was calculated at the same level of theory. The value of  $\sigma_{iso}$  for TMS obtained by us is very close to that obtained after correction by vibrational averaging, for bulk susceptibility, for temperature, and in relation to a secondary standard, 185.4 ppm.<sup>25</sup> These results confirm the appropriateness of the basis set and functional used in our chemical shifts calculation. All quantum chemical calculations are performed using the Gaussian 03 program package.<sup>26</sup>

\* Authors to whom correspondence should be addressed. (P.J.O.) E-mail: pedro@fq.uh.cu; (G.H.) E-mail: gunther.hennrich@uam.es.

<sup>†</sup> Departamento de Química Orgánica, Universidad Autónoma de Madrid.

<sup>‡</sup> Universidad de La Habana.

<sup>§</sup> Departamento de Química-Física Aplicada, Universidad Autónoma de Madrid.

<sup>||</sup> Present address: Departamento de Química Inorgánica, Universidad de La Habana, La Habana 10400, Cuba.

## SCHEME 2: Molecular Structure of Biphenyl

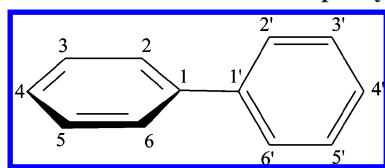


TABLE 1: Calculated and Experimental Torsional Barriers and Equilibrium Angle of Biphenyl

	$\Delta E$ (0°) (kJ/mol)	$\Delta E$ (90°) (kJ/mol)	$\theta^\circ$ (equilibrium)
experimental	$6.0 \pm 2.1^{15}$	$6.5 \pm 2.1^{15}$	$44.4 \pm 1.2^{16}$
calculated <sup>14</sup>	8.0	8.3	39.5
calculated <sup>a</sup>	9.0	8.3	40.6

<sup>a</sup> This work.TABLE 2: Experimental and Calculated <sup>13</sup>C NMR Chemical Shifts Differences between the Acetylenic Carbon Atoms ( $\Delta\delta_{\text{CI}=\text{CII}}$  (ppm) =  $\delta_{\text{CI}} - \delta_{\text{CII}}$ )

molecule			
X	Y	$\Delta\delta_{\text{CI}=\text{CII}}$ (ppm) calculated	$\Delta\delta_{\text{CI}=\text{CII}}$ (ppm) experimental
OC <sub>10</sub> H <sub>21</sub>	Pyr	+7.2	+7.4 <sup>28</sup>
OC <sub>10</sub> H <sub>21</sub>	NO <sub>2</sub>	+9.1	+6.9 <sup>28</sup>
OC <sub>10</sub> H <sub>21</sub>	COOCH <sub>3</sub>	+4.3	+3.3 <sup>28</sup>
COOCH <sub>3</sub>	OC <sub>10</sub> H <sub>21</sub>	-3.9	-3.2 <sup>28</sup>
COCH <sub>3</sub>	NH <sub>2</sub>	-5.6	-6.3 <sup>29</sup>

**2.2. <sup>13</sup>C NMR Spectra.** NMR spectra were recorded at 300 K in partially deuterated chloroform (deuteration grade 99.80%) on a Bruker AC 300 spectrometer (75 MHz for <sup>13</sup>C), and the chemical shifts,  $\delta$ (ppm), were referenced to the residual CDCl<sub>3</sub> signal. The g-HMBC (gradient-heteronuclear multiple bond correlation) was recorded at 300 K using a Varian NMR System 400 (100 MHz for <sup>13</sup>C).

### 3. Validation of the Theoretical Level Used in the Present Work

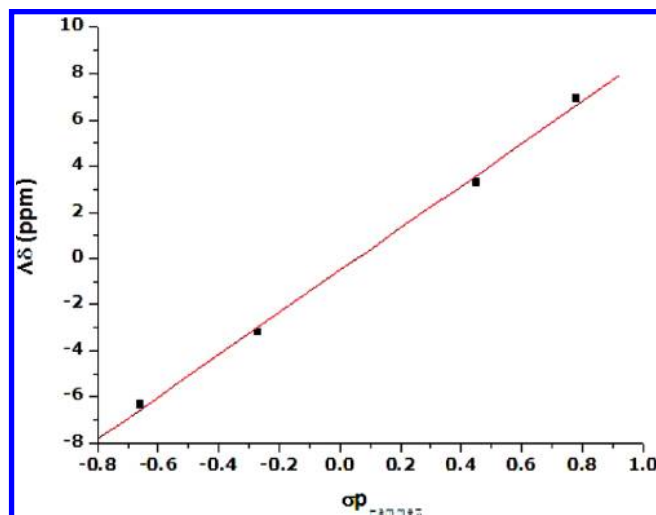
**3.1. Torsional Barriers and Equilibrium Angle.** The twisted structure of the biphenyl fragment is explained by the balance between ortho hydrogen–hydrogen steric repulsion and the electronic conjugation of the two phenyl rings<sup>27</sup> (Scheme 2).

Table 1 shows that the values for the torsional barriers in the biphenyl fragment obtained in the present work are in good agreement with both experimental data and data obtained using a very high level of theory.<sup>14</sup> The experimental equilibrium angle is larger than the theoretical one obtained at zero temperature, but it is in good agreement with most related methods.<sup>14</sup> Thermal corrections have a large effect on the equilibrium angle because potential energy near the minimum is very shallow, however, for our calculus these corrections are irrelevant.

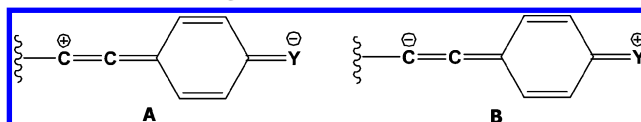
**3.2. <sup>13</sup>C NMR Chemical Shifts: Experimental and DFT-GIAO Calculation.** Table 2 shows a good agreement between the experimental and theoretical values of the chemical shifts differences between the acetylenic carbon atoms.

The <sup>13</sup>C NMR chemical shift DFT-GIAO calculation shows that  $\delta_{\text{CI}} > \delta_{\text{CII}}$  when Y = electron-withdrawing group and  $\delta_{\text{CI}} < \delta_{\text{CII}}$  when Y = electron-donating group, in correspondence with a Hammett plot (Figure 1).

The values of  $\Delta\delta$ (ppm) =  $\delta_{\text{CI}} - \delta_{\text{CII}}$  contain useful information on the molecular structure of these compounds because they are related with the polarization of the acetylenic triple bond.<sup>30–32</sup> The increased polarization of this bond enhances the

Figure 1. Experimental <sup>13</sup>C NMR chemical shifts,  $\Delta\delta_{\text{CI}=\text{CII}}$  (ppm) vs  $\sigma_{\text{pHammett}}$  plot.

### SCHEME 3: Charge Effect on CI Acetylenic Carbon Atom: Y-Electron-Withdrawing (A) or Y-Electron-Donating (B) Substituent



cumulenlic character and therefore increases efficient  $\pi$ -conjugation (Scheme 3).

An important result of our analysis is the unequivocal assignment of the C<sub>I</sub> and C<sub>II</sub> chemical shifts in the <sup>13</sup>C NMR spectra. Figure 2 shows the g-HMBC spectra of the compound COCH<sub>3</sub>/NH<sub>2</sub> (a) and OC<sub>10</sub>H<sub>21</sub>/NO<sub>2</sub> (b), respectively. This 2D NMR technique detects heteronuclear connectivities through two and three bonds, and it is very useful for the identification of quaternary carbon atoms. For simplicity, <sup>13</sup>C NMR spectra are not shown in Figure 1 (ppm).

In accordance with the numeration of the atoms, see Scheme 1, three bonds exist from H<sub>3'</sub> to C<sub>I</sub>, as well as from H<sub>2''</sub> to C<sub>II</sub>. We will use the proton spectrum-like reference to determine the relative positions of C<sub>I</sub> and C<sub>II</sub> in the <sup>13</sup>C NMR spectrum through the cross-peaks of the g-HMBC spectrum.

In the region corresponding to aromatic protons of both molecules the signals corresponding to three different spin systems are observed. The signals of H<sub>3'</sub> and H<sub>2'</sub> protons are easily identifiable in both proton spectra. The signals of C<sub>I</sub> and C<sub>II</sub> atoms are in the region of 80–100 ppm of the <sup>13</sup>C NMR spectra.

The cross-peaks in Figure 2a show that for the compound COCH<sub>3</sub>/NH<sub>2</sub> the carbon atom C<sub>I</sub> is more shielded than C<sub>II</sub>, while in Figure 2b it is observed that for the OC<sub>10</sub>H<sub>21</sub>/NO<sub>2</sub> compound, the carbon atom C<sub>I</sub> is more deshielded than C<sub>II</sub>. Thus, by means of the g-HMBC spectra, a totally sure determination of the acetylenic carbon atom relative position in the <sup>13</sup>C NMR spectra is achieved for the studied series of compounds. Those relative positions vary as a function of the electronic characteristic of the Y substituent.

It is important to highlight that by means of the GIAO–DFT method we arrived to the same conclusion in our work. It is firm evidence of the predictive capacity of this theoretical method, at the level we have used it, to predict NMR chemical shifts in the series of studied compounds. The NMR/DFT combination has been also successfully employed in other molecular systems.<sup>33–36</sup>

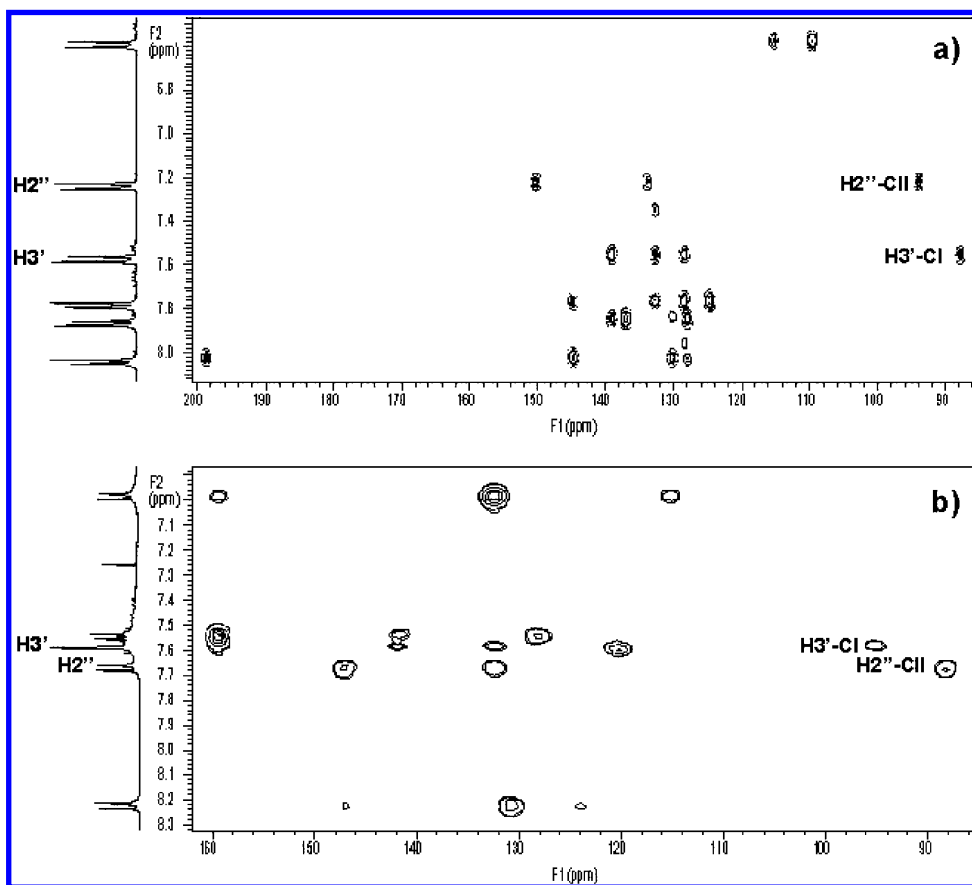


Figure 2. g-HMBC spectra of (a) X = COCH<sub>3</sub>/Y = NH<sub>2</sub> and (b) X = OC<sub>10</sub>H<sub>21</sub>/Y = NO<sub>2</sub>.

TABLE 3: Calculated Energetic, Geometric, and Spectroscopic Parameters for a Substituent

molecule		$\theta_{eq}$	$E_{eq}$ (a.u.)	bar 0°	bar 90°	$\Delta\delta_{C_{II}=C_{II}}$ (ppm)
X	Y			(kJ/mol)	(kJ/mol)	
H	H	38.7	-770.70329	8.02	9.20	-0.5
H	NO <sub>2</sub>	38.5	-975.25956	8.04	9.30	+8.0
H	COOCH <sub>3</sub>	38.6	-998.64509	8.04	9.21	+3.2
H	OCH <sub>3</sub>	38.5	-885.25746	7.99	9.25	-2.6
H	NH <sub>2</sub>	38.5	-826.07788	7.95	9.34	-4.4
NO <sub>2</sub>	H	37.6	-975.25983	7.46	10.37	-4.1
COOCH <sub>3</sub>	H	37.8	-998.64523	7.55	10.13	-2.2
OCH <sub>3</sub>	H	37.4	-885.25698	7.20	10.12	-0.1
NH <sub>2</sub>	H	36.3	-826.07701	6.62	10.98	+0.6

#### 4. Torsional Barriers, Equilibrium Angle, and $\Delta\delta_{C_{II}=C_{II}}$ (ppm) of 4-X-4'-[(4-Y-Phenyl)]ethynyl]biphenyl Series

**4.1. The Effect of a Substituent.** Table 3 summarizes the theoretical values of X- or Y-substituted biphenylacetylene systems. For comparison, the values obtained for X = Y = H are added. The changes in  $\theta_{eq}$  upon Y-substitution are negligible, but a slight decrease upon the X-substitution can be observed. The biggest effect corresponds to X = NH<sub>2</sub>, which is a strong electron-donor substituent.

As can be observed in Table 3, the electronic energy is practically insensitive to the substituent change, and the numeric values indicate that these are stable molecules in all cases. A considerable influence on the torsional barriers is observed for X-substituents.  $\Delta E(0^\circ)$  decreases and  $\Delta E(90^\circ)$  increases with respect to X = H, and the highest effect is observed when X = NH<sub>2</sub>. This result is in agreement with that obtained for the equilibrium angle  $\theta_{eq}$ , and it is a consequence of the variation of the electron density in the corresponding phenyl ring. The decrease of  $\theta_{eq}$  results in a stronger repulsion of the hydrogen

TABLE 4: Calculated Critical Interatomic Distances for  $\theta = 0^\circ$ ,  $\theta_{eq}$ , and  $90^\circ$  of the Monosubstituted Compounds

molecule		$d_{C_I-C_{I'}}$ ( $\theta_{eq}$ ) (Å)	$d_{C_I-C_{I'}}$ (0°) (Å)	$d_{C_I-C_{I'}}$ (90°) (Å)	$d_{H_2-H_2'}$ ( $\theta_{eq}$ ) (Å)	$d_{H_2-H_2'}$ (0°) (Å)
X	Y					
H	H	1.494	1.494	1.495	2.371	1.950
H	NO <sub>2</sub>	1.493	1.490	1.494	2.369	1.951
H	COOCH <sub>3</sub>	1.493	1.490	1.494	2.371	1.951
H	OCH <sub>3</sub>	1.493	1.490	1.494	2.371	1.953
H	NH <sub>2</sub>	1.493	1.494	1.494	2.371	1.954
NO <sub>2</sub>	H	1.491	1.487	1.493	2.352	1.949
COOCH <sub>3</sub>	H	1.482	1.488	1.493	2.357	1.952
OCH <sub>3</sub>	H	1.491	1.487	1.494	2.359	1.962
NH <sub>2</sub>	H	1.490	1.490	1.494	2.342	1.954

atoms in the ortho positions of both phenyl rings and therefore an increase in the energy barrier  $\Delta E(90^\circ)$ . The effect for the Y-substituent is insignificant.

On the other hand, the effect of the Y-substituent on  $\Delta\delta_{C_{II}=C_{II}}$  (ppm) is very significant and shows a behavior similar to that described in Section 3.2, with the biggest calculated value of  $\Delta\delta_{C_{II}=C_{II}}$  (ppm) for Y = NO<sub>2</sub>. The effect is small for the electron-donor substituents OCH<sub>3</sub> and NH<sub>2</sub> but remarkable for the NO<sub>2</sub> group.

It is interesting to observe the relative positions of the acetylenic carbon atoms in the <sup>13</sup>C NMR spectrum when one electron-withdrawing substituent occupies the X or Y positions. C<sub>I</sub> is the more deshielded nucleus when X = NO<sub>2</sub> and C<sub>II</sub> is the more deshielded nucleus when Y = NO<sub>2</sub>.

The energetics of the internal rotation around the central C–C bond in the biphenyl moiety has proven to be problematic.<sup>37</sup> Although a commonly accepted interpretation exists,<sup>27</sup> a different approach outlines that the hydrogen–hydrogen interaction would in fact be attractive and that the reason for nonplanarity instead

TABLE 5: Calculated Energetic, Geometric and Spectroscopic Parameters for Two Substituents

molecule		$\theta_{eq}$	$E_{eq}$ (a. u.)	bar 0° (kJ/mol)	bar 90° (kJ/mol)	$d_{C1-C1'}$ (Å)	$d_{H2-H2'}$ (Å)	$\Delta\delta_{C1=CII}$ (ppm)
X	Y							
H	H	38.7	-770.70329	8.02	9.20	1.494	2.371	-0.5
COOCH <sub>3</sub>	NO <sub>2</sub>	38.0	-1203.20111	7.65	9.91	1.493	2.357	+7.2
COCH <sub>3</sub>	NO <sub>2</sub>	37.8	-1127.94671	7.48	9.95	1.494	2.342	+7.0
OCH <sub>3</sub>	NO <sub>2</sub>	36.8	-1089.81355	6.94	10.28	1.494	2.359	+9.1
OCH <sub>3</sub>	COOCH <sub>3</sub>	37.2	-1113.19890	7.09	10.32	1.493	2.352	+4.3
OCH <sub>3</sub>	Pyr	37.2	-901.29520	7.11	10.37	1.494	2.369	+7.2
COOCH <sub>3</sub>	OCH <sub>3</sub>	37.5	-1113.19954	7.40	10.28	1.494	2.371	-3.9
COCH <sub>3</sub>	NH <sub>2</sub>	37.1	-978.76583	7.11	10.62	1.494	2.371	-5.6

is caused by an unfavorable lengthening of the central C—C bond when the two benzene rings become more coplanar.<sup>38</sup>

In order to understand the nature of phenyl–phenyl interactions, in Table 4 we summarize the effect of the X- or Y-substituents on critical interatomic distances for the dihedral angle  $\theta$  equal to 0°,  $\theta_{eq}$ , and 90°. As can be seen in the table, the bond length of bridging C—C bond,  $d_{C1-C1'}$ , does not change upon substitution for all dihedral angles.

It is noticeable that  $d_{C1-C1'}$  is almost the value of a single bond distance. At the same time,  $d_{C1-C1'}(\theta_{eq}) \approx d_{C1-C1'}(0^\circ)$  and  $d_{H2-H2'}(\theta_{eq}) > d_{H2-H2'}(0^\circ)$  for each molecule. These results support the classical interpretation of the twisted structure of the biphenyl unit.

The calculation method used by us predicts that the X-substituent has the most marked effect on both  $\theta_{eq}$  and the torsional barriers  $\Delta E(0^\circ)$  and  $\Delta E(90^\circ)$ , while the difference between the chemical shifts of the C<sub>I</sub> and C<sub>II</sub> carbon atoms are more sensitive to the Y-substituent. It also correctly predicts the substitution effect on the geometric and electronic situation, which varies depending on the electronic nature of the substituent.

**4.2. The Effect of Two Substituents.** Table 5 shows the calculations for X-Y combinations of practical interest in the context of liquid crystals. Obtaining information on the geometric, energetic, and electronic parameters of this series of compounds is especially important.

The effect of X,Y-disubstitution on electronic energy is similar to that observed in monosubstitution. In accordance with the analysis carried out in Section 4.1, we interpret the values of  $\theta_{eq}$ ,  $\Delta E(0^\circ)$ ,  $\Delta E(90^\circ)$ ,  $d_{C1-C1'}$ , and  $d_{H2-H2'}$  in terms of the Y-substituent effects on the X-substituted compounds, and the  $\Delta\delta_{C1=CII}$  (ppm) values due to variation of the X-substituent in the Y-substituted compounds. For calculated combinations of X and Y, the following results are obtained, in all cases referenced to the unsubstituted compound (X = Y = H):  $\theta_{eq}$  shows little variation, while the torsional barriers  $\Delta E(0^\circ)$  and  $\Delta E(90^\circ)$  are smaller and bigger, respectively, when they are compared with those of X = Y = H. These results indicate that X-Y double substitution lightly favors the minor  $\theta_{eq}$  in all cases.

On the other hand, the values of  $d_{C1-C1'}$  and  $d_{H2-H2'}$  are practically insensitive to the double substitution, as well as in the case of the monosubstitution. Furthermore,  $d_{C1-C1'}(\theta_{eq}) \approx d_{C1-C1'}(0^\circ)$  and  $d_{H2-H2'}(\theta_{eq}) > d_{H2-H2'}(0^\circ)$ , supporting the classical interpretation of the twisted biphenylic structure.

The other important calculated parameter is  $\Delta\delta_{C1=CII}$  (ppm). Molecules with Y = NO<sub>2</sub> show the highest values of  $\Delta\delta_{C1=CII}$  (ppm), with the highest value for the combination OCH<sub>3</sub>/NO<sub>2</sub>. The relative position of the C<sub>I</sub> and C<sub>II</sub> carbon atoms in the <sup>13</sup>C NMR spectra is in accordance with that obtained for the monosubstituted compounds.

TABLE 6: Calculated Electronic Dipole Moments,  $\mu$ (D), for Mono- and Disubstituted Molecules

molecule			molecule		
X	Y	$\mu$ (D)	X	Y	$\mu$ (D)
H	H	0.17	H	H	0.17
H	NO <sub>2</sub>	6.61	COOCH <sub>3</sub>	NO <sub>2</sub>	5.49
H	COOCH <sub>3</sub>	2.43	COCH <sub>3</sub>	NO <sub>2</sub>	4.49
H	OCH <sub>3</sub>	1.84	OCH <sub>3</sub>	NO <sub>2</sub>	8.07
H	NH <sub>2</sub>	2.84	OCH <sub>3</sub>	COOCH <sub>3</sub>	3.21
NO <sub>2</sub>	H	5.96	OCH <sub>3</sub>	Pyr	4.98
COOCH <sub>3</sub>	H	2.10	COOCH <sub>3</sub>	OCH <sub>3</sub>	3.01
OCH <sub>3</sub>	H	1.80	COCH <sub>3</sub>	NH <sub>2</sub>	5.95
NH <sub>2</sub>	H	2.79			

## 5. Molecular Dipole Moment

Since practical applications of liquid crystals are based on the response of those substances to external electric fields, we will pay special attention to the calculation of the molecular dipole moment.

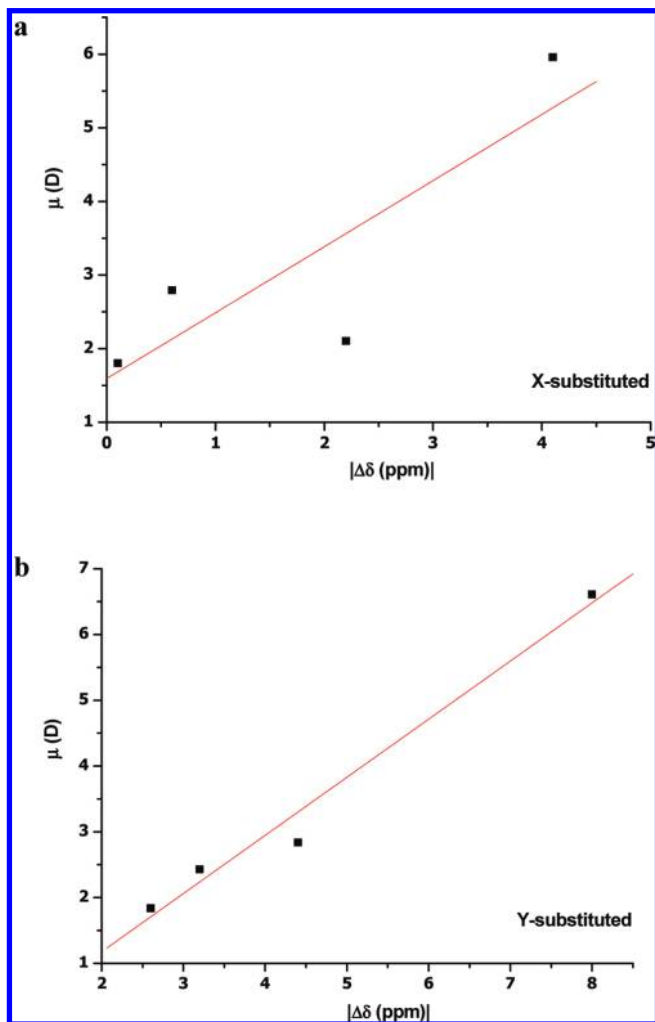
**5.1. Calculated Dipole Moments.** In Table 6 it can be seen that all substituted compounds obviously have a higher dipole moment compared to the unsubstituted reference. The  $\mu$ (D) value for one substituent is slightly higher when it occupies the Y-position than when it occupies the X-position in the molecule. In the series of monosubstituted compounds, the biggest effect in  $\mu$ (D) corresponds to the NO<sub>2</sub> group, that takes a significantly high value compared to those calculated for the rest of substituents.

Table 6 shows that the substituent combinations electron-donating (B)/electron-withdrawing (A) lead to an increase of  $\mu$ (D) increment regarding the monosubstituted compounds, while the substituent combinations A/B give a relative decreases of  $\mu$ (D). The highest value in the whole series of compounds is found for OCH<sub>3</sub>/NO<sub>2</sub> ( $\mu$  = 8.07 D). In this case there are two substituents with complementary electronic effects.

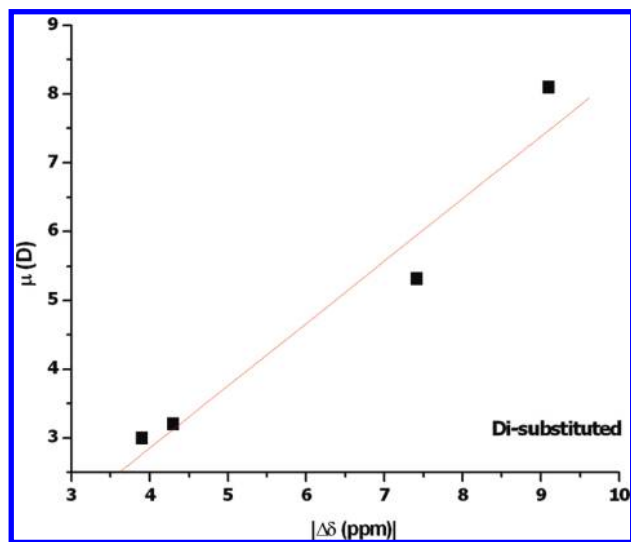
**5.2. Relationship between  $\mu$ (D) and  $|\Delta\delta_{C1=CII}|$  (ppm).** With the objective of obtaining information on the relationship between  $\mu$ (D) and the acetylenic triple bond polarization, figure 3 shows the  $\mu$ (D) vs  $|\Delta\delta_{C1=CII}|$  (ppm) plot for monosubstituted compounds. A linear relationship exists for Y-substituents (Figure 3b), that we interpret in terms of the polarization of the triple bond induced by the Y. The great dispersion of data points observed for the X-substitution (Figure 3a) is evidence of a more complicated relationship between the molecular structure and the electronic conjugation in the  $\pi$ -system.

We have drawn a similar plot (Figure 4), choosing four disubstituted compounds, for which the liquid crystalline properties of their corresponding experimental homologous have been proven experimentally.<sup>28</sup> Figure 4 shows an equally linear relationship as the one observed for Y-substituted compounds (Figure 3b). This is an evidence of the similarity between the





**Figure 3.** Theoretical  $\mu$ (D) vs  $|\Delta\delta_{C\equiv CII}|$  (ppm) plot of (a) X- and (b) Y-monosubstituted compounds.



**Figure 4.** Theoretical  $\mu$ (D) vs  $|\Delta\delta_{C\equiv CII}|$  (ppm) plot of disubstituted compounds which display liquid crystal properties.

electronic transmission mechanisms in these molecules, and about the contribution of the acetylenic triple bond to this mechanism.

## 6. Conclusions

In this work we have been able to obtain and to systematize valuable information on the 4-X-4'-[(4''-Y-phenyl)ethynyl]biphenyl

homologous series of compounds by means of the DFT theory using the B3LYP functional and 6-311G(d,p) bases of functions.  $^{13}\text{C}$  NMR chemical shifts calculations carried out by means of the GIAO method, at the same theory level, are equally satisfactory. The equilibrium angle ( $\theta_{eq}$ ) is in the range of  $38.5\text{--}36.3^\circ$ , and the method of calculus also predicts correctly the  $\Delta E(0^\circ)$  and  $\Delta E(90^\circ)$  torsional barriers, in good agreement with that obtained by means of others theoretical and experimental methods for the biphenyl and its para,para'-disubstituted derivatives. In the series that we study, these parameters are dependent on the X-substitution. In general, those molecules of the series that have substituents with high electronic effects, i.e., the combinations electron-donating/electron-withdrawing and electron-withdrawing/electron-donating, are effective to obtain high electric dipolar moment  $\mu$ (D) values. It is a very important parameter because of its relationship with the liquid crystal properties of these compounds. The functional relationship between  $\mu$ (D) and  $|\Delta\delta_{C\equiv CII}|$ (ppm) is similar for both Y- and disubstituted molecules (the latter with properties like those of liquid crystals).

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## References and Notes

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(29) 4-Ethanone-yl-4'-[(4''-aminophenyl)ethynyl]biphenyl (X = COCH<sub>3</sub>/Y = NH<sub>2</sub>) as a yellow solid. Yield: 95 mg; 31%; <sup>1</sup>H NMR: δ = 8.04 ppm (d, *J* = 8.1 Hz, 2 H); 7.85 (d, *J* = 8.1, 2 H); 7.77 (d, *J* = 8.2, 2 H); 7.56 (d, *J* = 8.2, 2 H); 7.24 (d, *J* = 8.0, 2 H); 6.60 (d, 2 H); 2.60 (s, 3 H). <sup>13</sup>C NMR: δ = 198.1 ppm; 149.8, 144.0, 138.0, 136.2, 133.6, 132.0, 129.6, 127.8, 127.4, 123.9, 113.9, 109.2, 93.2, 86.9, 26.8; MALDI-HRMS found: 311.3879; calculated for C<sub>22</sub>H<sub>7</sub>ON: 311.3869. *R*<sub>f</sub> (Hex/EtOAc 1:1): 0.28.

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