

## Synthesis, Molecular Structure of Diethyl Phenylenebis(Methylene)Dicarbamates and FTIR Spectroscopy Molecular Recognition Study with Benzenediols

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The synthesis, density functional theory (DFT) molecular structure and Fourier transform infrared spectroscopy (FTIR) molecular recognition study of diethyl phenylenebis(methylene) dicarbamates with 1,2- and 1,3-benzenediols is described. The formation of the complexes was confirmed by the shift of the O-H stretching bands in the IR spectra of the complexes compared with the IR spectra of the noncomplexed benzenediols.

**Keywords:** carbamates, xylylenediamines, molecular recognition, FTIR, DFT

### Introduction

Molecular recognition is the basis of supramolecular chemistry. It involves complementarily that should exist between the functional groups of two molecules to form a host-guest complex by noncovalent interactions.<sup>1</sup> Hydrogen bond (HB) is the most important noncovalent interaction used in the design of supramolecular systems. HB is particularly important from a biological point of view because of its involvement in several biological processes, such as the stabilization of the double helix of DNA,<sup>2</sup> peptide three-dimensional structures (helices, sheets or turns),<sup>3</sup> enzyme-substrate interactions,<sup>4</sup> recognition among proteins<sup>5</sup> and drug-acceptor interactions.<sup>6</sup> Amide based receptors have been exploited as HB donors and acceptors.<sup>7-9</sup> Carbamates are composed by N-H, C=O and O-R functionalities, which allow them to form HB interactions. In this context, xylylenediamine amide derivatives have been exploited as molecular hosts in macrocyclic<sup>10-12</sup> and non-macrocyclic<sup>13,14</sup> forms.

On the other hand, benzenediols has been used as supramolecular building blocks in the design of

supramolecular systems due its ability as HB donors.<sup>15-19</sup> Fourier transform infrared spectroscopy (FTIR) have been employed as routine tool for the characterization of hydrogen bonded molecular complexes.<sup>20-22</sup>

Computational chemistry methods, such as density functional theory (DFT) calculations, and spectroscopic techniques such nuclear magnetic resonance (NMR) are used in order to obtain information about the molecular structure of a new compound when there is not X-ray molecular structure.<sup>23-25</sup>

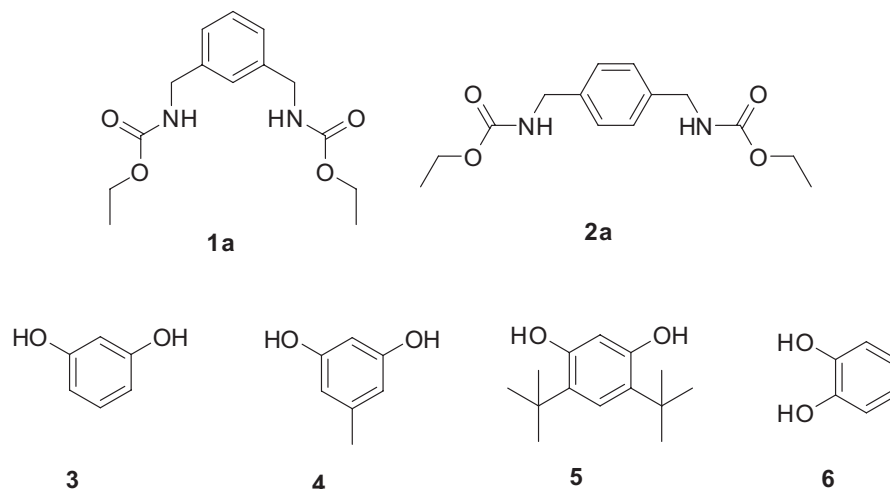
In this contribution, we report the synthesis, and the optimized DFT molecular structure of two diethyl phenylenebis(methylene)dicarbamates (**1a** and **2a**), as well as, the preliminary complexation study by FTIR spectroscopy, with 1,2- and 1,3-benzenediols: resorcinol (**3**), orcinol (**4**), 4,6-di-*tert*-butyl-1,3-benzenediol (**5**) and catechol (**6**) (Scheme 1).

### Results and Discussion

Synthesis of the compounds

The compounds were synthesized by the condensation of *meta*- and *para*- xylylenediamine with ethyl chloroformate

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**Scheme 1.** Compounds involved in the molecular recognition study.

(Scheme 2). The structures of **1a** and **2a** were confirmed by the spectral data (Table 1). The N-H frequencies in IR and  $^1\text{H}$ NMR spectra [see Supplementary Information (SI) section] confirmed the formation of the compounds. The IR spectra of compounds **1a** and **2a** displayed characteristic absorption bands at  $3310\text{ cm}^{-1}$  and  $3308\text{ cm}^{-1}$  for N-H, at  $1687\text{ cm}^{-1}$  and  $1685\text{ cm}^{-1}$  strong bands for the C=O groups and, in the region of  $1247\text{--}1248\text{ cm}^{-1}$  corresponding to C-O vibrations, respectively. The  $^1\text{H}$  NMR spectra showed the NH signal at 5.03 ppm for **1a** and 5.01 ppm for **1b**. The  $^{13}\text{C}$  NMR chemical shift C(7)-N bond appeared at 44.8 and 44.6 ppm for **1a** and **2a**, respectively; the carbonyl chemical shifts were observed at the characteristic high frequencies of 156.6 ppm in both compounds.

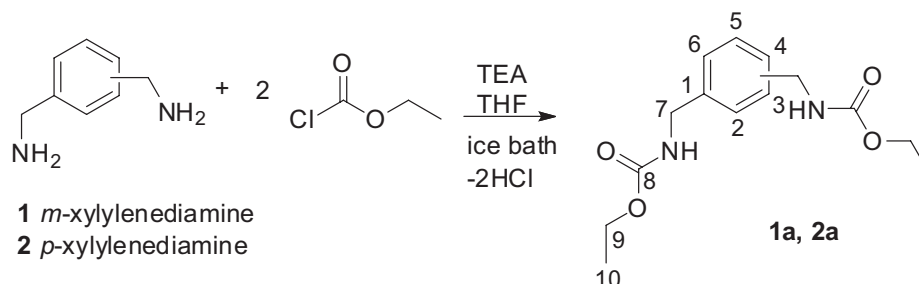
#### FTIR molecular recognition study

The molecular recognition ability of the phenylenebis(methylene)dicarbamates to benzenediols was evaluated by a mechanochemical complexation study. Mixtures in a 1:1 ratio of crystalline powders of **1a** or **2a** with the 1,2- or 1,3-benzenediol (**3-6**) were ground with dichloromethane in a porcelain mortar until complete 5 min. 1,4-benzenediols were not included in this study because in these positions, the O-H groups are located at  $180^\circ$  between

them. At the end of the grinding time, in all the experiments performed, a semisolid sticky (similar to honey) product was obtained as consequence of the grinding process (**1a-3-6** and **2a-3-6** complexes). FTIR spectra of the semisolid ground products, the phenylenebis(methylene)dicarbamates (**1a** and **2a**) and the benzenediols (**3-6**) were obtained with a FTIR attenuated total reflection (ATR) system. The O-H and N-H stretching bands are presented in Figure 1 (full spectra of the compounds are presented as SI).

The complex formation was confirmed because the O-H stretching bands in the IR spectra of the semisolid product are shifted with respect to the O-H stretching bands in the spectra of the respective benzenediol. This shift suggests the formation of the phenylenebis(methylene)dicarbamate-benzenediol complex involving the intermolecular O-H...O=C hydrogen bond interaction as consequence of the mechanochemical reaction.<sup>17</sup> In all the IR spectra of the semisolid complexes (**1a-3-6** and **2a-3-6**) the O-H stretching bands are overlapped with the N-H stretching band of **1a** or **2a**.

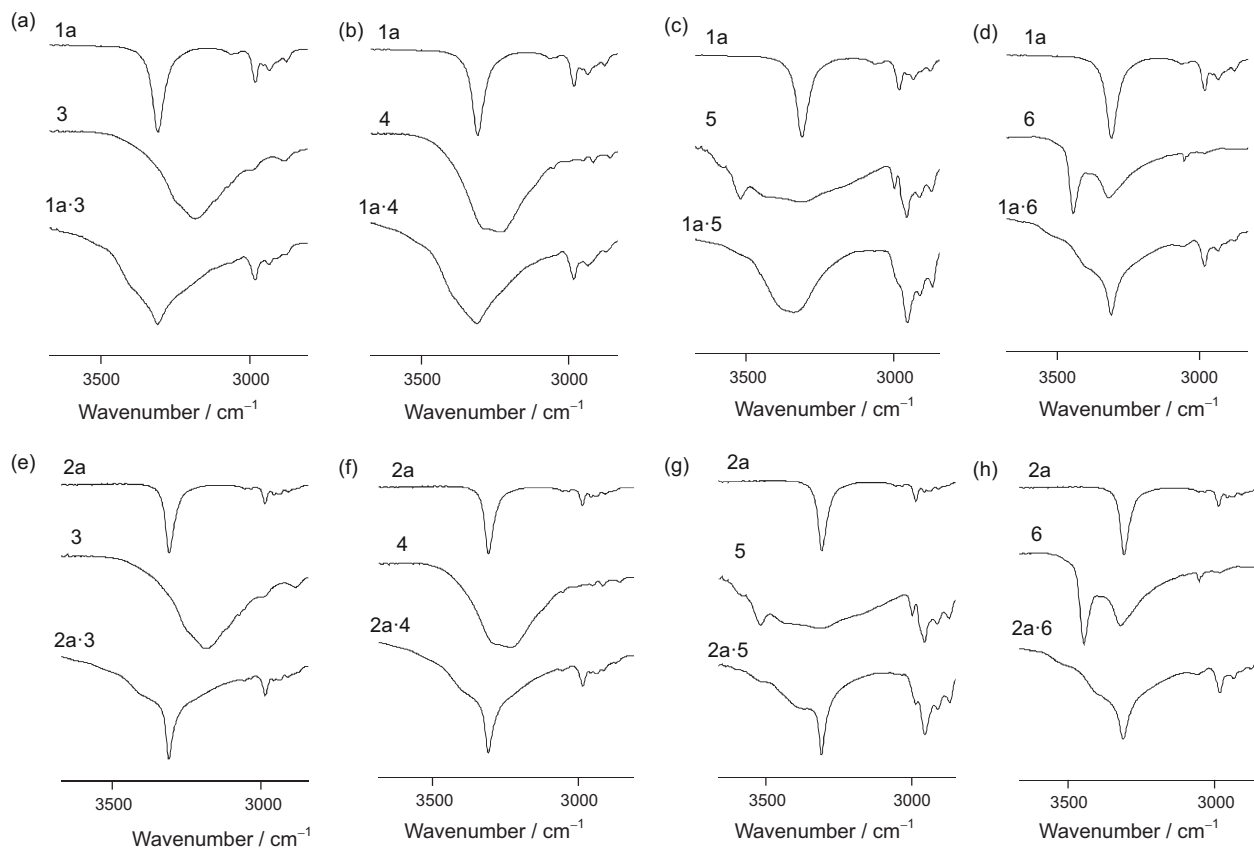
The IR spectra of the noncomplexed forms of **3** and **4** showed a single broad O-H stretching band at  $3183\text{ cm}^{-1}$  and  $3227\text{ cm}^{-1}$  (Table 2) respectively, meanwhile in the **1a-3-4**, **2a-3-4**, complexes, the O-H stretching band is shifted to higher frequencies (Figures 1a, 1b, 1e and 1f).



**Scheme 2.** Synthetic procedure for **1a** and **2a**. TEA = triethylamine, THF = tetrahydrofuran.

**Table 1.** Spectroscopic characterization of **1a** and **2a**

$\delta$ $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ ), $J$ in Hz										
Compound	H2	H3	H4	H5	H6	H7	NH	H9	H10	
<b>1a</b>	7.22	–	7.19	7.30	7.19	4.36 $^3J = 5.6$	5.03	4.16 $^3J = 7.2$	1.27 $^3J = 7.2$	
<b>2a</b>	7.27	7.27	–	7.27	7.27	4.35 $^3J = 6.0$	5.01	4.15 $^3J = 7.2$	1.25 $^3J = 7.2$	
$\delta$ $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )										
Compound	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
<b>1a</b>	139.1	126.5	139.1	129.0	126.5	129.0	44.8	156.6	61.0	14.6
<b>2a</b>	137.9	127.8	127.8	137.9	127.8	127.8	44.6	156.6	61.0	14.6
IR frequencies, $\nu$ in $\text{cm}^{-1}$										
Compound	N-H	=C-H (Ar)	C-H (Alk)	C=O	C-C (Ar)	C-O				
<b>1a</b>	3310	3065	2981	1687	1530 (s)	1247, 1045				
<b>2a</b>	3308	3054	2986	1685	1527 (s)	1248, 1051				

**Figure 1.** O-H and N-H stretching bands of the noncomplexed compounds and (a) **1a**·**3**, (b) **1a**·**4**, (c) **1a**·**5**, (d) **1a**·**6**, (e) **2a**·**3**, (f) **2a**·**4**, (g) **2a**·**5** and (h) **2a**·**6** complexes.

Two O-H stretching bands were observed in the IR spectra of noncomplexed **5** at  $3517\text{ cm}^{-1}$  (sharp) and  $3320\text{ cm}^{-1}$  (broad). After the complexation, in the **1a**·**5** and **2a**·**5** (Figures 1c and 1g) complexes, a single broad O-H stretching band is showed at  $3339\text{ cm}^{-1}$  and  $3382\text{ cm}^{-1}$ , respectively.

The IR spectra of **6** showed two O-H stretching bands: the band at  $3444\text{ cm}^{-1}$  belongs to the “free” O-H group, and the band at  $3320\text{ cm}^{-1}$  is the band of the intramolecular hydrogen bonded O-H group. In the **1a**·**6** and **2a**·**6** complexes (Figure 1d and 1h), both, the “free” and the intramolecular hydrogen bonded O-H bands

are shifted to lower frequencies as consequence of the intermolecular hydrogen bond. This has been reported in the complexation between catechol and hydrogen bonding acceptors.<sup>18,19</sup>

In very diluted solutions of alcohols and phenols, the “free” O-H stretching frequencies are observed as sharp and strong bands in the 3700-3584 cm<sup>-1</sup> range. As the concentration increases, the O-H band is shifted to lower frequencies (3550-3200 cm<sup>-1</sup>) and broadens, as consequence of the intermolecular hydrogen bonding between the O-H groups, leading to the formation of self-assembled O-H...O-H polymeric structures.<sup>26</sup> The O-H stretching bands of the noncomplexed forms of **3** and **4** are in the lower limit of the intermolecular hydrogen bonded frequencies (3183 cm<sup>-1</sup> and 3227 cm<sup>-1</sup>, respectively), due to their great ability to form intermolecular hydrogen bonds. Meanwhile, in the noncomplexed forms of **5** and **6**, the steric hindrance and the formation of intramolecular hydrogen bonds respectively, decreases this ability, causing the O-H stretching bands to appear at higher frequencies than **3** and **4**.

It is noteworthy that, after the complexation, the frequency of the O-H stretching bands in the IR spectra of **1a**·**3**-**6** and **2a**·**3**-**6** complexes, measured from the semisolid ground product, are in the 3308-3339 cm<sup>-1</sup> intermolecular hydrogen bond range, suggesting a rearrangement in the intermolecular hydrogen bond pattern, from the O-H...O-H in the noncomplexed forms, to the C=O...O-H in the complexes. This is in agreement with the reported for phenyldioxalamate-1,3-benzenediols complexes.<sup>17</sup> This rearrangement “breaks” the highly O-H...O-H intermolecular hydrogen bonded self assembly of the noncomplexed form of **3** and **4**, and shifts to higher

frequencies the O-H stretching band in the complexes **1a**·**3**-**4** and **2a**·**3**-**4**. Unlike **4** and **5**, whose formation of the **1a**·**5**-**6** and **2a**·**5**-**6** complexes favors the formation of intermolecular hydrogen bonds and shifts to lower frequencies de O-H stretching bands with regard to the noncomplexed form.

The small shifts of the C=O stretching bands are characteristic of the O-H...O=C complexes.<sup>17,27,28</sup> On the other hand, the small shift of the N-H stretching bands indicates that the N-H group is not involved in the complex formation.

#### Molecular structure of **1a** and **2a**

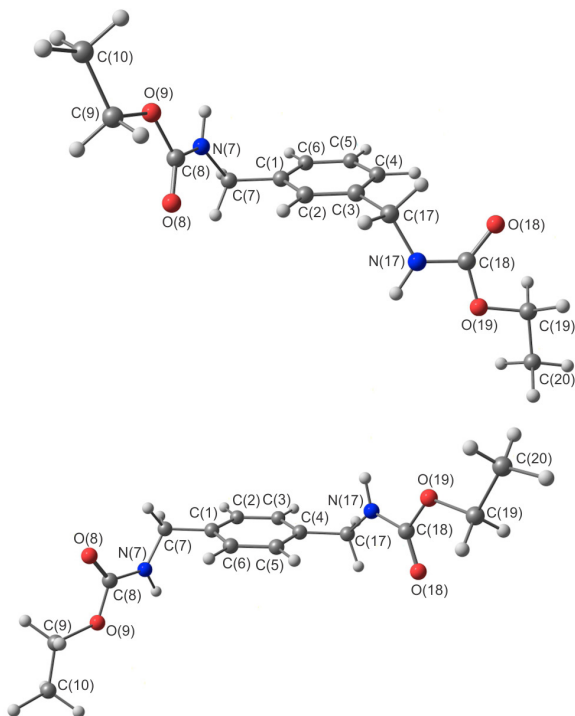
In order to gain more information about the molecular structure of the **1a** and **2a** compounds, DFT calculations at B3LYP/6-31+G\*\* level were performed using the GAUSSIAN 09 program.<sup>29</sup> In order to obtain the most stable conformer according to the arrangement of the diethyl carbamate “side arms” with respect to the plane of the aromatic ring, each conformer was obtained by the twisting of the C(2)-C(1)-C(7)-N(7) torsion angle (see SI). Each 10° turn conformer was geometry optimized to a local minimum.

In the global minimum energy conformations of **1a** and **2a** (Figure 2), the ethyl carbamate side “arms” are *trans*-positioned between them, in relation to the mean plane of the phenylene ring. In **1a**, the values of the C(2)-C(1)-C(7)-N(7) and C(2)-C(3)-C(17)-N(17) torsion angles are 110.69° and 69.08°, respectively, meanwhile in **2a**, the values of C(2)-C(1)-C(7)-N(7) and C(5)-C(4)-C(17)-N(17) are -59.03° and -55.20°, respectively. It is

**Table 2.** O-H, N-H and C=O stretching frequencies (cm<sup>-1</sup>) of **1a** and **2a** and their complexes in the ground products

Compound	$\nu_{\text{O-H}}$	$\Delta(\nu_{\text{O-H}})$	$\nu_{\text{N-H}}$	$\Delta(\nu_{\text{N-H}})$	$\nu_{\text{C=O}}$	$\Delta(\nu_{\text{C=O}})$
<b>1a</b>	–	–	3310	–	1687	–
<b>2a</b>	–	–	3308	–	1685	–
<b>3</b>	3183	–	–	–	–	–
<b>1a</b> · <b>3</b>	3313	+130	3313	+3	1683	-4
<b>2a</b> · <b>3</b>	3309	+126	3309	-1	1685	0
<b>4</b>	3227	–	–	–	–	–
<b>1a</b> · <b>4</b>	3312	+85	3312	+4	1685	-2
<b>2a</b> · <b>4</b>	3308	+81	3308	0	1685	0
<b>5</b>	3517, 3320	–	–	–	–	–
<b>1a</b> · <b>5</b>	3339	-178, +19	3339	+29	1689	+2
<b>2a</b> · <b>5</b>	3309	-136, +12	3382	+1	1684	-1
<b>6</b>	3444, 3320	–	–	–	–	–
<b>1a</b> · <b>6</b>	3311	-133, -9	3311	+1	1686	-1
<b>2a</b> · <b>6</b>	3308	-136, -12	3308	0	1684	-1

noteworthy that the *trans* conformation is also adopted by X-ray diffraction structures of similar compounds.<sup>30,31</sup>



**Figure 2.** Optimized molecular structures and atomic numbering of **1a** and **2a**.

On the other hand, the torsion angles from H(7)-C(7)-N(7)-H moiety of **1a** and **2a** are  $55.52^\circ$  and  $67.05^\circ$ , respectively for a synperiplanar conformation, meanwhile for an antiperiplanar conformation the values are  $171.24^\circ$  and  $-177.24^\circ$ , respectively. Using the experimental heteronuclear Karplus curves,<sup>24,25</sup> which correlates the NMR coupling constants with the dihedral angle, we found that the torsion angles of theoretical optimization are according to the  $^3J_{\text{H7-NH}}$  coupling constant of 5.6 Hz and 6.0 Hz obtained from the  $^1\text{H}$  NMR spectra of **1a** and **2a** (Table 1), which denote a torsion angle from  $28^\circ$  and  $23^\circ$  for synperiplanar, and  $134^\circ$  and  $137^\circ$  for antiperiplanar conformation, respectively.

## Conclusions

It was synthesized and characterized two new diethyl phenylenebis(methylene)-dicarbamates and its minimum energy molecular structure was determined by DFT calculations and  $^1\text{H}$  NMR. The FTIR spectroscopy study allowed to determinate the mechanochemical complexation of the phenylenebis(methylene)dicarbamates and benzenediols by the shift of the phenolic O-H stretching bands. This shift suggests a rearrangement

in the intermolecular hydrogen bond pattern, from the O-H...O-H in the noncomplexed forms, to the C=O...O-H in the complexes. As consequence of the results of the FTIR molecular recognition study, future studies with solution and solid state techniques will be performed in order to gain more information about the molecular structure of the complexes and their binding constants.

## Experimental

Melting points (m.p.) were determined using an Electrothermal IA9300 apparatus and are uncorrected. IR spectra were recorded from solid samples on a Bruker Tensor-27 FTIR spectrophotometer with ATR system. Mass spectra were obtained in a Bruker Esquire 6000 spectrometer with an electron ionization mode.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance III 400 ( $^1\text{H}$ , 400.1 MHz;  $^{13}\text{C}$ , 100.6 MHz) instrument in  $\text{CDCl}_3$  solutions, measured with  $\text{SiMe}_4$  as the internal reference, the chemical shift values are recorded on  $\delta$  scale and are in ppm; the coupling constants ( $J$ ) are in Hertz.

General procedure for the synthesis of the diethyl phenylenebis(methylene)-dicarbamates (**1a-2a**)

To a THF (100 mL) solution of 5 g (36.7 mmol) of the xylylenediamine and 10.2 mL (7.4 g, 73.4 mmol) of TEA were added dropwise 7.0 mL (7.9 g, 73.4 mmol) of ethyl chloroformate with vigorous stirring in an ice bath. The reaction mixture was additionally stirred for 24 h at room temperature. The suspension was filtered and the THF solution was evaporated to dryness. The obtained solid was solubilized in ethyl acetate and filtered to separate the insoluble solids. The ethyl acetate solution was evaporated to obtain the solid product.

Diethyl 1,3-phenylenebis(methylene)dicarbamate (**1a**)

Yield 78.9%; colorless flakes; m.p. 95-98  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  1.27 (t, 6H,  $J = 7.2$  Hz,  $\text{CH}_3$ ), 4.16 (q, 4H,  $J = 7.2$  Hz, O- $\text{CH}_2$ - $\text{CH}_3$ ), 4.36 (d, 4H,  $J = 5.6$  Hz, Ar- $\text{CH}_2$ ), 5.03 (s, 2H, NH), 7.19-7.30 (m, 4H, Ar);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ),  $\delta$  14.6, 44.8, 61.0, 126.5, 129.0, 139.1, 156.6; IR (neat)  $\nu_{\text{max}}/\text{cm}^{-1}$  3310 (NH), 1687 (C=O); GC-MS (EI)  $[M + 1]^+ = 281.1$   $m/z$ , anal. calcd. for  $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_4$ : C 59.99, H 7.19, N 9.99; found: C 60.06, H 7.28, N 9.91.

Diethyl 1,4-phenylenebis(methylene)dicarbamate (**2a**)

Yield 59.0%; white colorless flakes; m.p. 135-138  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  1.25 (t, 6H,  $J = 7.2$  Hz,  $\text{CH}_3$ ),

4.15 (q, 4H,  $J = 7.2$  Hz, O-CH<sub>2</sub>-CH<sub>3</sub>), 4.35 (d, 4H,  $J$  6.0 Hz, Ar-CH<sub>2</sub>), 5.01 (s, 2H, NH), 7.27 (s, 4H, Ar); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  14.6, 44.6, 61.0, 127.8, 137.9, 156.6; IR (neat)  $\nu_{\max}/\text{cm}^{-1}$  3305 (NH), 1683 (C=O); GC-MS (EI)  $[M + 1]^+ = 281.0$   $m/z$ , anal. calcd. for C<sub>14</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>: C 59.99, H 7.19, N 9.99; found: C 59.91, H 7.25, N 10.00.

### Mechanochemical complexation with benzenediols

Benzendiols **3-6** were purchased from commercial sources and used as received.

Mixtures in a ratio of 1:1 of 0.1 g of the xyllylene bis-carbamate (**1a**, **2a**) and the equivalent of benzenediol (**3-6**) were ground in a porcelain mortar with aid of 0.5 mL of dichloromethane. The grind time was completed until 5 min. A semisolid (similar to honey) product was obtained.

### Theoretical calculations

The density functional theory (DFT)<sup>32-34</sup> calculations were performed using the GAUSSIAN 09 package.<sup>26</sup> B3LYP hybrid functional<sup>35</sup> was employed. 6-31+G\*\* basis set<sup>36-38</sup> for C, H, O, and N atoms was also employed. Harmonic frequency analysis was made to verify optimized minima at the potential energy surface. The results were visualized in the Chemcraft program.<sup>39</sup>

### Supplementary Information

Supplementary information (Figures S1-S20: characterization of **1a** and **2a**, conformational study and FTIR full spectra of the molecular complexation study) is available free of charge at <http://jbc.sbq.org.br> as PDF file.

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