A Density Functional Theory Study on Interactions in Water-Bridged Dimeric Complexes of Lignin

Jurgen Lange Bregado,[*,1,2] Argimiro R. Secchi,[1,2] Frederico W. Tavares[1,2]

[1] Chemical Engineering *Program, COPPE, Universidade Federal do Rio de Janeiro, Cidade Universitária, Rio de Janeiro CP: 21941-914, Brazil.*

[2] Chemical and Biochemical Process Engineering Program , *Escola de Química, Universidade Federal do Rio de Janeiro, Cidade Universitária, Rio de Janeiro. CP: 21941-909, Brazil.*

Corresponding author, email: jurgenlange1967@gmail.com (J. L. B)

This file includes: 9 pages, 4 tables, 4 figures

Figure S1. (a) Structure of the water-bridged dimeric complexes: G⋯G inferred by radial distribution functions (RDFs) from MD study.[1] **(b)** Optimized structure of S⋯G by Density Functional Theory starting from structure depicted in **(a)** adding one -OCH3 group on the fragment 1 (**Figure 2**). Methyl groups (depicted with dashed black circles) were inserted at the O8 position to represent etherification by β – O – 4 linkages in the WBDCs. Dashed green lines represent hydrogen bond distances, whereas dashed black lines account for distance (d) and interplanar angle (θ) between phenolic rings in the dimeric complex (**Table S1**). Despite the structure (**b**) is dissimilar from (**a**) by a -OCH3 group, their conformations as to ring orientation are not very different (**Table S1**).
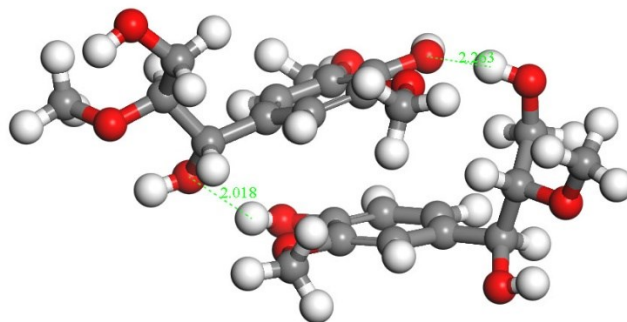
Figure S2. Optimized structure of S···G complex without water by Density Functional Theory at M06-2X/6-31++G (d, p) theory level. Dashed green lines represent hydrogen bond (H-bond) distances between O7···HO4 (2.018 Å) and O4···HO9 (2.263 Å). Stronger interactions of these H-bonds with much shorter distances (1.838 and 2.012 Å for O7···HO4 and O4···HO9, respectively) are observed in hydrated S···G complex (**Figure S1b**), indicating that water molecules participate in the stabilization of WBDCs.
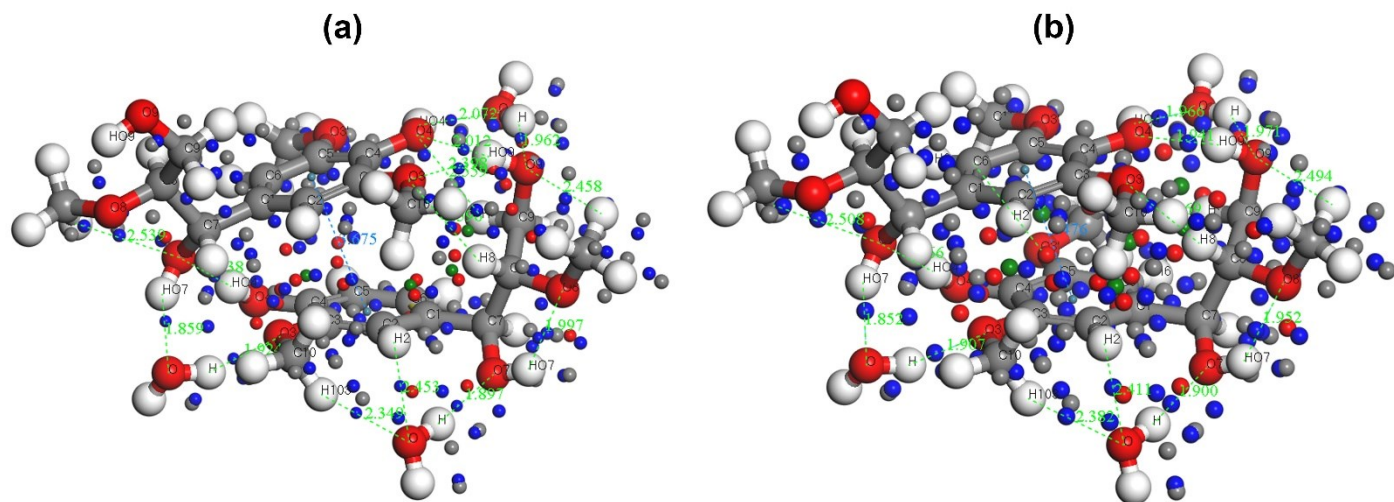
Figure S3. Structure of the water-bridged dimeric complexes: (**a**) S⋯G and (**b**) S⋯S showing all bond critical points (BCPs) determined by AIM's theory. Bonded carbon, oxygen and hydrogen atoms in the complexes are represented by big gray, red and white balls, respectively. Smaller size balls with gray, red, blue and green color illustrate the BCPs (3,-3), (3+1), (3,-1) and (3,+3) type. The light green dashed lines represent hydrogen bonds (H-bonds) connecting two atoms and intercepting the BCP (3,-1) type. On these lines are written the values of H-bonds distance.

Table S1. Comparison of geometric characteristic of water-bridged dimeric complexes (WBDCs) by Density Functional Theory (DFT) and Molecular dynamics (MD)

WBDCs	Number of methoxy groups	d [a) [Å]	θ [a) [°]	d [a) [Å]	θ [a) [°]
		DFT		MD	
S ⋯ G	3	3.60	23.74	3.904	23.89
S ⋯ S	4	3.52	23.11		

[a] d and θ mean distance and interplanar angle between centroids of aromatic rings (**Figure S1**). When d < 3.80 Å, and θ < 20°, face-to-face π-π stacking (Cofacial "sandwich") interactions will exist.[2]

Table S2. Electrostatic properties of hydrogen bonds in water-bridged dimeric complexes

WBDCs	H-bond	Atom charges [b]	Charges product	H-bond distance [Å]	Electrostatic Force [c] [pN]
	[1] O7H ⋯ O [W1] [a]	+0.482 ⋯ -0.800	-0.3856	1.859	-2573.46
	[1] O7 ⋯ HO4 [2]	-0.608 ⋯ +0.542	-0.32954	1.838	-2249.84
	[1] O4H ⋯ O [W2]	+0.462 ⋯ -0.563	-0.2616	2.072	-1509.28
	[1] O4 ⋯ HO9 [2]	-0.563 ⋯ +0.499	-0.28094	2.012	-1600.64
	[1] O3 ⋯ HO9 [2]	-0.264 ⋯ +0.499	-0.13174	2.398	-528.38 [d]
	[1] O4 ⋯ H9 [2]	-0.563 ⋯ +0.211	-0.11879	2.559	-418.40 [d]
S ⋯ G	[1] O3 ⋯ H8 [2]	-0.264 ⋯ +0.405	-0.10692	2.596	-365.92 [d]
	[2] O3 ⋯ H [W1]	-0.421 ⋯ +0.475	-0.19998	1.924	-1245.96
	[2] O9 ⋯ H [W2]	-0.484 ⋯ +0.436	-0.21102	1.962	-1264.37
	[2] O7H ⋯ O8 [2]	+0.430 ⋯ -0.231	-0.09933	1.997	-574.46 [d]
	[2] O7 ⋯ H [W3]	-0.433 ⋯ +0.476	-0.20611	1.897	-1320.99
	[2] H103 ⋯ O [W3]	+0.212 ⋯ -0.761	-0.16133	2.349	-674.36 [d]
	[2] H2 ⋯ O [W3]	+0.109 ⋯ -0.761	-0.08295	2.453	-317.95 [d]
	[1] O7H ⋯ O [W1]	+0.482 ⋯ -0.800	-0.3856	1.852	-2592.95
	[1] O7 ⋯ HO4 [2]	-0.612 ⋯ +0.556	-0.34027	1.866	-2253.94
	[1] O4H ⋯ O [W2]	+0.501 ⋯ -0.798	-0.3998	1.966	-2385.69
	[1] O4 ⋯ HO9 [2]	-0.556 ⋯ +0.473	-0.26299	1.941	-1609.99
	[1] H103' ⋯ O3' [2]	+0.245 ⋯ -0.200	-0.049	2.452	-187.97 [d]
S ⋯ S	[1] O3 ⋯ H8 [2]	-0.207 ⋯ +0.676	-0.13993	2.369	-575.078 [d]
	[2] O3 ⋯ H [W1]	-0.400 ⋯ +0.479	-0.1916	1.907	-1215.16
	[2] O9 ⋯ H [W2]	-0.486 ⋯ +0.449	-0.21821	1.971	-1295.53
	[2] O7H ⋯ O8 [W2]	+0.439 ⋯ -0.230	-0.10097	1.952	-611.18 [d]
	[2] O7 ⋯ H [W3]	-0.461 ⋯ +0.462	-0.21298	1.900	-1360.74
	[2] H103 ⋯ O [W3]	+0.213 ⋯ -0.763	-0.16252	2.382	-660.63 [d]
	[2] H2 ⋯ O [W3]	+0.103 ⋯ -0.763	-0.0786	2.411	-329.99 [d]

[a] Numbers 1 and 2 between brackets indicate the fragment or unit in the water-bridged dimeric complex from which the donor or acceptor come (**Figure 2** in the text). Here the notations [W1], [W2] and [W3] also indicate fragments, but they are referred to water molecules: water 1, water 2 and water 3 respectively.

[b] Mulliken's charges on the atoms.

[c] Electrostatic forces were calculated by employing Coulomb's law, with the atoms being considered as point charges.[3] The charges on the atoms (Mulliken charges) have been determined from quantum chemical calculations at M06-2X/6-31++G(d,p) theory level.

[d] Based on low electron density (0.0093 – 0.0122) and positive energy density (0.0016 – 1.6777 au) values at BCP (**Table 2** in the text), we specify by this subscript the H-bonds that are rather governed by electrostatic forces. Hydrogen bonding is not only governed by electrostatic forces as often seen, but there are another forces involved in its formation, as for instance charge-transfer interactions, π-resonance assistance, steric repulsion, cooperative effects, dispersion interactions and secondary electrostatic interactions.[4]

Table S3. The main electron donor–acceptor interactions in π - stacking for the S···G complex and their second-order perturbation stabilization energies ($E(2)$) at M06-2X/6-31++g(d,p) level

| WBDC | π - stacking interaction | | |
	Donor(i)	Aceptor(j)	$E(2)$ [b] [kcal mol^{-1}]
	π C1 – C2 [1] [a]	π^* C2 – C3 [2] [a]	0.55
	π C1 – C2 [1]	σ^* C3 – O3 [2]	0.1
	π C1 – C2 [1]	σ^* O3 – C10 [2]	0.06
	π C1 – C2 [1]	π^* C3 – C4 [1]	NF [c]
	π C1 – C2 [1]	π^* C4 – C5 [2]	NF
	π C1 – C2 [1]	σ^* O4 – HO4 [2]	NF
	π C1 – C6 [1]	π^* C2 – C3 [2]	NF
	π C1 – C6 [1]	π^* C3 – C4 [2]	NF
	π C1 – C6 [1]	σ^* C2 – H2 [2]	NF
	π C1 – C6 [1]	σ^* O3 – C10 [2]	NF
S ··· G	π C1 – C6 [1]	π^* C5 – C6 [2]	NF
	π C1 – C6 [1]	σ^* C5 – O3' [2]	NE
	π C1 – C6 [1]	σ^* O4 – HO4 [2]	NF
	π C2 – C3 [2]	π^* C1 – C2 [1]	0.07
	π C2 – C3 [2]	π^* C3 – C4 [1]	0.12
	π C3 – C4 [1]	σ^* C2 – H2 [2]	NF
	π C3 – C4 [1]	π^* C2 – C3 [2]	0.07
	π C3 – C4 [1]	σ^* C5 – O3' [2]	NE [c]
	π C3 – C4 [1]	π^* C5 – C6 [2]	NF
	π C4 – C5 [1]	π^* C3 – C4 [2]	NF
	π C4 – C5 [1]	π^* C5 – C6 [2]	NF
	π C5 – C6 [1]	π^* C4 – O4 [2]	0.07
	π C5 – C6 [1]	σ^* O4 – HO4 [2]	0.19
	π C5 – C6 [1]	π^* C3 – C4 [2]	NF
	π C5 – C6 [1]	π^* C4 – C5 [2]	0.31
	π C5 – C6 [1]	π^* C5 – C6 [2]	NF
	π C5 – C6 [2]	π^* C5 – C6 [1]	NF

[a] Numbers 1 and 2 between brackets indicate the fragment or unit in the water-bridged dimeric complex from which the donor or acceptor come (**Figure 2** in the text).

[b] The total value of $E(2)$ (=1.54 kcal mol^{-1}) is in the range from 1.19 to 9.56 kcal mol^{-1}, which is the typical range of energy for π-stacking.[5]

[c] NF and NE stand for not-found and not-existent interaction in the geometry, respectively.

Table S4. The main electron donor–acceptor interactions in π - stacking for the S···S complex and their second-order perturbation stabilization energies ($E(2)$) at M06-2X/6-31++g(d,p) level

WBDC	Donor(i) [a]	Aceptor(j) [a]	$E(2)$ [b] [kcal mol^{-1}]
		π - stacking interaction	
	π C1 – C2 [1]	π^* C2 – C3 [2]	0.09
	π C1 – C2 [1]	σ^* C3 – O3 [2]	NF [c]
	π C1 – C2 [1]	σ^* O3 – C10 [2]	NF
	π C1 – C2 [1]	π^* C3 – C4 [2]	NF
	π C1 – C2 [1]	π^* C4 – C5 [2]	NF
	π C1 – C2 [1]	σ^* O4 – HO4 [2]	NF
	π C1 – C6 [1]	π^* C2 – C3 [2]	0.10
	π C1 – C6 [1]	π^* C3 – C4 [2]	0.06
	π C1 – C6 [1]	σ^* C2 – H2 [2]	0.27
	π C1 – C6 [1]	σ^* O3 – C10 [2]	0.17
	π C1 – C6 [1]	π^* C5 – C6 [2]	0.38
	π C1 – C6 [1]	σ^* C5 – O3' [2]	0.58
S ··· S	π C1 – C6 [1]	σ^* O4 – HO4 [2]	1.02
	π C2 – C3 [2]	π^* C3 – C4 [1]	NF
	π C2 – C3 [2]	π^* C1 – C2 [1]	NF
	π C3 – C4 [1]	σ^* C2 – H2 [2]	NF
	π C3 – C4 [1]	π^* C2 – C3 [2]	NF
	π C3 – C4 [1]	σ^* C5 – O3' [2]	NF
	π C3 – C4 [1]	π^* C5 – C6 [2]	NF
	π C4 – C5 [1]	π^* C3 – C4 [2]	0.09
	π C4 – C5 [1]	π^* C5 – C6 [2]	0.14
	π C5 – C6 [1]	π^* C4 – O4 [2]	NF
	π C5 – C6 [1]	σ^* O4 – HO4 [2]	NF
	π C5 – C6 [1]	π^* C3 – C4 [2]	NF
	π C5 – C6 [1]	π^* C4 – C5 [2]	NF
	π C5 – C6 [1]	π^* C5 – C6 [2]	NF
	π C5 – C6 [2]	π^* C5 – C6 [1]	NF

[a] Numbers 1 and 2 between brackets indicate the fragment or unit in the water-bridged dimeric complex from which the donor or acceptor come (**Figure 2** in the text)

[b] The total value of $E(2)$ (= 2.81 kcal mol^{-1}) is in the range from 1.19 to 9.56 kcal mol^{-1}, which is the typical range of energy for π-stacking.[5]

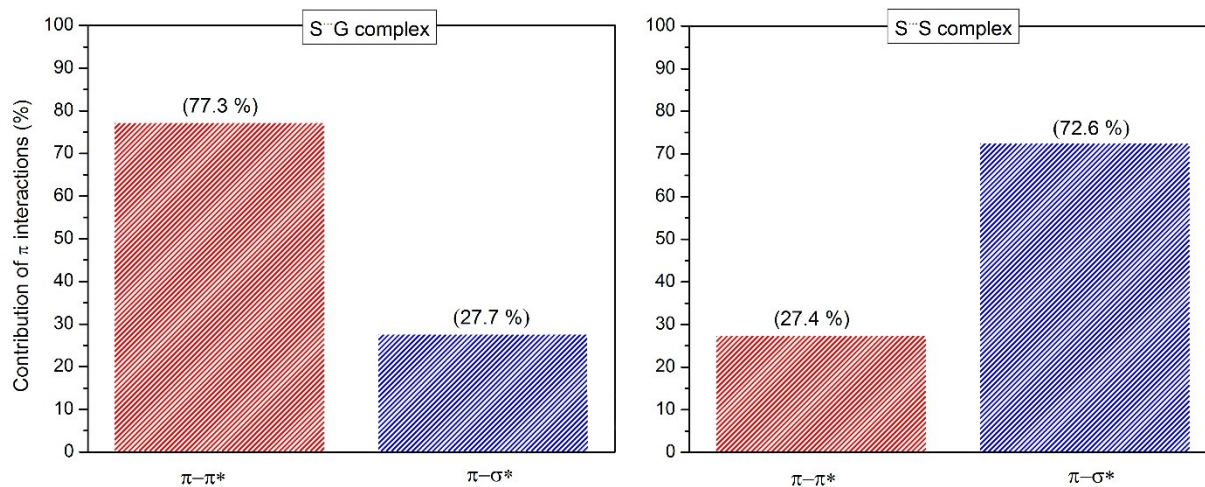[c] NF stands for not-found interaction in the geometry, respectively

Figure S4. Energetic contribution $((\sum_{bond-type} E(2)_i)/\sum_{all-bonds} E(2)_i)$ of $\pi - \pi^*$ and $\pi - \sigma^*$ interactions in the water-bridged dimeric complexes (S···G and S···S). The individual interaction energies between bond orbitals collected in **Table S3** and **S4** were used to calculate these contributions.

Table S5. Values of thermodynamics properties: internal energy (*E*), enthalpy (*H*), entropy (*S*) and Gibbs energy (*G*) of units (S, G, water) and WBDCs (S⋯S, S⋯G) calculated at M06-2X/6-31++g(d,p) level

Structures	Thermodynamic property [a]			
	E	*H*	*S*	*G*
	[Hartree]	[Hartree]	[kcal mol^{-1} K^{-1}]	[Hartree]
S	-918.7778	-918.75762	0.143958	-918.82601
G	-804.33221	-804.31446	0.132842	-804.37757
Water	-76.373456	-76.36968	0.046455	-76.39175
S⋯S	-2067.42214 [b]	-2066.8349	0.273911	-2066.8349
S⋯G	-1952.94164 [b]	-1952.259670	0.269645	-1952.38779

[a] The properties were calculated at room condition (T = 298 K, P = 1atm).

[b] Counterpoise corrected energies.

References

(1) Bregado, J. L.; Souto, F.; Secchi, A. R.; Tavares, F. W.; Calado, V. Molecular Dynamics Study of Thermophysical and Mechanical Properties in Hydrated Lignin with Compositions Close to Softwood. *ACS Sustainable Chem. Eng.* **2023**, *11*, 238. **DOI**: 10.1021/acssuschemeng.2c05264

(2) Li, X.; Long, Y.; Zhang, C.; Sun, C.; Hu, B.; Lu, P.; Chen, J. Hydrogen Bond and π-π Stacking Interaction: Stabilization Mechanism of Two Metal Cyclo-N5–-Containing Energetic Materials. *ACS Omega* **2022**, *7*, 8, 6627. **DOI**: 10.1021/acsomega.1c05961

(3) Tiwari, M. K.; Vanka, K. Exploiting directional long range secondary forces for regulating electrostatics-dominated noncovalent interactions. *Chem. Sci.* **2017**, *8*, 1378. **DOI**: 10.1039/C6SC03642B

(4) van der Lubbe, S. C. C.; Guerra, C. F. The Nature of Hydrogen Bonds: A Delineation of the Role of Different Energy Components on Hydrogen Bond Strengths and Lengths. *Chemistry - An Asian Journal* **2019**, *14*, 2759. **DOI**: 10.1002/asia.201900717

(5) Dhotel, A.; Chen, Z.; Delbreilh, L.; Youssef, B.; Saiter, J.-M. Tan L. Molecular Motions in Functional Self-Assembled Nanostructures. *Int. J. Mol. Sci.* **2013**, *14*, 2303. **DOI**: 10.3390/ijms14022303