

Theoretical analysis of hydrogen bonding in catechol- n (H_2O) clusters ($n=0\dots3$)

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1. Simulated annealing configurational search of complex formation

A structural study was carried out within the framework of the molecular mechanics approach by means of the simulated annealing method¹, implemented in the HyperChem² program, in order to choose the initial geometries for their later quantum chemical full optimization. The AMBER³ force field and its Amber-99 functional form was used due to its ability to deal with polar molecules. The Polak-Ribiere algorithm was employed for all the molecular mechanics optimizations. A simulated annealing protocol was repeated in 100 independent searches for analyzing the number of similar final configurations obtained. The catechol previously optimized structure at this level was confined in a periodic box of size 10 by 10 by 10 Å surrounded by 25 water molecules. For each simulation, the initial intermolecular arrangement was randomly chosen followed by an optimization, the simulated annealing, and the analysis of the final configurations. The hydrogen bonds (HB) formed between the water molecules and the catechol moiety were then identified using the default geometrical parameters defined by the program: the distance between the donated hydrogen and acceptor atoms should be less than 3.2 Å and the donor-hydrogen-acceptor angle greater than 150°. The settings for the simulated annealing protocol were: 0.1, 0.5, and 0.4 ps for heating, run and cooling times, respectively, with a time step size of 1.0×10^{-3} ps; the starting, simulation and final temperatures were 100, 600, and 0 K, respectively, with a temperature step of 20 K.

2. Final configurations analysis from the classical search

The number of HBs formed was used to classify the final configurations obtained from the simulated annealing protocol. The following numbering scheme was used. The oxygen atoms

from the catechol hydroxyls can act as hydrogen donors as well as acceptors and in the final configurations classification they are addressed by their position related to the free catechol, O1 and O2, Fig. 1 of the article. In addition, *d* and *a* stand for hydrogen donor acceptor atoms, respectively. In this form, a configuration labeled “O1d2a” (Fig. 1a) indicates that there are two HBs formed with the catechol O1 as donor and the O2 as hydrogen acceptor, and a “O2d” configuration, Fig. 1b, denotes a HB formed between the catechol donor O2 with one water molecule.

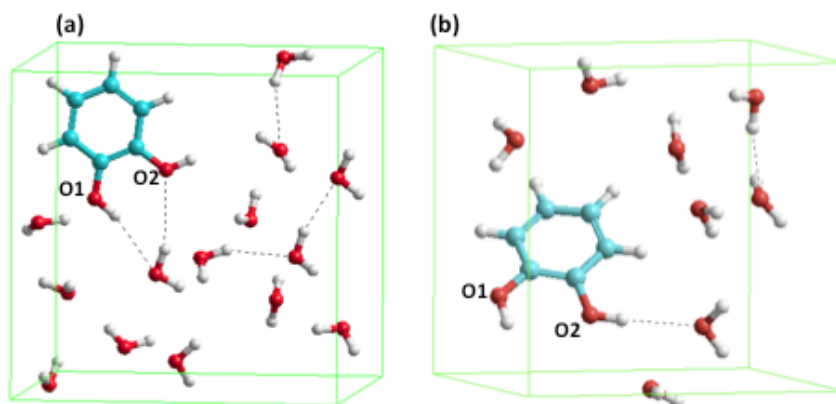


Fig. I. Two of the final configurations for the catechol- n (H₂O) system obtained with the simulated annealing protocol using HyperChem and classified according to the text, (a) O1d2a, and (b) O2d. The majority of the initial 25 water molecules were removed from the periodic box in the diagrams for the sake of clarity.

A summary of the obtained and classified final configurations, Table I, shows that from the 100 sample, there were 36 simulations that finished with no HB formed between the catechol and at least one water molecule. This does not imply that there was no intermolecular interaction at all but that the geometrical criteria needed for the HB was not met.

From the 64 final configurations that exhibited HB interactions, in 7 of them the symmetry of the catechol moiety within the complex was C_{2v} , and in 57 it was C_s . Configurations with one HB interaction are preferred over two and three HBs because the frequencies were 38, 20 and 6, respectively. 78% of the configurations have at least one of the catechol hydroxyls acting as hydrogen donor, and among them, the O1d and O2d configurations are the favored ones but with no significant frequency difference between them. Hence, from this results, 30 initial

configurations were chosen to continue with the optimization at the B3PW91/cc-pVTZ level, including also those that appeared only once.

Table I. Final configurations obtained from the simulated annealing search and their frequency (number of similar final configurations). They classified in terms of the catechol oxygen position O1 or O2, and its donor or acceptor (d or a) role in the hydrogen bond.

Catechol-(H₂O) configurations	Frequency	Catechol-2(H₂O) Configurations	Frequency	Catechol-3(H₂O) configurations	Frequency
O1a	5	O1ad	3	O1d – O2ad	2
O1d	13	O2aa	3	O1aa – O2d	1
O2a	6	O2ad	4	O1ad – O2d	1
O2d	14	O1d – O2d	4	O1ad – O2a	2
		O1a – O2d	4		
		O1d – O2a	2		
Total	38	Total	20	Total	6

3. Structure and energetics of the stable catechol-n(H₂O) complexes.

From the 50 initial structures for the catechol-n(H₂O) clusters that involves configurations from the annealing study, the conformers from Jang et al work⁴, and random arrangements as well, twenty three local minima on the potential energy surface at the quantum level were obtained and confirmed by means of a vibrational analysis. The molecular graphs for the catechol stable conformers and the stable catechol-n(H₂O) (n= 1, 2, 3) complexes are shown in figures II, III, and IV, and arranged by their energy relative to the most stable complex in each case. The complexes are labeled according to the notation used in the Darwinian family tree, Figure 5 of the article, for which the rules defined by Michaux et al.⁵ are closely followed. Also, the three most stable structures for catechol in the presence of one to three water molecule are labeled according to the main text.

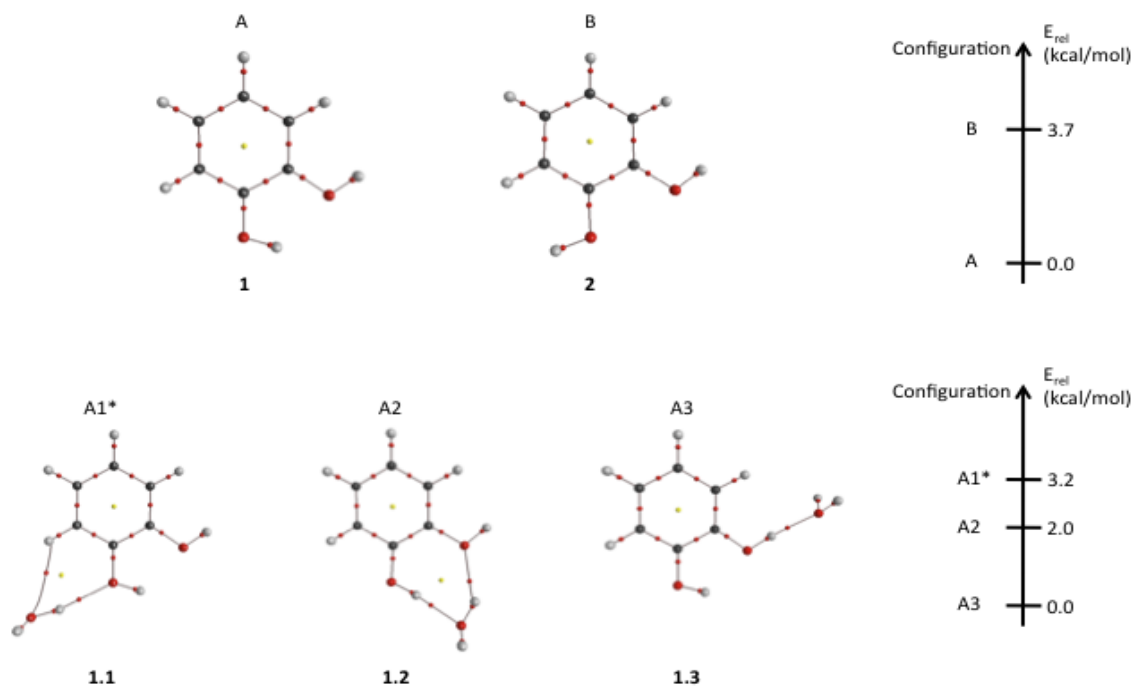


Fig. II. Molecular graphs for the stable catechol conformers and catechol-(H₂O) complexes. Their relative energies are shown on the right-hand side. The bond and ring critical points are denoted by small red and yellow spheres. The structures are labeled according to the notation of figures 1 and 2 of the paper. The notation used in the Darwinian family, Figure 5 of the article, is also used closely following the rules defined by Michaux et al.⁵.

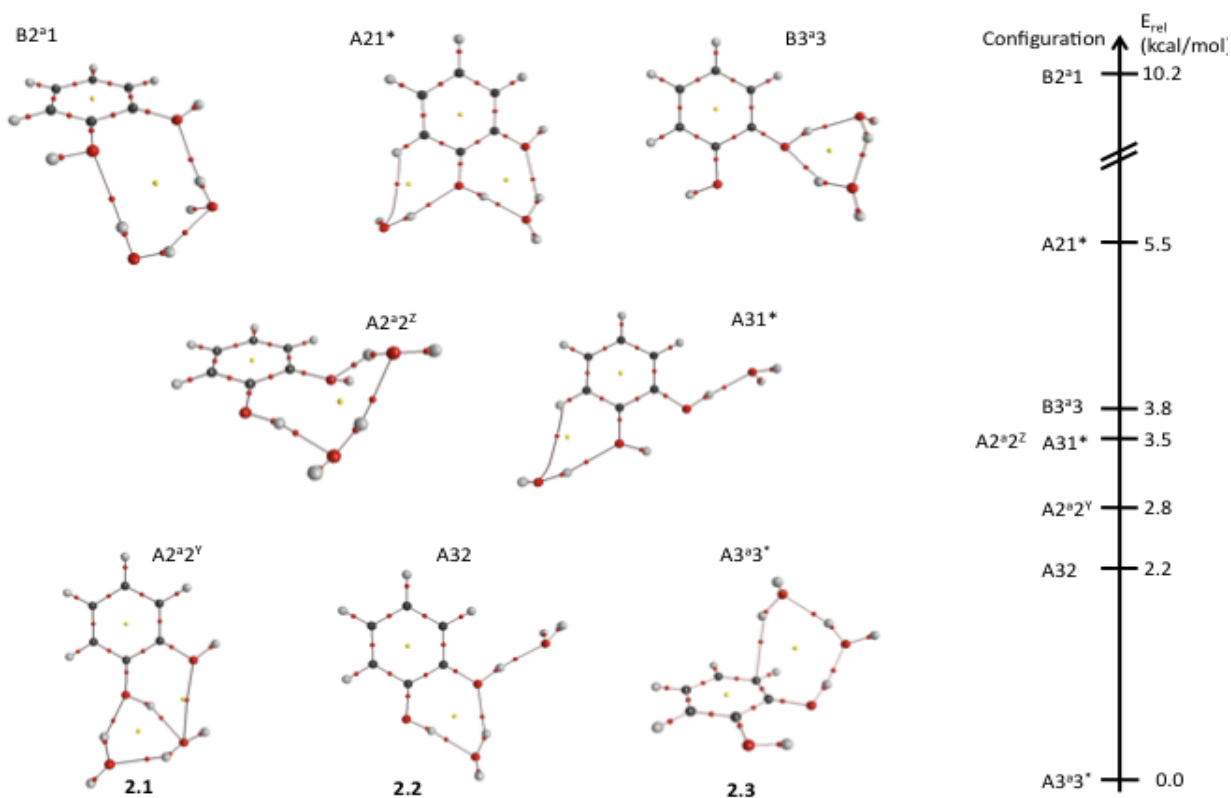


Fig. III. Molecular graphs for the stable catechol-2(H₂O) complexes. Their relative energies are shown on the right-hand side. The bond and ring critical points are denoted by small red and yellow spheres. The structures are labeled according to the notation of Figure 2 of the paper. The notation used in the Darwinian family, Figure 5 of the article, is also used closely following the rules defined by Michaux et al.⁵.

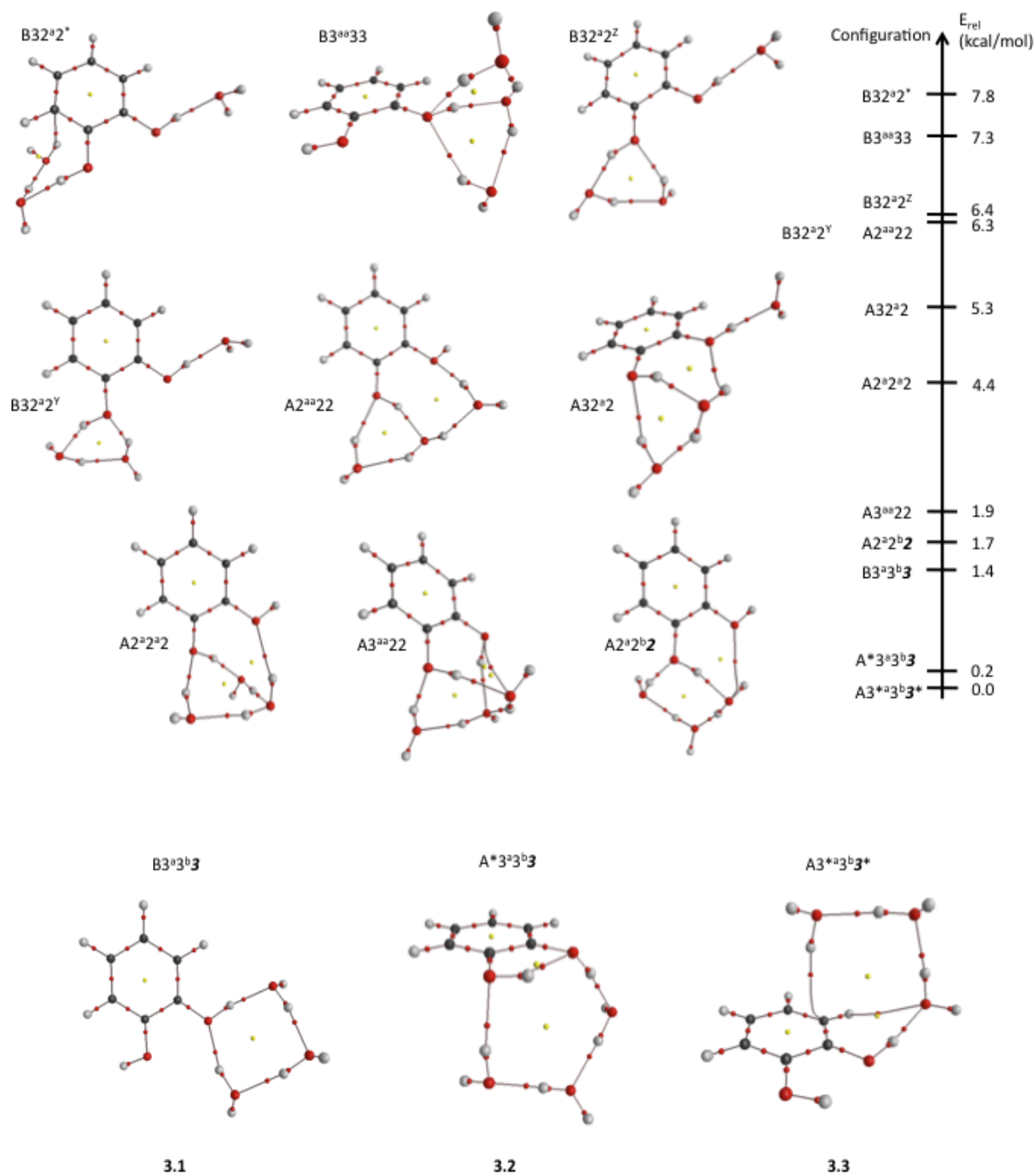


Fig. IV. Molecular graphs for the stable catechol-3(H₂O) complexes. Their relative energies are shown on the right-hand side. The bond and ring critical points are denoted by small red and yellow spheres. The structures are labeled according to the notation of Figure 2 of the paper. The notation used in the Darwinian family, Figure 5 of the article, is also used closely following the rules defined by Michaux et al.⁵.

Finally, the complete E_{int} and E'_{int} values, according to equations (1) and (2), are given in Table II for all 23 stable catechol- $n(\text{H}_2\text{O})$ complexes as well as their relative energies.

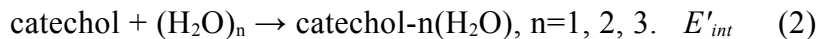
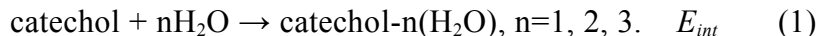


Table II. E_{int} and E'_{int} values, according to equations (1) and (2), for all 23 stable catechol- $n(\text{H}_2\text{O})$ studied complexes as well as their relative energies. Values are given in kcal/mol.

Configuration	E_{int}	E'_{int}	E_{rel}
A1* (1.1)	-1.0	-1.0	3.2
A2 (1.2)	-2.1	-2.1	2.0
A3 (1.3)	-4.1	-4.1	0.0
B2 ^a 1	0.9	2.8	10.2
A21*	-3.7	-1.8	5.5
B3 ^a 3	-5.4	-3.5	3.8
A2 ^a 2 ^z	-5.7	-3.8	3.5
A31*	-5.7	-3.8	3.5
A2 ^a 2 ^y (2.1)	-6.4	-4.5	2.8
A32 (2.2)	-7.1	-5.2	2.2
A3 ^a 3* (2.3)	-9.2	-7.4	0.0
B32 ^a 2*	-7.7	-0.3	7.8
B3 ^{aa} 33	-8.2	-0.8	7.3
B32 ^a 2 ^z	-9.1	-1.7	6.4
B32 ^a 2 ^y	-9.2	-1.8	6.3
A2 ^{aa} 22	-9.2	-1.8	6.3
A32 ^a 2	-10.2	-2.8	5.3
A2 ^a 2 ^a 2	-11.1	-3.7	4.4
A3 ^{aa} 22	-13.6	-6.2	1.9
A2 ^a 2 ^b 2	-13.8	-6.4	1.7
B3 ^a 3 ^b 3 (3.1)	-14.1	-6.7	1.4
A*3 ^a 3 ^b 3 (3.2)	-15.3	-7.9	0.2
A3* ^a 3 ^b 3* (3.3)	-15.5	-8.1	0.0

References

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