

THE NATURE OF STACKING INTERACTIONS OF THE RESONANCE-ASSISTED HYDROGEN-BRIDGED RINGS

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ABSTRACT

The Symmetry Adapted Perturbation Theory (SAPT) energy decomposition analysis is applied for studying the nature of stacking interaction occurring in homodimers of resonance-assisted hydrogen-bridged (RAHB) rings and heterodimers of RAHB and benzene rings. The contribution of various energy terms is dependent on the composition of a RAHB ring and can be rationalized based on electrostatic potential maps.

INTRODUCTION

The existence of mutual stacking interaction between Resonance-Assisted Hydrogen-Bridged (RAHB) rings (Figure 1a), as well as stacking interactions between RAHB and C₆-aromatic rings is confirmed by analysing the crystal structures from the Cambridge Structural Database (CSD) and by quantum-chemical calculations in the gas phase [1,2]. It is observed that both RAHB/RAHB and RAHB/C₆-aromatic rings form parallel layers in the crystal structures and that these layers are in both cases separated by 3.0-4.0 Å in the majority of the structures. Thus, contacts between the layers can be assigned to stacking interactions. Namely, we used malonaldehyde molecule (Figure 1b), its mononitrogen (Figure 1c) and dinitrogen analogue (Figure 1d) as prototypes for the RAHB rings, since these rings are the most frequently present in both sets of structures in the CSD (RAHB/RAHB rings and RAHB/C₆-aromatic rings) [1,2]. We used benzene molecule as a prototype for a C₆-aromatic molecule. In this work, we present a Symmetry Adapted Perturbation Theory (SAPT2+3, [3]) energy decomposition, calculated for RAHB/RAHB and RAHB/benzene stacking interactions and discuss the nature of these interactions.

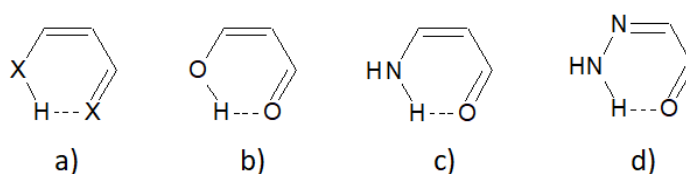


Figure 1. Examples of the RAHB rings; a) general formula, electronegative atoms, usually N, O and S forming intramolecular hydrogen bond are connected by a π -system; b) malonaldehyde; c) the mononitrogen analogue of malonaldehyde; d) the dinitrogen analogue of malonaldehyde

METHODS

On the basis of the SAPT energy decomposition scheme the interaction energy is consisted of the electrostatic, induction, dispersion and exchange-repulsion terms. Dispersion and exchange-repulsion terms are sometimes combined into a net dispersion term [4]. A SAPT2+3 energy decomposition analysis was performed in this work on structures corresponding to the lowest minima on the RAHB/RAHB and the RAHB/benzene potential energy curves [1,2]. The SAPT2+3 calculations were performed at cc-pVQZ level, since it was shown to be in good agreement with CCSD(T) method at the Complete Basis Set limit (CCSD(T)/CBS) [1,2]. To perform SAPT2+3 calculations we used PSI4 program package [5]. The electrostatic potential maps were calculated at the outer contour of electron density of 0.001 a. u. using Wavefunction Analysis Surface Analysis Suite (WFA-SAS) program [6] by the wavefunctions calculated in Gaussian09 [7] at MP2/cc-pVTZ level.

RESULTS AND DISCUSSION

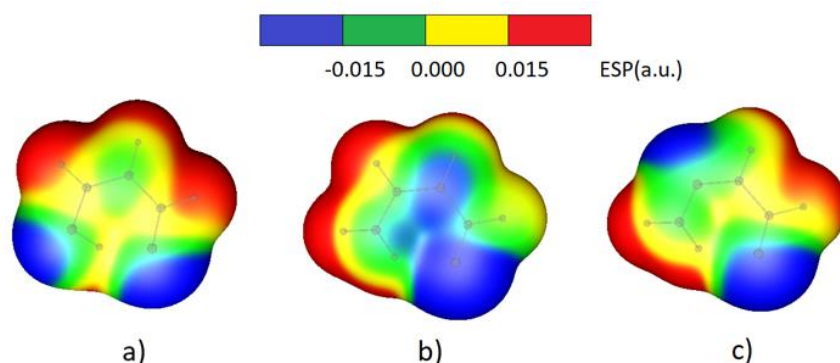
The dispersion term is dominant in all studied systems (Table 1), but it is significantly cancelled or even surpassed by the exchange-repulsion term. Thus, when we compare RAHB/RAHB stacked systems [1] we can see that the electrostatic term is dominant in $\text{H}_4\text{C}_3\text{O}_2/\text{H}_4\text{C}_3\text{O}_2$ and $\text{H}_5\text{C}_3\text{NO}/\text{H}_5\text{C}_3\text{NO}$ systems, since net dispersion is quite small (in $\text{H}_4\text{C}_3\text{O}_2/\text{H}_4\text{C}_3\text{O}_2$ system) or even repulsive (in $\text{H}_5\text{C}_3\text{NO}/\text{H}_5\text{C}_3\text{NO}$ system). The main reason for significantly smaller total interaction energy in $\text{H}_4\text{C}_2\text{N}_2\text{O}/\text{H}_4\text{C}_2\text{N}_2\text{O}$ system, compared to the other two RAHB /RAHB stacking interactions is a smaller electrostatic contribution. On the other hand, in this system, net dispersion contribution is almost equal to the electrostatic contribution (Table 1).

Similar observations apply to RAHB/benzene stacked dimers [2]. Dispersion terms are almost cancelled in $\text{H}_4\text{C}_3\text{O}_2/\text{benzene}$ and $\text{H}_5\text{C}_3\text{NO}/\text{benzene}$ systems, while net dispersion significantly contributes to the interaction in $\text{H}_4\text{C}_2\text{N}_2\text{O}/\text{benzene}$ system. However, even in this system the electrostatic contribution is more pronounced than net dispersion (Table 1). Electrostatic contribution is dominant in $\text{H}_4\text{C}_3\text{O}_2/\text{benzene}$ and $\text{H}_5\text{C}_3\text{NO}/\text{benzene}$. Induction energy term contributes to the interaction energy in all studied RAHB/RAHB and RAHB/benzene systems, but to a smaller extent (Table 1).

Table 1. SAPT2+3 energy decomposition analysis; all energy values are in kcal/mol. Net dispersion is a sum of exchange-repulsion and dispersion terms.

Model system	ELST	EXCH	IND	DISP	NET DISP	SAPT 2+3
H ₄ C ₃ O ₂ /H ₄ C ₃ O ₂	-3.55	5.92	-0.60	-6.10	-0.18	-4.32
H ₅ C ₃ NO/H ₅ C ₃ NO	-4.81	7.86	-1.12	-6.74	1.12	-4.81
H ₄ C ₂ N ₂ O/H ₄ C ₂ N ₂ O	-0.89	3.76	-0.33	-4.64	-0.88	-2.09
H ₄ C ₃ O ₂ /benzene	-2.68	6.51	-0.80	-6.63	-0.12	-3.60
H ₅ C ₃ NO/benzene	-2.60	6.51	-0.92	-6.52	-0.01	-3.53
H ₄ C ₂ N ₂ O/benzene	-1.61	4.70	-0.51	-5.69	-0.99	-3.11

We can observe that differences occur in the nature of RAHB stacking interactions for the three rings. These differences can be explained by electrostatic potential maps (Figure 2). It can be seen that H₄C₃O₂ and H₅C₃NO molecules both have a dipole moment. At the other hand, a clearly pronounced dipole moment can not be observed in case of H₄C₂N₂O molecule. Thus, significant contribution of electrostatic interaction in antiparallel H₄C₃O₂/H₄C₃O₂ and H₅C₃NO/H₅C₃NO can be attributed to antiparallel dipole-dipole interactions. Benzene molecule does not possess a dipole moment, but it possesses a quadrupole moment, thus a smaller electrostatic term in H₄C₃O₂/benzene and H₅C₃NO/benzene systems than in the corresponding RAHB/RAHB systems is a consequence of a dipole-quadrupole interaction. For that reason, the overall interaction is stronger in H₄C₃O₂/H₄C₃O₂ and H₅C₃NO/H₅C₃NO systems than in H₄C₃O₂/benzene and H₅C₃NO/benzene systems. Since H₄C₂N₂O molecule does not possess a clearly pronounced dipole moment, the electrostatic terms are less dominant than in systems involving H₄C₃O₂ and H₅C₃NO molecules. Also, net dispersion is significant, which can be attributed to the smaller exchange-repulsion term (Table 1).

**Figure 2.** The electrostatic potential maps of a) malonaldehyde; b) the mononitrogen analogue of malonaldehyde; c) the dinitrogen analogue of malonaldehyde (Figure 1)

CONCLUSION

The SAPT2+3 energy decomposition analysis is performed on RAHB/RAHB and RAHB/benzene model systems. The dispersion contribution is dominant in all studied systems. Depending on the dipole moment intensity, the electrostatic term is dominant or comparable with a net dispersion term, which is often presented as a sum of dispersion and exchange-repulsion terms. In a system that does not possess a pronounced dipole moment, the electrostatic contribution is smaller than in systems with a pronounced dipole moment. Also, exchange-repulsion term is smaller, which leads to a more significant net dispersion term. The induction energy term contributes to the stacking interaction energy in all systems, but not to a large extent.

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REFERENCES

- [1] J. P. Blagojević Filipović, M. B. Hall, S. D. Zarić, *Cryst. Growth Des.* 2019, 19, 5619-5628.
- [2] J. P. Blagojević Filipović, M. B. Hall, S. D. Zarić, *Phys. Chem. Chem. Phys.* 2020, 22, 13721-13728.
- [3] T. M. Parker, L. A. Burns, R. M. Parrish, A. G. Ryno, C. D. Sherrill, *J. Chem. Phys.* 2014, 140, 094106.
- [4] E. G. Hohenstein, C. D. Sherrill, *J. Phys. Chem. A*, 2009, 113, 878-886.
- [5] R. M. Parrish, L. A. Burns, D. G. A. Smith, A. C. Simmonett, A. E. DePrince, E. G. Hohenstein, U. Bozkaya, A. Y. Sokolov, R. Di Remigio, R. M. Richard, et al. *J. Chem. Theory Comput.*, 2017, 13, 3185-3197.
- [6] F. A. Bulat, A. Toro-Labbé, T. Brinck, J. S. Murray, P. J. Politzer, *Mol. Model.* 2010, 16, 1679–1691.
- [7] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, et al. *Gaussian 09, Revision D.01*; Gaussian, Inc., 2016.