



PHYSICAL CHEMISTRY 2016

*13th International Conference on
Fundamental and Applied Aspects of
Physical Chemistry*

*Proceedings
Volume I*

BELGRADE
September 26-30, 2016

ISBN 978-86-82475-34-7

Title: Physical Chemistry 2016 (Proceedings)

Editors: Željko Čupić and Slobodan Anić

Published by: Society of Physical Chemists of Serbia, Studentski trg 12-16, 11158, Belgrade, Serbia.

Publisher: Society of Physical Chemists of Serbia

For Publisher: S. Anić, President of Society of Physical Chemists of Serbia

Printed by: "Jovan", Printing and Publishing Company; 200 Copies.

Number of pages: 6+502; Format B5; printing finished in September 2016

Text and Layout: "Jovan"

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BENCHMARK STUDY FOR 2-BUTENE PARALLEL INTERACTIONS

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ABSTRACT

The interactions in model systems of unsaturated molecules with *cis*- and *trans*-double bonds were studied using quantum chemical calculations. We present benchmark study of *cis*- and *trans*-2-butene dimer model systems with various methods and different basis sets. Root Mean Square Deviation (RMSD) values are represented and results showed that the best agreement with CCSD(T)/CBS values has B3LYP-D3 method with cc-pVTZ basis set, with the lowest RMSD value of 0.032.

INTRODUCTION

Non-covalent interactions of molecules with double bonds are important and have been studied with great interest [1-5]. Presence of double bonds can affect the properties and behavior of various systems and processes [6]. For example, molecules with double bonds, like fatty acids, have a significant role in living organisms, effecting on human health [7]. Most of the studies on non-covalent interaction of molecules with double bonds have been done on ethene (ethylene) molecule. Interactions in ethene dimer, as the simplest model system with double bonds, have been studied using different quantum chemical methods [2-5].

In previous study, in order to find differences in interactions of *cis*- and *trans*-unsaturated molecules, *cis*- and *trans*-2-butene have been studied, as the smallest model system [8]. Potential differences in interactions of model systems was performed using high level quantum chemical methods including very accurate CCSD(T) at complete basis set (CBS) approximation [9].

In the previous work we compared a few methods for two *cis*-2-butene dimers, while in this work detailed benchmark study using MP2 and several DFT-D methods, with various basis sets, on model systems of all five 2-

butene dimers (Figure 1), has been performed in order to find the best method and basis set for interactions of these molecules.

METHODOLOGY

The benchmark study was performed using MP2, BLYP-D3, M05-D3, M052X-D3, M06-D3, M06HF-D3, B3LYP-D3, BP86, TPSS, and PBE1PBE methods and the four basis sets (cc-pVDZ, cc-pVTZ, aug-cc-pVDZ and 6-31++G**) for each method.

The geometries of interactions of *cis*- and *trans*-2-butene used for the calculations in this work were obtained in previous work, as minima on potential curves [8]. The potential energy curves were calculated by keeping

monomer geometries rigid and varying the offset, r (parallel displacement) and normal distance between the planes of the two molecules, R [8]. Offset is the distance between double bond centre in one molecule and the projection of the double bond centre of the other molecule on the plane of the first molecule. The monomer geometries were optimized using MP2 method, while the potential curves were calculated using M052X-D3 method with cc-pVDZ basis set [8]. All calculations on interaction energies in 2-butene dimers have been performed in Gaussian 09 (version D.01) [10].

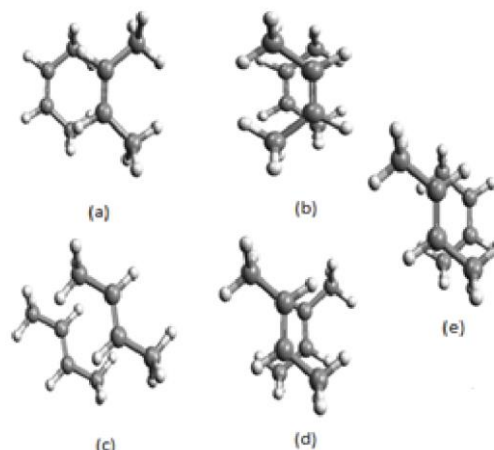


Figure 1. Model systems used in benchmark study

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RESULTS AND DISCUSSION

We have performed detailed benchmark study using ten methods, and four basis sets for each of the methods, by comparing calculated interaction energies at various level of theory with CCSD(T)/CBS energies, since CCSD(T)/CBS method is considered golden standard in quantum chemistry. The benchmark study was performed using five possible geometries for interactions in *cis*- and *trans*-2-butene dimers shown on Figure 1: (a) *cis*-2-butene dimer with parallel orientation ($r=2.4$, $R=3.3$), (b) *cis*-2-butene dimer with anti-parallel orientation ($r=1.0$, $R=3.7$), (c) *trans*-2-butene dimer with parallel orientation ($r=2.3$, $R=3.3$), (d) *trans*-2-butene dimer with anti-parallel orientation ($r=0.8$, $R=3.6$) and (e) *cis*-2-butene / *trans*-2-butene ($r=1.4$, $R=3.7$).

The results show that influence of the basis set is the largest on MP2 method, while on DFT-D methods it is much smaller. It was shown that the MP2, M06HF-D3, B3LYP-D3 methods underestimate interaction energies in comparison to values of CCSD(T)/CBS interaction energies.

Table 1. RMSD values for each methods with various basis sets (without(-) and with dispersion correction (D3) in kcal/mol

Methods	Basis sets							
	cc-pVDZ		cc-pVTZ		aug-cc-pVDZ		6-31++G**	
	-	D3	-	D3	-	D3	-	D3
MP2		1.34		0.245		0.071		0.805
BLYP	2.91	0.139	2.45	0.187	2.39	0.137	2.68	0.058
M05	1.64	0.263	1.56	0.349	1.43	0.483	1.36	0.553
M052X	1.06	0.095	0.86	0.103	0.66	0.303	0.70	0.269
M06	1.03	0.283	0.75	0.565	0.29	1.03	0.11	1.22
M06HF	1.13	0.255	1.16	0.287	0.71	0.190	0.52	0.353
B3LYP	4.00	0.103	3.89	0.032	3.91	0.052	3.99	0.105
BP86	4.64	0.258	4.47	0.388	4.40	0.418	4.56	0.352
TPSS	3.65	0.188	3.59	0.228	3.52	0.248	3.62	0.222
PBE1PBE	2.84	0.185	2.71	0.278	2.64	0.298	2.71	0.302

In Table 1 the data for Root Mean Square Deviation, RMSD, for each theory level are shown. It is shown that dispersion correction has influence on the interaction energy and have a much better agreement with CCSD(T) values. RMSD values are much lower with dispersion correction then without. However, one can notice that results without correction are better for Minnesota functionals, while dispersion is very important for other functionals. When considering the data with dispersion correction only a few levels have very large errors, above 1.0 kcal/mol.

The best level of theory for *cis*- and *trans*-2-butene dimers is B3LYP-D3/cc-pVTZ with RMSD value of 0.032, the second best is B3LYP-D3/aug-cc-pVDZ basis set with RMSD value of 0.052. Five levels of theory (B3LYP-D3/cc-pVTZ, B3LYP-D3/aug-cc-pVDZ, BLYP-D3/6-31++G**, MP2/aug-cc-pVDZ and M052X/cc-pVDZ) have RMSD values below 0.1, indicating that all these level sare very reliable for calculations on 2-butene dimers.

After obtained the best level of theory (B3LYP-D3/cc-pVTZ), we recalculated the potential curves using B3LYP-D3/cc-pVTZ. The

geometries at potential curves minima did not changed much, offset and normal distance are almost the same. The energies of new potential curves are somewhat more stable(up to 0.32kcal/mol).

CONCLUSION

Benchmarking study of *cis*- and *trans*-2-butene dimers was performed with various methods and basis sets. The study used ten methods and four basis sets for each of the method. The best method is B3LYP-D3 with cc-pVTZ basis set, where value of RMSD is 0.032. Five of 40 levels of theory, that we tested, have RMSD values below 0.1, indicating that these methods are good in reproducing interaction energies.

Acknowledgement

This work was supported by the Education, Science and Technology Development, Republic of Serbia Projects no. OI172063 and III46010.

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