BioChem Press

Inter*net* Electronic Journal of
Molecular Design

Theoretical Studies on the Validity of B3LYP Density Functional Theory for Symmetrical Electrocyclic Reactions

Shogo Sakai

Department of Information Systems Engineering, Osaka Sangyo University, Daito 574-8530 Japan

Citation of the article:
S. Sakai, Theoretical Studies on the Validity of B3LYP Density Functional Theory for Symmetrical Electrocyclic Reactions, *Internet Electron. J. Mol. Des.* **2002**, *1*, 462–466, http://www.biochempress.com.

Theoretical Studies on the Validity of B3LYP Density Functional Theory for Symmetrical Electrocyclic Reactions[#]

Shogo Sakai*

Department of Information Systems Engineering, Osaka Sangyo University, Daito 574-8530 Japan

Abstract
Motivation. The reactions including orbital symmetry allowed and forbidden mechanisms are studied by theoretical multireference correlation molecular orbital methods such as complete active space (CAS) self–consistent field (SCF) or broken symmetry unrestricted methods. Although the CASSCF MO method can describe the electronic states between the singlet electronic coupling state and the singlet diradicals state, no information is available regarding the accuracy of the broken symmetry unrestricted method for these electronic states. We compared the validity of the geometry parameters and the relative energies for three symmetrical electrocyclic reaction systems by broken symmetry unrestricted and restricted methods on the basis of the (U)B3LYP density functional theory with those by CASSCF and MP2–CASSCF levels.

Method. (U)B3LYP density functional methods with 6–31G(d) basis set are used in this study.

Results. The geometry parameters of the stationary points for three symmetrical electrocyclic reactions and their relative energies are calculated by (U)B3LYP methods.

Conclusions. The geometry parameters of the stationary points determined by the (U)B3LYP method agreed well with those by CASSCF levels. The relative energies calculated by the (U)B3LYP method agreed qualitatively with those by MP2-CASSCF levels, but the energy difference by both methods is significant.

Keywords. Pericyclic reactions; butadiene; hexa–1,3,5–triene; *o*–xylylene; CASSCF MO; (U)B3LYP.

1 INTRODUCTION

The reaction mechanisms including conrotatory and disrotatory paths for electrocyclic reactions are very important for organic molecular design and have been studied by theoretical and experimental chemists [1,2]. One reaction path of the conrotatory or disrotatory mechanisms for symmetrical electrocyclic reaction is a orbital symmetry forbidden reaction from the orbital symmetry rules as the Woodward–Hoffamnn rule [3] or the frontier orbital theory [4], and the other path is a orbital symmetry allowed reaction. Therefore the non–dynamical electron correlation for the molecular orbital calculations is very important to treat these reaction systems with the same

---

[#] Dedicated to Professor Haruo Hosoya on the occasion of the 65th birthday.
* Correspondence author; E–mail: sakai@ise.osaka-sandai.ac.jp.

level of accuracy. The systems of orbital symmetry forbidden are usually treated by multi–reference molecular orbital methods as CASSCF and MRCI methods. Recently the density functional theory (DFT) [5] has been widely used for many chemical systems. Because DFT in the spin–restricted Kohn–Sham formulation is unable to describe the potential energy surface for singlet diradicals, structures with suspected diradical character are sometimes computed with the broken symmetry, spin–unrestricted method.

In this paper we investigate if the (U)B3LYP theoretical model, despite its plausible predictions, is indeed appropriate for studying the symmetrical electrocyclic reactions.

2 TEORETICAL METHODS

Calculations were carried out with the 6–31G(d) basis set [6], using Becke's hybrid exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP) [7,8]. The stationary points of the reactants, the products, and the transition states for symmetry allowed reactions were calculated by the B3LYP method, and those for symmetry forbidden reactions were calculated by the UB3LYP method. A vibrational analysis was performed at each stationary point found, to confirm its identity as an energy minimum or a transition state structure. All electronic structure calculations were carried out with the Gaussian98 suite of programs [9].

3 RESULTS AND DISCUSSION

3.1 Geometry

Some geometry parameters of the transition states on the conrotatory and disrotatory paths for the electrocyclic reactions of butadiene, hexa–1,3,5–triene, and *o*–xylylene are listed in Table 1. In this table, C_1 and C_n indicate the terminal carbon atoms of active site, and H_A and H_B denote the hydrogen atoms bonding to the terminal carbon atom C_1. Also, in Table 1 the values estimated by CASSCF method are taken from previous studies [10,11,12]. For the active site in all systems treated here, the distances of $R(C_1–C_n)$ optimized by the (U)B3LYP method are about 7–4 % less than those by the CASSCF calculation levels. The difference between the dihedral angles, $H_A–C_1–C_2–C_3$ and $H_B–C_1–C_2–C_3$, obtained by the (U)B3LYP and CASSCF methods is under 7%, except for $H_A–C_1–C_2–C_3$ angle of the conrotatory transition state of *o*–xylylene. The dihedral angle for the conrotatory transition state of *o*–xylylene probably relates to the stabilization energies between the delocalized and the Kekulé structures. Consequently, we conclude that the geometry parameters for electrocyclic reactions estimated by the (U)B3LYP method agree well with those by CASSCF calculation levels.

3.2 Energy

The relative energies of the reactants (open structures with C_2 symmetry) for the stationary points of electrocyclic reactions of butadiene, hexa–1,3,5–triene, and *o*–xylylene are listed in Table 2. The relative energies estimated by the CASSCF and MP2–CASSCF methods in the table are taken from previous studies [10,11,12].

Table 1. Some geometry parameters of the transition states on the conrotatory and disrotatory paths for electrocyclic reactions of butadiene, hexa–1,3,5–triene, and *o*–xylylene. Bond lengths of $R(C_1–C_n)$ are in angstroms and dihedral angles in degrees

	(U)B3LYP	CASSCF	Difference (%)
Butadiene (Conrotatory)			
$R(C_1–C_n)$	2.144	2.235	–4.1
$H_A–C_1–C_2–C_3$	61.5	64.9	–5.2
$H_B–C_1–C_2–C_3$	145.0	148.5	–2.4
Butadiene (Disrotatory)			
$R(C_1–C_n)$	2.668	2.849	–6.4
$H_A–C_1–C_2–C_3$	80.6	77.7	3.7
$H_B–C_1–C_2–C_3$	114.5	123.6	–7.4
Hexa–1,3,5–triene (Conrotatory)			
$R(C_1–C_n)$	2.339	2.508	–6.7
$H_A–C_1–C_2–C_3$	39.9	37.6	6.1
$H_B–C_1–C_2–C_3$	165.9	167.3	–0.8
Hexa–1,3,5–triene (Disrotatory)			
$R(C_1–C_n)$	2.282	2.291	–0.4
$H_A–C_1–C_2–C_3$	57.3	60.0	–4.5
$H_B–C_1–C_2–C_3$	160.0	159.4	0.4
o–Xylylene (Conrotatory)			
$R(C_1–C_n)$	2.291	2.396	–4.4
$H_A–C_1–C_2–C_3$	55.6	63.6	–12.6
$H_B–C_1–C_2–C_3$	148.6	142.6	4.2
o–Xylylene (Disrotatory)			
$R(C_1–C_n)$	2.571	2.703	–4.9
$H_A–C_1–C_2–C_3$	73.8	71.3	3.5
$H_B–C_1–C_2–C_3$	123.0	131.1	–6.2

For butadiene, the relative energies of the reactants with C_s symmetry and the products calculated with the B3LYP method agrees very well with those at the MP2–CASSCF level, but not at the CASSCF level. The CASSCF values do not include the dynamic electron correlation. The energy barrier height of the conrotatory transition state estimated with the B3LYP method is lower by 5.4 kcal/mol than that obtained with the MP2–CASSCF method, and the energy barrier height of the disrotatory transition state with the UB3LYP method is 1.6 kcal/mol lower. The energy difference between the conrotatory and disrotatory transition states calculated with the (U)B3LYP method is about 4 kcal/mol larger than that with the MP2–CASSCF method.

For the reactions of hexa–1,3,5–triene, the relative energies of the reactants with C_s symmetry and the products estimated with the B3LYP method also agree with those obtained at the MP2–CASSCF calculation level. However, the energy barriers for the conrotatory and disrotatory transition states obtained with the UB3LYP and B3LYP methods are 8.1 kcal/mol and 16.4 kcal/mol less than those from MP2–CASSCF calculations, respectively. The difference between the

energy barrier heights of the conrotatory and disrotatory transition states estimated with the (U)B3LYP method is about half of those by the MP2–CASSCF and/or CASSCF calculation levels. For *o*–xylylene, the relative energies of the products, benzocyclobutene, and both transition states calculated by the (U)B3LYP method are lower than those computed with the CASSCF and MP2–CASSCF methods. These lower energies probably arise from the difference in evaluating the aromatic stabilization energy by both methods. It is known [12] that the six–membered ring part of *o*–xylylene has the character of a Kekulé structure and the six–membered ring part of benzocyclobutene is delocalized and aromatic. The reactants and the products for butadiene and hexa–1,3,5–triene are polyenes. Accordingly, the relative energies for the reactants and the products of butadiene and hexa–1,3,5–triene estimated with the B3LYP method agree well with those from the MP2–CASSCF method.

Table 2. The relative energies from the reactants (open structure with C_2 symmetry) for electrocyclic reactions of butadiene, hexa–1,3,5–triene, and *o*–xylylene. (kcal/mol)

	(U)B3LYP	CASSCF	MP2–CASSCF
Butadiene (C_2)	0.0	0.0	0.0
Conrotatory TS	43.9	52.6	49.3
Cyclo–butene (C_2)	8.3	16.0	8.9
Butadiene (C_s)	0.3	0.3	0.8
Disrotatory TS	66.9	66.0	68.5
Cyclobutene (C_s)	8.3	16.0	8.9
Hexa–1,3,5–triene (C_2)	0.0	0.0	0.0
Conrotatory TS	39.6	46.8	47.7
Cyclohexadiene (C_2)	−24.7	−16.7	−24.1
Hexa–1,3,5–triene (C_s)	0.8	1.3	0.9
Disrotatory TS	20.3	36.8	36.7
Cyclohexadiene (C_s)	−22.8	−14.9	−21.7
o–Xylylene (C_2)	0.0	0.0	0.0
Conrotatory TS	28.0	36.8	35.0
Benzocyclobutene (C_2)	−15.6	−1.8	−9.0
o–Xylylene (C_s)	0.1	0.0	0.0
Disrotatory TS	40.1	44.1	43.1
Benzocyclobutene (C_s)	−15.6	−1.8	−9.0

In the comparison of the energy barrier heights of the transition states obtained with the (U)B3LYP and MP2–CASSCF the difference of the energy barrier heights for the symmetry forbidden reactions estimated by both methods is less than that for the symmetry allowed. Namely, the treatment for the spin state as diradicals estimated with UB3LYP gives more accurate relative energies than those for the closed shell singlet spin state from the B3LYP method.

4 CONCLUSIONS

The electrocyclic reactions of butadiene, hexa–1,3,5–triene, and *o*–xylylene were studied with the density functional theory (U)B3LYP method. The geometry parameters and the relative energies for these reactions obtained with the (U)B3LYP method were compared with those from the CASSCF and MP2–CASSCF calculation levels. The difference between the geometry parameters

for active sites estimated by the (U)B3LYP and the CASSCF is under 7 %, except for the dihedral angle, H_A–C_1–C_2–C_3, for the conrotatory transition state of *o*–xylylene.

The relative energies of the reactants and the products for butadiene and hexa–1,3,5–triene reactions calculated with the (U)B3LYP method agree well with those from the MP2–CASSCF level. The activation barrier heights for butadiene and hexa–1,3,5–triene estimated with the (U)B3LYP method are lower by 2–16 kcal/mol than those from the MP2–CASSCF calculations. The relative energies for *o*–xylylene system obtained with the B3LYP method are about 3–7 kcal/mol lower than those at the MP2–CASSCF calculation level. The differences between the relative energies for all systems estimated by the UB3LYP and MP2–CASSCF methods are smaller than those from the B3LYP and MP2–CASSCF methods. In conclusion, the accuracy of the geometry parameters optimized by the B3LYP level is good, but the relative energies evaluated at the (U)B3LYP level are lower than those from MP2–CASSCF.

5 REFERENCES

[1] K. H. Houk, Y. Li, and J. D. Evanseck, Transition structures of hydrocarbon pericyclic reactions, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 682–708.

[2] K. N. Houk, J. Gonzalez, and Y. Li, Pericyclic reaction transition states: Passions and punctilios, 1935–1995, *Acc. Chem. Res.* **1995**, *28*, 81–90.

[3] R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag, Weinheim, Germany, 1970.

[4] K. Fukui, *Chemical reactions and orbital of electrons*, Maruzen Press, 1976.

[5] R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989.

[6] P. C. Haviharan and J. A. Pople, The influence of polarization functions on molecular orbital hydrogenation energies, *Theor. Chim. Acta*, **1973**, *28*, 213–222.

[7] A. D. Becke, Density functional exchange energy approximation with correct asymptotic behavior, *Phys. Rev. A* **1988**, *38*, 3098–3100.

[8] C. Lee, W. Yang, and R. G. Parr, Development of the Colle–Salvetti correlation energy formula into a functional of the electron density, *Phys. Rev. B* **1988**, *37*, 785–789.

[9] K. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al–Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cislowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Comperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. DeFrees, J. Baker, J. P. Stewart, M. Head–Gordon, C. Gonzalez, J. A. Pople, GAUSSIAN98, Gaussian, Inc.: Pittsburgh, PA, **1998**.

[10] S. Sakai, Theoretical studies on the electrocyclic reaction mechanisms for *s*–cis butadiene and disilylbutadiene, *J. Mol. Struc.* (*Theochem*) **1999**, *461–462*, 283–295.

[11] S. Sakai and S. Takane, Theoretical studies of the electrocyclic reaction mechanisms of hexatriene to cyclohexadiene, *J. Phys. Chem. A* **1999**, *103*, 2878–2882.

[12] S. Sakai, Theoretical studies of the electrocyclic reaction mechanisms of *o*–xylylene to benzocyclobutene, *J. Phys. Chem. A* **2000**, *104*, 11615–11621.