Chem 412
Project 1

Using Ab initio and DFT calculations to study the electocyclization of (Z)-Hexa-1,3,5-triene and its heterosubstituted analogues

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Introduction

The original paper is *J.Org.Chem*. **1999**, 64, 6842-6848. The author is Jesus Rodriquez-Otero from Spain. The general goal of the paper is to study the electrocyclization of hexatriene, dienimine and pentadienal structures shown in Figure 2 of the paper) by using ab initio and DFT calculations. This kind of reactions has been studied experimentally and theoretically (mostly with semiempirical and low level ab initio methods). The problem is that the computational data could poorly reproduce the experimental data. That is the reason that they author performed further computational work with higher lever methods and basis sets.

The author concentrated on the calculation of the activation energy for the electrocyclization of the three compounds and provided his explanation for the different reactivity of the reactions. Reaction thermodynamics has also been studied. The author calculated the reaction enthalpies to reveal the relative stability of reactants and products. The experimental structural character, activation energies and enthalpies were reproduced fairly well.

Computational Data

Table 1. Calculated Relative Energies (kcal/mol? for the Compounds of Figure 2

		QCISD(T)	MP4SDTQ	B3LYP
Hexatriene	tZt	0.00	0.00	0.00
	tZc	2.85	2.81	3.86
	cZc	7.43	7.50	9.77
TS		32.23	30.30	30.11
cycclohexadiene		-15.59	-16.27	-12.21
(E)-dienimine	tZt	0.00	0.00	0.00
	tZc	2.59	2.60	3.68
	cZc	6.11	5.87	6.23
	cZt	1.57	1.36	1.31
TS		25.94	22.11	20.58
dihydropyridine		-5.59	-6.80	-6.98
(Z)- dienimine	tZt	0.00	0.00	0.00

	tZc	2.72	2.70	3.81
	cZc	5.95	6.10	8.08
	cZt	2.18	2.20	3.18
TS		39.73	37.53	37.12
dihydropyridine		-6.07	-7.20	-7.19
pentadienal	tZt	0.28	0.33	0.45
	tZc	2.89	2.93	3.69
	cZc	5.24	5.19	4.84
	cZt	0.00	0.00	0.00
TS		24.80	22.92	21.52
2H-pyran		2.76	2.96	3.44

Table 2 Calculated Activation Energies and Enthalpies of Reaction (kcal/mol) for the Electrocyclization of Hexatriene to 1,3-cyclohexadiene at 400 K

	Ea	ΔH
Experimental	29.9+/-0.5	-17.5
MP4SDTQ/6-31G*//MP2/6-31G*	30.4	-17.8
MP4SDTQ/6-31G**//MP2/6-31G**	30.0	-17.7
MP4SDTQ/6-311G**//MP2/6-311G*	28.6	-17.8
QCISD(T)/6-31G**//MP2/6-31G**	31.9	-17.0
QCISD(T)/6-311G**//MP2/6-31G**	30.8	-17.2
B3LYP/6-31G**//B3LYP/6-31G**	29.8	-13.5
B3LYP/6-311+G*//MP2/6-31G*	30.6	-11.8
B3LYP/6-311++G**//B3LYP/6-31G**	30.4	-11.3

Table 3. Wiberg bond Orders Based on the Natural Atomic Orbitals (NAOs) Density Matrix for the Transition States as Calculated from MP2 and B3LYP Densities

	hexatriene	(E)-dienimine	(Z)-dienimine	pentadienal
C2-X1	1.398(1.476)	1.526(1.635)	1.311(1.412)	1.412(1.487)
C3-C2	1.309(1.434)	1.197(1.285)	1.361(1.474)	1.234(1.339)
C4-C3	1.354(1.423)	1.406(1.481)	1.294(1.367)	1.349(1.405)
C5-C4	1.309(1.434)	1.267(1.373)	1.384(1.505)	1.313(1.425)
C6-C5	1.398(1.476)	1.425(1.484)	1.322(1.405)	1.388(1.433)
X1-C6	0.349(0.433)	0.327(0.382)	0.423(0.489)	0.335(0.382)

Table 4. Bond Orders of the Natural Localized Molecular Orbitals (NLMOs) for the Interaction between Atoms X1 and C6 in the Transition State

	bond order	NLMO
hexatriene	+0.086(+0.094) +0.086(+0.094)	π(5-6) π(1-2)

	+0.079(+0.086)	π(3-4)
(E)-dienimine	+0.083(+0.098)	LP(1)
	+0.046(+0.051)	π(1-2)
	+0.040(+0.039)	π(3-4)
	+0.040(+0.035)	π(5-6)
(Z)-dienimine	+0.726(+0.666)	(1-6)
	-0.078(-0.067)	π(2-3)
	-0.054(-0.026)	π(4-5)
pentadienal	+0.094(+0.103)	LP(1)
	+0.047(=0.056)	π(1-2)
	+0.037(+0.035)	π(3-4)
	+0.031(+0.026)	π(5-6)

Question Section

1. (SCL) What computational methods did the author use? Please provide both computational levels and basis sets. Which level is theoretically higher? Are the methods and basis sets the author chose reasonable? Why? Is a higher level calculation with a further expansion of basis set always better? Why?
2. (RQD) Using Table 1 and necessary information in the paper, rationalize the relative stability of different conformations of the same compound, hexatriene, dienimine, and pentadieneal, respectively.
3. (RQD) We did not learn NBO and NLMO calculations. But could you use your own knowledge with the information from the paper to explain why the author used these two calculations to rationalize the reactivity? What information can we get from these two calculations? How does the data in Table 3 agree with the fact the activation barrier of (Z)-dienimine is higher than others' ?
4. (EVL) The author came up with an explanation for the relative reactivity of hexatriene, (E)-dienimine, (Z)-dienimine and pentadienal. What is his explanation and do you agree with it totally, partially, or not? Why?