

An ab Initio theoretical study about the dimerization of cyclobutadiene using CASSCF computational methods.

“The Hueckelberries”

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Introduction

This paper is based solely on the paper “The Dimerization of Cyclobutadiene. An ab Initio CASSCF Theoretical Study” by Yi Li and K. N. Houk, *J. Am. Chem. Soc.* **1996**, *118*, 880-885. Cyclobutadiene (CB), or (C₄H₄) under normal conditions exists as a dimer. Li and Houk studied the mechanism by which CB dimerizes. Using computational methods they located transition states, second order saddle points, and minima on the potential energy diagram.

Cyclobutadiene is “essentially” a diradical and therefore highly reactive. One specific question to ask would be whether the dimerization prefers a concerted or step by step pathway. A concerted mechanism can maintain some aromaticity, but a step by step mechanism destroys the aromaticity. Since CB is highly reactive, does it’s transition to a dimer have any advantage in a concerted pathway?

Computational Data

Several computational methods were used to study the dimerization of CB. RHF/3-21G and RHF/6-31G* were used to optimize the structure. The geometries were described by using the 8-electron, 8-orbital complete active space multiconfiguration self-consistent field theory (CASSCF) and the 3-21G basis set. Several species were also studied by CASSCF/6-31G* calculations. The CASSCF calculations were performed with the GAMESS program and the RHF and MP2 calculations were performed using the Gaussian 90 program.

Table 1. Calculated Relative Energies(kcal/mol) of Stationary Points and Numbers of Imaginary Frequencies (roman numeral)

	HF /3-21G	RHF /6-31G*	RMP2 /6-31G*	CASSCF /3-21G	CASSCF /6-31G*	
1	0 (O)	0	0	0		0
2	-104.6 (O)	-94.6	-104.8	-72.9		
3	-113.2 (O)	-102.3	-112	-80.1		
4	9.3 (I)	16.4	-9.6	12.2 (II)		
5	-10.1 (II)	6.1	-50.1	-4.4 (II)		6.8
6	-68.9 (I)	-52.8	-82.4	-43 (I)		
7	-55.1			12.2		15.2
8a	-91.4					
8b	-87.8			-26.2 (I)		
9a	-95.5			-33.1 (O)		
9b	-95.5			-33.4 (O)		

**1: (2 cyclobutadienes); 2: (syn adduct) 3: (anti-adduct) 4: (anti-saddle point)
5: (second order saddle) 6: (Cope TS) 7: (anti TS) 8a: (singlet eclipsed)
8b: (triplet eclipsed) 9a: (singlet anti) 9b: (triplet anti)**

The singlet of CB is rectangular and is 7 kcal/mol more stable than the square triplet. The syn product **2** is less stable than the anti adduct, **3**, by about 8 kcal/mol according to calculation, but the syn product is kinetically favored experimentally.

A symmetrical stationary point was found, **5**, that was consistently lower in energy than the anti-saddle point, **4**. This suggests that the antiaromaticity of CB decreases in the syn stationary point. Note that **5** is also square in geometry as in the triplet state and also has two degenerate vibrational imaginary modes. Relaxation may lead to transition structure, **6**, which can happen in four different ways or, it may also degenerate in four ways to form the syn adduct **2**. The latter is the steepest pathway.

The transition structure **6** is lower in energy than **5**. In turn, **5** is lower in energy than 2 cyclobutadienes on the RHF/3-21G level, higher on the 6-31G*, and ridiculously lower on the MP2 level. This is because **6** has so much biradical character. For this reason, Li and Houk use CASSCF for a better description of diradical species.

Two CB's may also come together to form the product without passing through **5** or **6** at all. This happens when the attractive interactions are so great that they combine

without activation and are deposited in the ground state surface for the degenerate Cope rearrangement. The energy of concert is zero for this reaction.

Yi and Houk failed to locate either an asynchronous saddle point or a singlet biradical intermediate for the syn addition, suggesting that syn dimerization is spontaneous when two cyclobutadienes approach each other in a staggered face-to-face orientation.

In conclusion, two cyclobutadienes will react to form the dimer with no potential energy barrier. The energy lowering upon interaction is greatest in a concerted syn geometry, but passage through syn diradical geometries is also favorable.

Questions

- 1.) What conditions make a concerted pathway more favorable than a stepwise pathway? (ICR)
- 2.) How can you tell in Fig.1 (**4**) that this is a Diels Alder reaction and not a [2+2] addition? (SCL)
- 3.) What makes cyclobutadiene “essentially” a diradical? (SCL)
- 4.) Why is CASSCF calculations better for diradical species? (FAR)
- 5.) Why is structure **4** in Table 1 a first order saddle point in HF/3-21G and a second order saddle point in CASSCF/3-21G? (EVL)

Group Actions and Dynamics

Sang and I each picked three or four papers on our own, then got together and decided on this one because it was relatively easy to understand and because it was a topic that has never been studied before. This took a couple of hours. Next, we got together to discuss what questions to ask. Again, we each came up with our own ideas first and then narrowed it down to five. This took about two hours. Then we tried to

figure out how to run the scanner, which took another hour. Writing the report took another two hours. It was difficult deciding what to include and what to leave out.

This project was more of a mental challenge than Sang and I had expected. We each went over every paragraph and referred to the tables and figures several times before we could get a firm understanding of what was going on. We discovered that we had more questions about the methods after reading it over and over.

Sang and I were both pulling our hair out, but it certainly was a good learning experience. We hope that after the peer review we will have an even better understanding of this paper.

