

Automerization of Cyclobutadiene and its Substituted Derivatives - An Ab Initio Study of the Barrier Height

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Outline

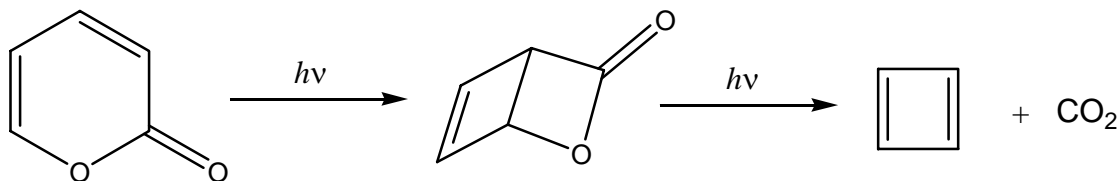
- Introduction
- Energy Barrier of Automerization of Cyclobutadiene and its Cyano Substituted Derivatives
- Lowest Triplet State of Cyclobutadiene
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Introduction

- cyclobutadiene has been fascinating both experimental and theoretical chemists for many decades
- cyclobutadiene is the smallest neutral compound that exhibits an antiaromatic character
- in the ground state, it is very unstable due to the antiaromaticity and high strain

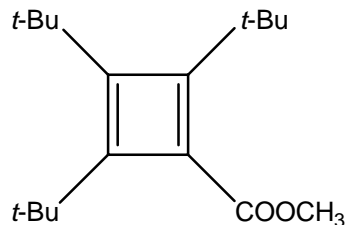
Introduction

- since cyclobutadiene is very unstable, it is isolated at the very low temperature (8 K) in the matrix of argon atoms



Chapman et al., 1973.

- some substituted cyclobutadienes, as well as complexes of cyclobutadiene were synthesized and characterized



Masamune et al., 1973.

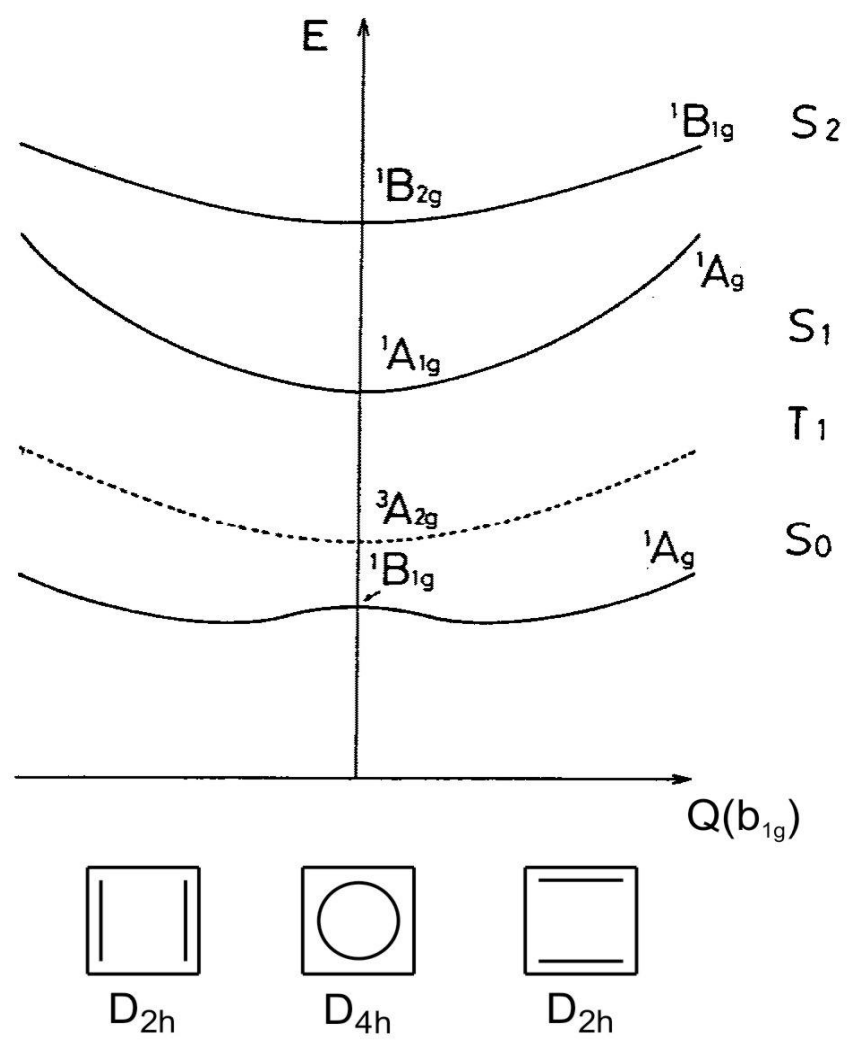
Introduction

- in spite of its relatively simple electronic structure, cyclobutadiene exhibits some very interesting electronic properties:
 - **the ground state is rectangle**
 - **the lowest triplet state is square**
 - the ground state exhibits antiaromatic character
 - the lowest triplet state exhibits aromatic character

Baird, 1972.

Gogonea et al., 1998.

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Energy Barrier of Automerization

Experimental facts:

- the energy barrier for automerization reaction of the parent molecule is in the range of 1.6 - 10 kcal mol⁻¹

Carpenter, 1983.

- the activation energy for automerization of tri-*t*-butylcyclobutadiene is less than 2.5 kcal mol⁻¹

Maier et al., 1982.

Energy Barrier of Automerization

Theoretical predictions of ΔE :

- HF: 30.2 kcal mol⁻¹ (Sancho-Garcia et al., 2000.)
- B3LYP: 25.3 kcal mol⁻¹ (Sancho-Garcia et al., 2000.)
- MR-CCSD(T): 6.6 kcal mol⁻¹ (Balkova and Bartlett 1994.)
- MC-SCF: 4.8 kcal mol⁻¹ (Nakamura et al., 1989.)
- MR-BWCCSD: 7.0 kcal mol⁻¹ (Sancho-Garcia et al., 2000.)

Energy Barrier of Automerization

- importance of both dynamic and non-dynamic electron correlation
- the ground state is closed shell singlet and it can be, in principle, well described with single reference methods
- the transition state is open shell structure - it can not be described by single reference methods
- **this calls for the use of multireference methods**

Lowest Triplet State of Cyclobutadiene

Theoretical predictions of ΔE :

- HF: -36.6 kcal mol⁻¹
- CCSD: -9.8 kcal mol⁻¹
- MR-CCSD(T): 6.9 kcal mol⁻¹
- MC-SCF: 12.7 kcal mol⁻¹

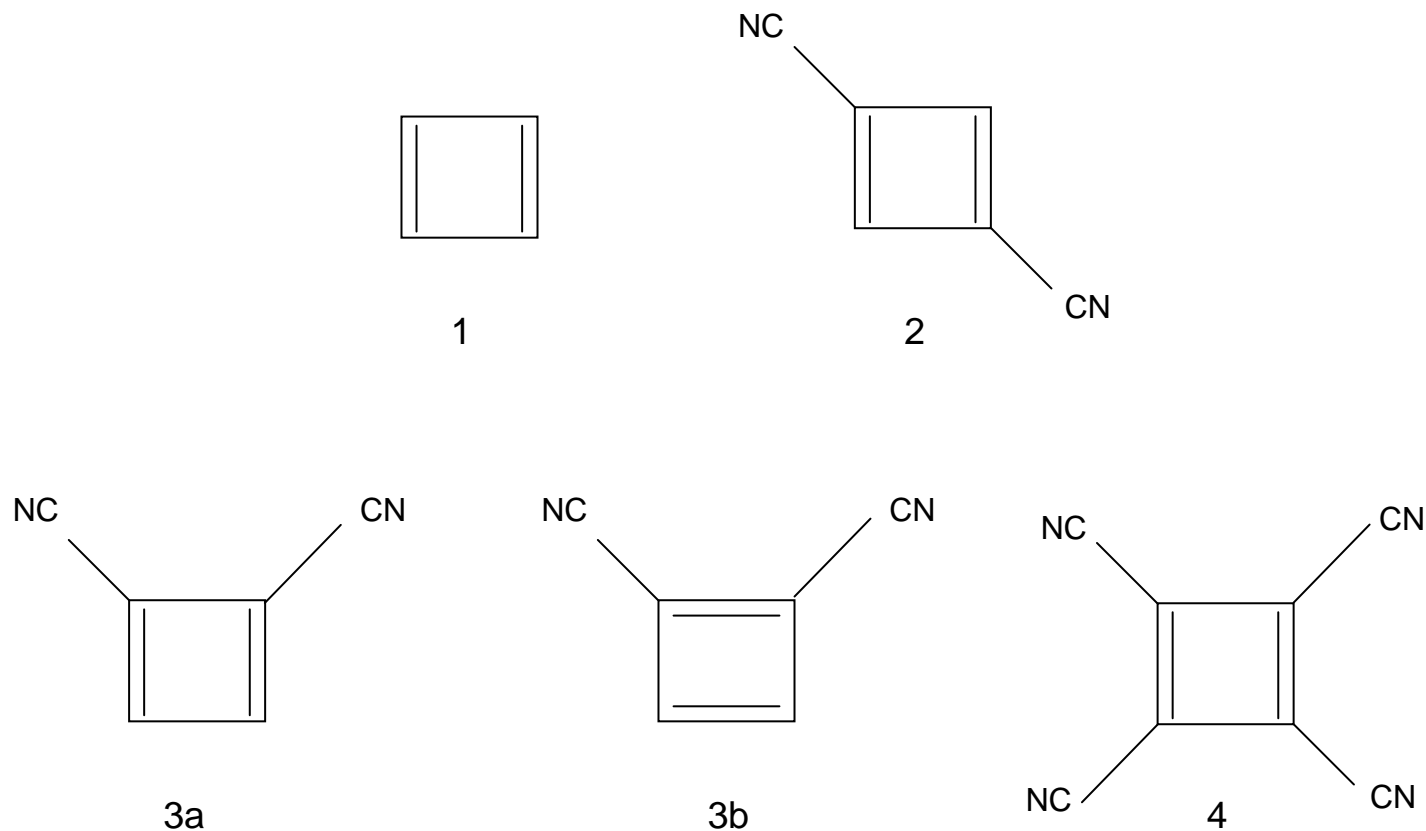
Balkova and Bartlett, 1994.

Nakamura et. al., 1989.

Lowest Triplet State of Cyclobutadiene

- single reference methods predict that the lowest triplet state is more stable than the transition state
- the inclusion of dynamic and non-dynamic correlation effects, predicts correct ordering of energy levels
- violation of Hund's rule
- **this calls for the use of multireference methods**

Cyano Substituted Derivatives of Cyclobutadiene



Computational Methods - Cyclobutadiene

- complete active space: CAS (4,4)
- inclusion of all 4 π electrons
- methods: MC-SCF, MR-CISD(Q), **MR-AQCC**
- basis sets: cc-pVDZ, aug-cc-pVDZ, cc-pVTZ, aug'-cc-pVTZ
- state averaging over four states
- COLUMBUS suite of codes

Lischka, Shepard, Shavitt et al.

Computational Methods – Cyano Derivatives

- complete active spaces:
 - CAS (4,4) – molecule **1**
 - CAS (8,8) – molecules **2, 3a, 3b**
 - CAS (12,11) – molecule **4**
- inclusion of all π electrons relevant to the system
- reference space (4,4)
- methods: MC-SCF, MR-AQCC
- basis set: 6-31G(d)
- COLUMBUS suite of codes

The Aims

- energy barrier for automerization reaction of cyclobutadiene and its cyano derivatives
- effect of zero-point vibrational energy
- singlet-triplet energy difference at transition state geometry for cyclobutadiene

Results

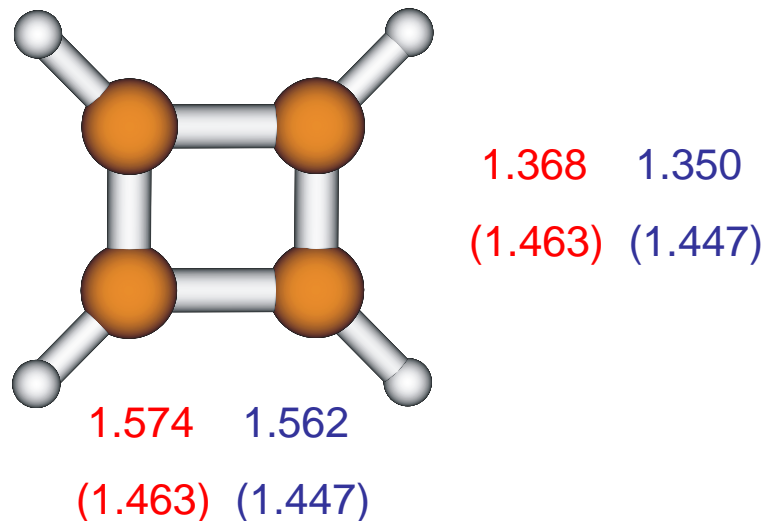
Ground State of Cyclobutadiene - Energies

	<i>rectangle</i>	<i>square</i>	<i>barrier</i>
cc-pVDZ	-154.225019	-154.213375	7.3 (4.8)
aug-cc-pVDZ	-154.244625	-154.232915	7.4 (4.9)
cc-pVTZ	-154.362540	-154.349137	8.4 (5.9)
aug'-cc-pVTZ	-154.365795	-154.352593	8.3 (5.8)

- MR-AQCC/SA-4-CASSCF
- ZPVE corrected values are given in parenthesis
(MR-AQCC/cc'-pVTZ level of theory)
- energies are given in a.u; barriers are in kcal mol⁻¹

Results

Ground State of Cyclobutadiene - Geometry



- bond lengths of ground state of cyclobutadiene for rectangle and square geometry (in parenthesis)
- MR-AQCC/aug-cc-pVDZ; MR-AQCC/aug'-cc-pVTZ

Results

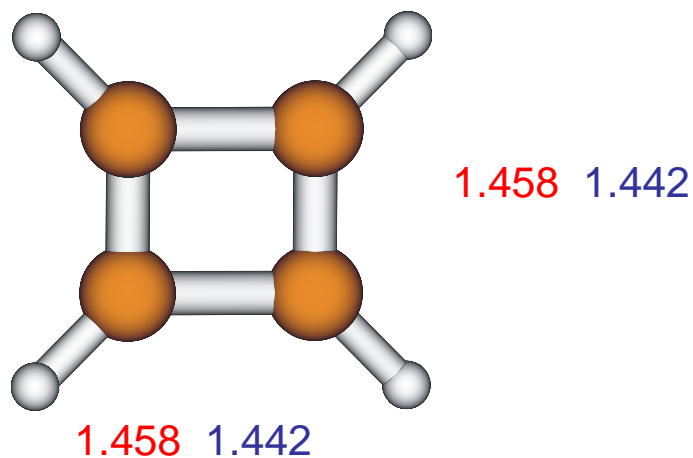
Lowest Triplet State of Cyclobutadiene - Energies

	1^1A_g	1^3A_{2g}	ΔE
cc-pVDZ	-154.213375	-154.203383	6.3 (8.2)
aug-cc-pVDZ	-154.232915	-154.223682	5.8 (7.7)
cc-pVTZ	-154.349137	-154.340338	5.5 (7.4)
aug'-cc-pVTZ	-154.352593	-154.343999	5.4 (7.3)

- energy differences between transition state and lowest triplet state of cyclobutadiene
- MR-AQCC/SA-4-CASSCF
- ZPVE corrected values are given in parenthesis
(MR-AQCC/cc-pVDZ level of theory)
- energies are given in a.u; ΔE values are in kcal mol⁻¹

Results

Lowest Triplet State of Cyclobutadiene - Geometry



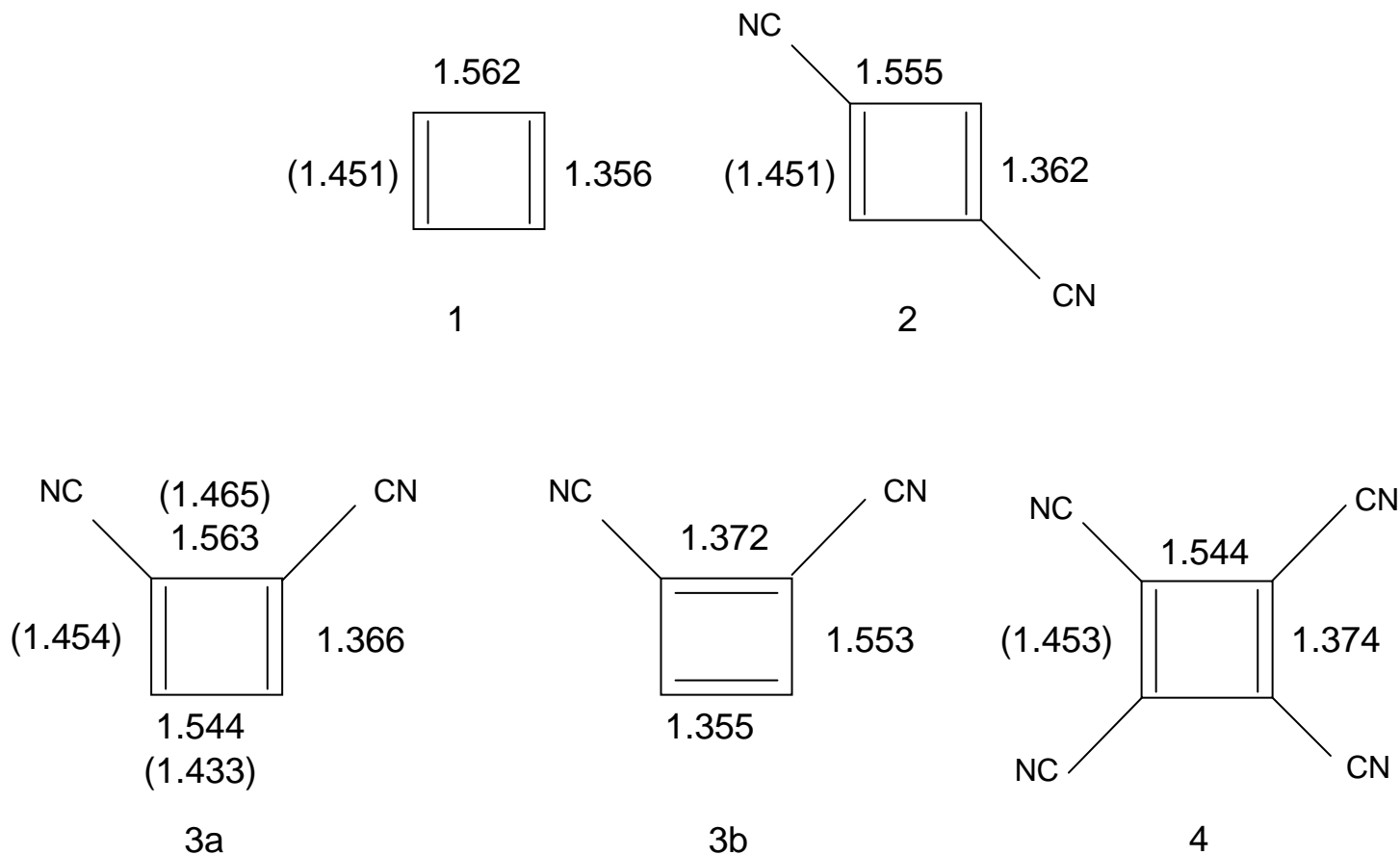
- bond lengths of the lowest triplet state of cyclobutadiene
- MR-AQCC/aug-cc-pVDZ; MR-AQCC/aug'-cc-pVTZ

Ground State of Cyano Derivatives of Cyclobutadiene - Energies

	<i>ground state</i>		<i>transition state</i>		<i>barrier</i>	
	MC-SCF	MR-AQCC	MC-SCF	MR-AQCC	MC-SCF	MR-AQCC
SS-CASSCF						
1	-153.70791	-154.18521	-153.69806	-154.17325	6.2 (3.7)	7.5 (5.0)
2	-337.23506	-338.19133	-337.22738	-338.18107	4.8 (2.3)	6.4 (3.9)
3a	-337.23310	-338.18888	-337.22644	-338.18125	4.2 (2.1)	4.8 (2.7)
3b	-337.23345	-338.18943	-337.22644	-338.18125	4.4 (2.3)	5.1 (3.0)
4	-520.69358	-522.17211	-520.68611	-522.16581	4.7 (2.6)	4.0 (1.9)

- ZPVE corrected values are given in parenthesis
(MC-SCF/6-31G(d) level of theory)
- different sizes of CAS spaces depending on the system studied
- energies are given in a.u; barriers are in kcal mol⁻¹

Ground State of Cyano Derivatives of Cyclobutadiene - Geometries



➤ bond stretch isomerism in molecule of 1,2-dicyanocyclobutadiene

Conclusions

- highly accurate MR-AQCC calculations are performed to evaluate energy barrier for automerization reaction of cyclobutadiene
- the most sophisticated method used, predicts that the barrier height is $8.3 \text{ kcal mol}^{-1}$ compared to the previous benchmark value of $6.6 \text{ kcal mol}^{-1}$
- inclusion of zero-point vibrational energy lowers the barrier by $2.5 \text{ kcal mol}^{-1}$, giving the value of $5.8 \text{ kcal mol}^{-1}$, which is $1.8 \text{ kcal mol}^{-1}$ higher than the benchmark value ($4.0 \text{ kcal mol}^{-1}$)
- the energy difference between the lowest triplet state and the transition state of cyclobutadiene is $5.4 \text{ kcal mol}^{-1}$ ($1.5 \text{ kcal mol}^{-1}$ lower than the MR-CCSD(T) result of $6.9 \text{ kcal mol}^{-1}$)

Conclusions

- cyano derivatives of cyclobutadiene show decrease of the energy barrier of automerization due to the steric destabilization of the ground state
- inclusion of dynamic correlation effect increases the barrier of the automerization reaction
- the barriers are decreasing in the range from 5.0 kcal mol⁻¹, for unsubstituted cyclobutadiene to 1.9 kcal mol⁻¹ for tetracyanocyclobutadiene with the zero-point vibrational energy included
- 1,2-dicyanocyclobutadiene shows an rare example of the bond-stretch isomerism

Acknowledgements

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Questions

