

Lawrence Berkeley National Laboratory

Recent Work

Title

ON THE ELECTRONIC STRUCTURE OF CUBENE C₈H₆

Permalink

<https://escholarship.org/uc/item/4sd6s9zm>

Authors

Takada, T.
Dupuis, M.

Publication Date

1982-09-01

NRCC NATIONAL RESOURCE FOR COMPUTATION IN CHEMISTRY

Submitted to: Chemical Physics Letters

ON THE ELECTRONIC STRUCTURE OF CUBENE, C_8H_6

T. Takada and M. Dupuis

September 1982

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782.*

**LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA**

LBL-14584
c. 2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

ON THE ELECTRONIC STRUCTURE OF CUBENE C_8H_6 *

T. Takada[†] and M. Dupuis^{††}

National Resource for Computation in Chemistry
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

[†]The James Franck Institute, University of Chicago, 5640 Ellis Avenue, Chicago, Illinois 60537

^{††}Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720.

*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098 and by the National Science Foundation under Grant No. CHE-7721305.

ON THE ELECTRONIC STRUCTURE OF CUBENE $C_8H_6^*$

T. Takada⁺ and M. Dupuis⁺⁺

National Resource for Computation in Chemistry
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Abstract

Hartree-Fock (HF) and Multiconfiguration Hartree-Fock (MCHF) wavefunctions of cubene C_8H_6 have been calculated which indicate that the ground state 1A_1 of the molecule is better described as a diradical than a CC double bonded structure. The 3B_2 state is found to lie ~ 0.94 eV above the ground state and the 1B_2 state ~ 4.4 eV above the ground state. The dissociation energy for β CH bond cleavage in the cubyl radical C_8H_7 to form $C_8H_6(^1A_1) + H$ is estimated to be 74 kcal/mol compared to 91 kcal/mol for CH bond cleavage in cubane C_8H_8 to form $C_8H_7 + H$. β CH bonds in the cubyl radical are much stronger than β CH bonds in acyclic alkyl radicals.

I. Introduction

One of the goals of experimental and theoretical investigations of the structure of radical is to determine how the radical center affects adjacent bonds of the molecule, and how it influences the reactivity of the radical. For example, recent studies¹ of acyclic alkyl radicals have shown that CH bonds β to the radical center and eclipsed with the half filled p-orbital of the radical are longer than CH bonds normally encountered in alkanes. In fact thermochemical studies indicate that the dissociation energy of β CH bonds is about 38 kcal/mol, in contrast to the ~ 98 kcal/mol required for cleavage of a CH bond in alkanes.

Recently, Schubert, et al.,² have calculated the structure of cubane, cubene, and the cubyl radical. They used the closed-shell Hartree-Fock (HF) formalism, and concluded that β CH bonds in the cubyl radical have the same length as the CH bonds in cubane. They estimated the β CH bond dissociation energy to be more than 100 kcal/mol, clearly much higher than for acyclic alkyl radicals.

The purpose of this note is to reconsider the theoretical description of the cubene molecule. Simple molecular orbital considerations indicate that electron correlation effects in cubene are significant. As shown below the energy lowering obtained with a two configuration wavefunction amounts to ~ 35 kcal/mol, and thus cubene is better described as a diradical than a CC double bonded structure.

While this finding does not alter the qualitative conclusions of Schubert, et al.,² mainly that cleavage of a β CH bond in the cubyl

radical requires much more energy than in acyclic alkyl radicals, it is worth noting that many molecules containing CC multiple bonds exhibit strong diradical character. Such is the case for ortho-benzyne,⁷ and for cyclopropyne⁸ and cyclobutyne.⁹

The theoretical considerations governing this study are given in Section II, a discussion of the results is presented in Section III.

II. Theoretical Considerations

The structure of "cubene" which has C_{2v} symmetry is shown on Fig. 1. The two adjacent carbon atoms C_1 do not have hydrogen atoms attached to them. All the carbon atoms can be described as being in an sp^3 hybridization state. While all four lobes of the hybridized state of the C_2 and C_3 atoms are covalently bonded to adjacent atoms (C or H), the two C_1 atoms each have an unpaired electron pointing in the diagonal direction.

Let us denote by P_{C_1} the half-filled orbital on the C_1 atoms. In C_{2v} symmetry, the two P_{C_1} orbitals form the basis for two molecular orbitals of a_1 and b_2 symmetry

$$a_1 = P_{C_1} + P_{C_1} \tag{1}$$

$$b_2 = P_{C_1} - P_{C_1}$$

If the two C_1 atoms were far apart, the two orbitals a_1 and b_2 would be degenerate in energy. At finite separation, the degeneracy is removed. The splitting of the a_1 and b_2 levels depends on the

overlap of the two half filled p_{C_1} orbitals. Since the two p_{C_1} orbitals are pointing away from each other, the overlap interaction is small, and therefore the a_1 and b_2 levels stay close in energy.

The electronic states resulting from the various orbital occupations are schematically represented in Fig. 2. When one electron occupies each orbital, we have the 3B_2 and 1B_2 state. When two electrons are paired in the a_1 and the b_2 orbitals we have two configurations of 1A_1 symmetry. The HF configuration of cubene is the third case shown in Fig. 2, with occupancy a_1^2 . However, the second configuration of 1A_1 symmetry with occupancy b_2^2 is expected to mix heavily with the HF configuration because of the near degeneracy of the a_1 and b_2 orbitals. Indeed the present calculated wavefunction indicates that the overlap of the two p_{C_1} orbitals is ~ 0.45 , that the energy lowering due to configuration mixing is ~ -0.58 a.u. (or ~ 36 kcal/mol), and that the coefficient of the a_1^2 configuration is ~ 0.935 and the coefficient of the b_2^2 configuration is -0.353 . The 3B_2 and 1B_2 states can be represented by a single configuration.

Ab initio Hartree-Fock (HF) calculations have been carried out on the 3B_2 and 1B_2 state of carbene, and multiconfiguration Hartree-Fock (MCHF) on the 1A_1 state of cubene. The gradient method³ was used to optimize all geometrical parameters. The calculations were done with the program HONDO⁴ and used the split valence 4-31G basis set.⁵

III. Results and Discussion

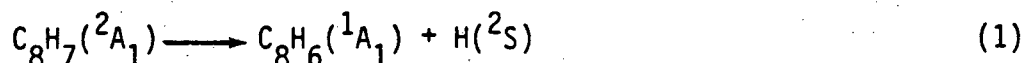
The energies and equilibrium geometrical parameters of the 1A_1 , 3B_2 , and 1B_2 states of cubene are given in Table 1. As described in the previous section the factors which contribute to the near degeneracy of the a_1 and b_2 orbitals are contained in the 1A_1 (MCHF) wavefunction. The results for this wavefunction are found in the corresponding labelled column. For comparison the double bonded structure obtained in ref. 2 is given in the column labelled 1A_1 (HF).

First, we note that the 3B_2 (HF) energy is lower than the 1A_1 (HF) energy. Taking into account the near degeneracy effect of the a_1 and b_2 orbitals, results in the 1A_1 state being the lowest state. The 1A_1 (MCHF) energy is 21.6 kcal/mol or 0.94 eV lower than the 3B_2 (HF) energy, and 100.7 kcal/mol or 4.36 eV lower than the 1B_2 (HF) energy.

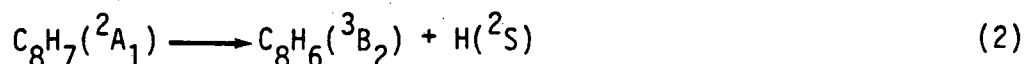
Second, we note that for the 1A_1 state the C_1-C_1 bond length is 0.051 Å longer in the MCHF model than in the HF model. The lengthening of the C_1-C_1 bond was expected since configuration mixing introduces the b_2^2 configuration which reflects the b_2 orbital's node between the two C_1 carbon atoms. In the 1A_1 (HF) state the two C_1 carbon atoms move toward the center of the molecule to make the in phase overlap of the radical orbital as large as possible. The configuration mixing of the 1A_1 (MCHF) help relieve the strain and therefore the molecule is not as "flat". The 1.418 Å C_1C_1 bond length of the 1A_1 (MCHF) state is still remarkably

shorter than any other CC bond of the diradical and of the cubyl radical ($\sim 1.56 \text{ \AA}$). The CH bond have about the same length as in the cubyl radical. All the CC bond lengths in the $^3B_2(\text{HF})$ structure of cubene are similar to the ones of the cubyl radical ($\sim 1.56\text{--}1.58 \text{ \AA}$). The $^3B_2(\text{HF})$ state structure looks very close to the perfect cube of cubane, while in the $^1B_2(\text{HF})$ state the C_1C_1 bond length is extremely long 1.845 \AA . In fact the two carbon atoms appear not bonded. They could be described as carbene-like entities. An argument similar to the one developed in the previous section suggest that near-degeneracy effects in the C_1C_1 bond of 1B_2 state are important, and should be accounted for by mixing the $C_1C_1(\sigma^2)$ and $C_1C_1(\sigma^{*2})$ configurations. Then one would expect the excitation energy of this state to be smaller than the 100 kcal/mol reported here.

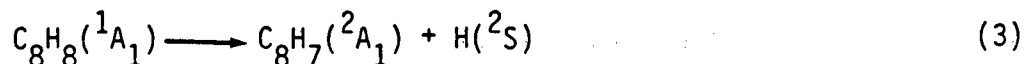
Using the calculated energies,⁶ we find that the enthalpy of reaction for



is 74 kcal/mol . The enthalpy of reaction for



is similarly determined to be 97 kcal/mol . From the bond energy of 91 kcal/mol given in ref. 2 for the reaction



it appears that β CH bonds in the cubyl radical are not as strong as CH bonds in cubane. Nevertheless, the qualitative conclusions presented by Schubert, et al.,² still hold: i.e., the energy required for β CH bond cleavage in the cubyl radical is clearly much higher than in acyclic alkyl radicals.

Conclusion

We have shown that configuration mixing plays an important role in the description of the ground electronic state of cubene. The near degeneracy of the a_1 and b_2 orbitals constructed from the radical center's half filled orbitals lowers the energy of the 1A_1 state by ~ 31 kcal/mol, to below the energy of the 3B_2 state. Thus cubene is better described as a diradical than a double bonded structure. Similar theoretical considerations are expected to be valid for many molecules.

Acknowledgment

The authors gratefully acknowledge many stimulating discussions with Dr. J. Pacansky (IBM Research Laboratory).

References

1. J. Pacansky and M. Dupuis, J. Chem. Phys. 68, 4276 (1978); J. Chem. Phys. 71, 2095 (1979); J. Chem. Phys. 73, 1867 (1980).
2. W. Schubert, M. Yoshimine, and J. Pacansky submitted to J. Chem. Phys.
3. For an overview see P. Pulay in H. F. Schaefer, III, "Methods of Electronic Structure Theory," Plenum, New York, 1977.
4. M. Dupuis, J. Rys, and H. F. King, J. Chem. Phys. 65, 111 (1976); M. Dupuis and H. F. King, J. Chem. Phys. 68, 3998 (1978).
5. R. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys. 54, 724 (1971).
6. See ref. 4 for the energy of H(2S). We use the energy given in ref. 2 for the cubyl radical.
7. M. Dupuis, to be published.
8. P. Saxe and H. F. Schaefer, III, J. Am. Chem. Soc. 102, 3239 (1980).
9. G. Fitzgerald and H. F. Schaefer, III, to be published.

Table 1. Optimized structural parameters of various electronic state of cubene (C_{2v} symmetry)

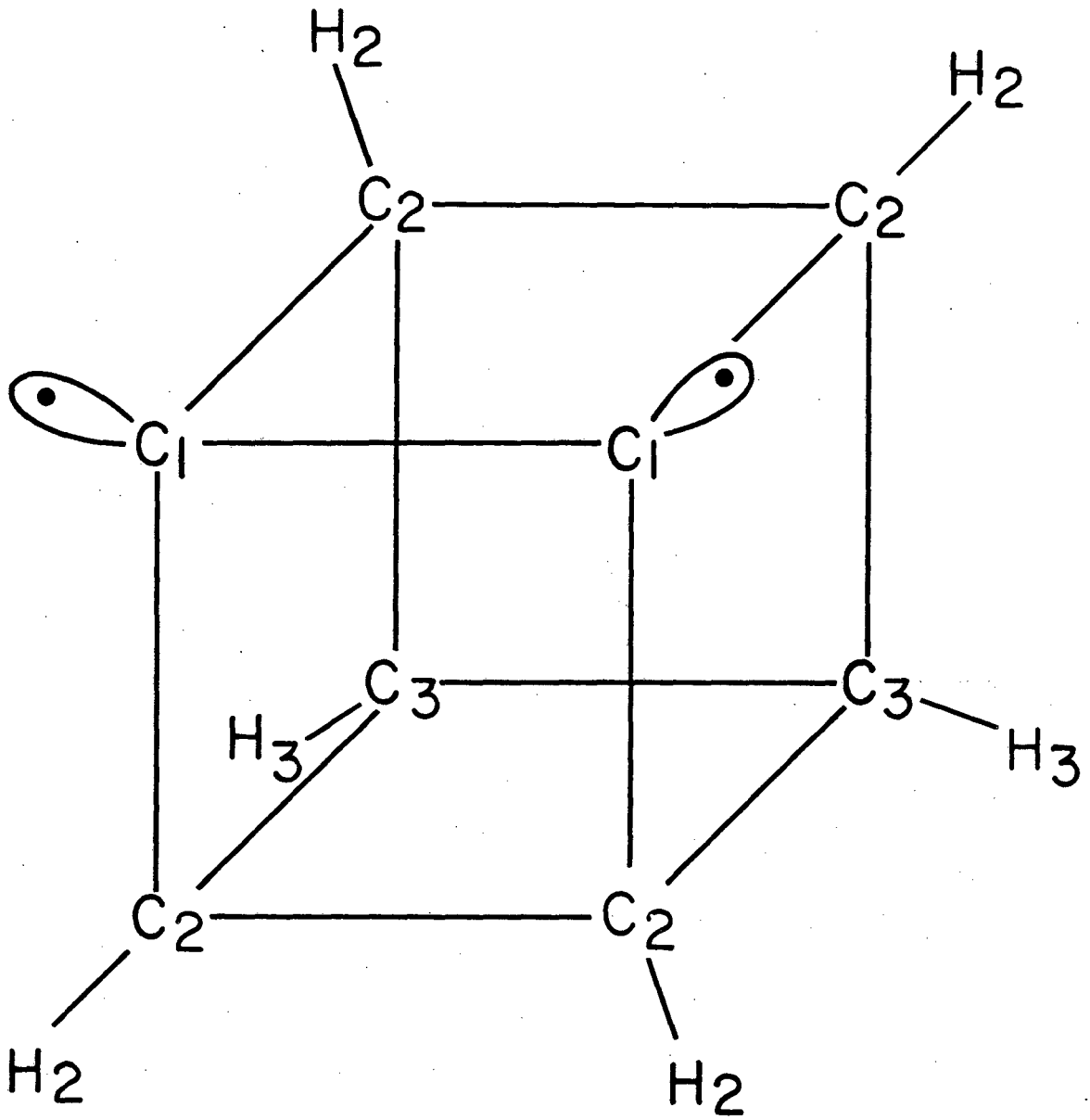
State	1A_1		3B_2	1B_2
	MCHF	HF	HF	HF
Energy (au)	-305.666723	-305.616603	-305.632313	-305.506333
Bond lengths (Å)				
C ₁ -C ₁	1.418	1.367	1.583	1.845
C ₂ -C ₂	1.579	1.575	1.585	1.553
C ₃ -C ₃	1.558	1.555	1.574	1.558
C ₁ -C ₂	1.568	1.570	1.565	1.574
C ₂ -C ₃	1.585	1.590	1.575	1.575
C ₂ -H ₂	1.073	1.073	1.073	1.073
C ₃ -H ₃	1.072	1.073	1.074	1.073
Bond angles (deg.)				
C ₁ -C ₁ -C ₂	92.9	93.8	90.0	84.7
C ₁ -C ₂ -C ₂	87.1	86.2	90.0	95.3
C ₂ -C ₂ -C ₃	89.6	89.6	89.8	88.9
C ₂ -C ₃ -C ₃	90.4	90.4	90.2	89.9
C ₂ -C ₁ -C ₂	95.6	97.3	91.2	90.9
C ₁ -C ₂ -C ₃	85.0	83.4	89.2	88.9
C ₂ -C ₃ -C ₂	94.2	95.7	90.4	90.8
C ₁ -C ₂ -H ₂	127.8	128.6	126.1	122.2
C ₂ -C ₂ -H ₂	128.3	129.0	124.7	123.6
C ₃ -C ₂ -H ₂	125.3	125.5	125.7	127.0
C ₂ -C ₃ -H ₃	123.7	123.2	125.1	124.5
C ₃ -C ₃ -H ₃	124.9	124.8	125.1	126.3

a. See Fig. 1 for labels.

Figure Captions

Fig. 1 Structure of Cubene with C_{2v} Symmetry

Fig. 2 The Electronic States of Cubene

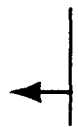


XBL 826-1403

Orbital b_2



Orbital a_1



State

3B_2

1B_2

1A_1

1A_1

=

XBL 826-1401

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720