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Schaefer, H.F.

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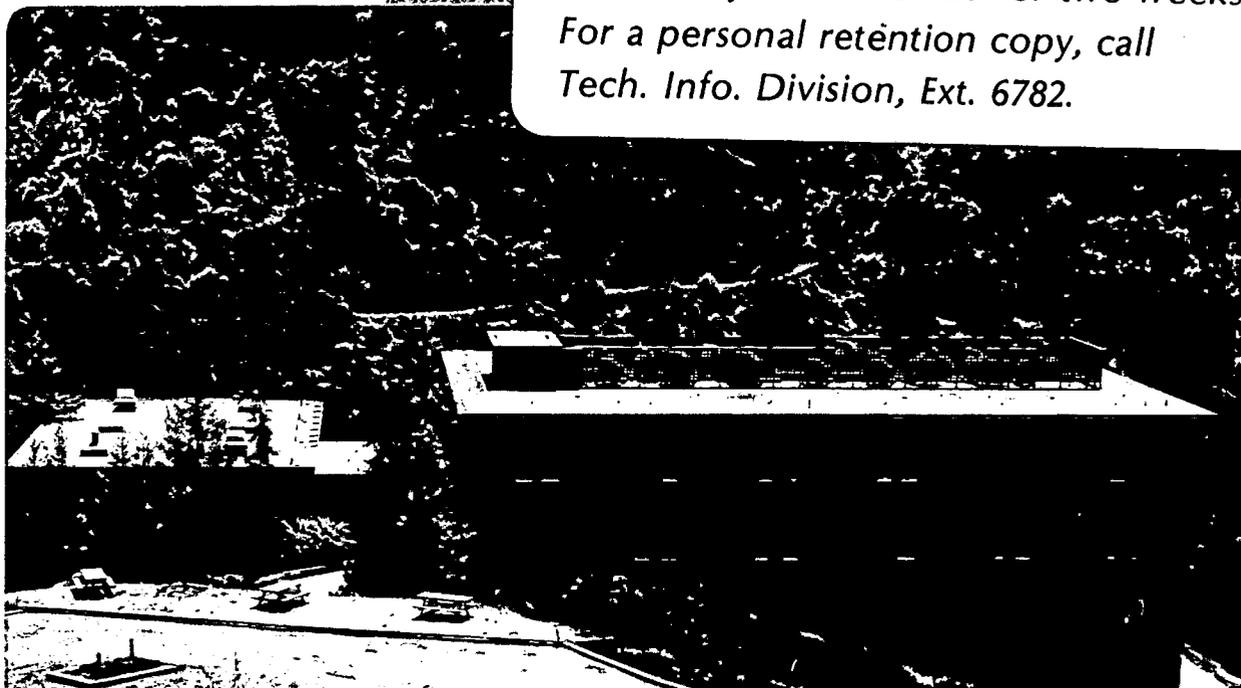
STRUCTURES, ENERGETICS, AND VIBRATIONAL
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George Fitzgerald and Henry F. Schaefer III

December 1982

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Structures, Energetics, and Vibrational
Frequencies of Cyclopropyne

George Fitzgerald^{*} and Henry F. Schaefer III

Department of Chemistry and Lawrence Berkeley Laboratory,
University of California,
Berkeley, California 94720

Abstract

The electronic structure of the lowest singlet and triplet states of cyclopropyne have been investigated using ab initio molecular quantum mechanics. Both double zeta (DZ) and double zeta plus carbon d function (DZ+d) basis sets have been used in conjunction with self-consistent-field (SCF), multiconfiguration (MC) SCF, and configuration interaction (CI) methods. Singlet cyclopropyne is predicted to be a transition state for the degenerate rearrangement of propadienylidene ($H_2C=C=C:$). However, triplet cyclopropyne is a minimum on the C_3H_2 potential energy hypersurface, and vibrational frequencies are predicted at two levels of theory. Structures and vibrational frequencies are compared with those of the relatively stable cyclopropene molecule.

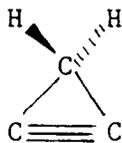
* National Science Foundation Predoctoral Fellow, 1980-83.

Background

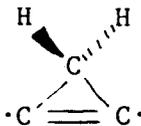
Small ring systems are of continuing interest in chemistry, and monocyclic otherwise saturated acetylenes have received particular attention in recent years.¹⁻⁴ One question which remains of fundamental interest concerns the size of the smallest such ring which can actually exist. Such a problem provides a challenge to the synthetic organic chemist, and, as well, should provide interesting insight into the limits of carbon-carbon bonding. Cyclooctyne⁵ is the smallest such ring for which a complete structural determination is available, but for years there has been evidence,¹⁻⁴ though largely indirect, for the transient existence of the smaller rings cycloheptyne, cyclohexyne, and cyclopentyne. Most recently, Chapman⁶ has obtained circumstantial support for the intermediacy of the smallest of these three.

Despite a lack of evidence for even the most transient existence of cyclobutyne,^{7,8} a recent theoretical study by our research group,⁹ predicted this four-membered ring to be a relative minimum on the C_4H_4 energy hypersurface. Furthermore, the predicted $C\equiv C$ stretching frequency (1911 cm^{-1}) and bond length (1.277 \AA) allow one to indeed classify this as a triple bond, though a weak one. Cyclobutyne is thus a potentially synthesizable molecule.

In an earlier study¹⁰ of cyclopropyne



it was reported that the 1A_1 electronic ground state did not represent a minimum on the energy hypersurface. However, because of the significant contribution of the diradical resonance structure



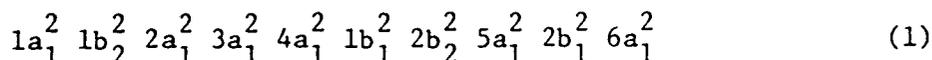
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a two-configuration self-consistent-field (TCSCF) procedure was required for an adequate description of the 1A_1 state; due to the lack of analytic TCSCF wave function gradients at that time, the reliable determination of force constants would have been difficult. The conclusion that singlet cyclopropyne is not a minimum was based solely on individual energies: movement of the CH_2 group in a direction parallel to the triple bond lowered the energy.

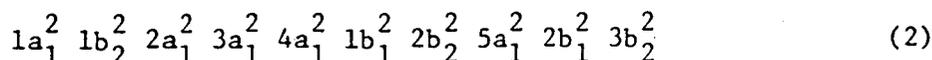
In this paper, we wish to explore the consequences of moving on to a higher level of theory. First, the basis set has been extended over that used in the original work. Our studies of cyclobutyne⁹ have indicated the influence of basis sets on molecular geometry and force constants for such strained ring systems. Secondly, force constants and the ensuing harmonic vibrational frequencies have been calculated for the TCSCF wave function. These frequencies provide a great deal more information about the molecule, including whether 1A_1 cyclopropyne truly represents a transition state, or perhaps something more outlandish.¹¹ That is, singlet cyclobutyne might be a stationary point with more than one imaginary vibrational frequency. These improvements will bring our earlier work¹⁰ up to the same level of theory employed in the cyclobutyne study⁹ and serves as a prelude to a study of the larger cycloalkynes.

Theoretical

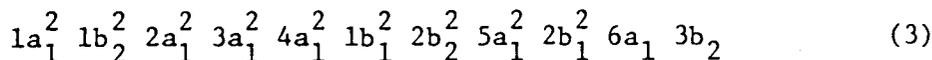
Consistent with the earlier cyclopropyne study,¹⁰ two electronic states were investigated. The wave function of the first, the 1A_1 state, is described primarily by the electron configuration



However, due to the strained nature of the ring, the configuration



which allows diradical character of the type shown in sketch 2, also contributes significantly to the wave function. For this reason a TCSCF procedure is required to properly describe this state in the zeroth order of approximation. In addition, the 3B_2 state, the lowest state qualitatively represented by a single configuration,



was studied.

Both singlet and triplet cyclopropyne were examined using two different basis sets. The first was the standard double-zeta (DZ) basis of Huzinaga¹² and Dunning,¹³ the same basis used in the earlier study.¹⁰ Next, the carbon atom basis was augmented with a set of d-like functions ($\alpha = 0.8$) identical to those employed in the cyclobutyne study.⁹ This latter basis set is labeled (DZ+d).

All molecular geometries were optimized within the confines of C_{2v} symmetry using analytic SCF gradient^{14,15} and analytic TCSCF gradient¹⁶

techniques. Quadratic force constants and the resulting harmonic vibrational frequencies were determined at each of these geometries. For the DZ basis sets, these were calculated using analytic SCF¹⁷ and TCSCF¹⁸ second derivative programs, while finite differences of analytic gradients were required for the larger DZ+d basis sets.

Finally, the effects of electron correlation were included by the method of configuration interaction (CI).^{19,20} For the 1A_1 state all singly and doubly excited configurations relative to both references (1) and (2) were included, with the exception that the three lowest energy (carbon 1s-like) orbitals remain doubly occupied and their corresponding virtual orbitals remain unoccupied in all configurations. This amounted to 5,724 1A_1 configuration with the DZ basis and 19,331 with the DZ+d set. For 3B_2 cyclopropyne all singly and doubly excited configurations relative to (3) were included, again with the exception of freezing the three lowest core and deleting the three highest virtual orbitals. This amount to 3,816 and 12,582 configurations for the DZ and DZ+d basis sets, respectively.

Presentation of Results

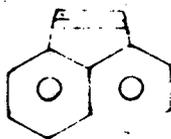
The predicted equilibrium geometries for singlet and triplet cyclopropyne are shown in Figure 1; those for cyclobutyne⁹ are given in Figure 2 for comparison. As shown in Table I, at all levels of theory, including those employing electron correlation, the 1A_1 state is predicted to lie lower in energy, by as much as 12 kcal/mole. The consequence of adding d functions to the basis set is to shorten the carbon-carbon bonds by $\sim 0.02-0.04$ Å, an effect comparable to that seen in cyclobutyne, so this discussion will center on the (more accurate) DZ+d structures.

Focusing first on the singlet structure, the carbon-carbon bond lengths are seen to be 1.522 Å and 1.241 Å for the single and multiple bonds, respectively. Each of this is substantially shorter (0.041 Å and 0.017 Å) than its corresponding bond in cyclobutyne.⁹ The single bond is in fact now shorter than the prototype C-C distance, 1.54 Å. The multiple bond is just 0.038 Å longer than the C≡C bond length²¹ of acetylene (1.203 Å), but almost 0.1 Å shorter than that of ethylene. This allows an unambiguous classification as triple bond, based solely on bond length.

The single C-C bond in triplet cyclopropyne is actually 0.014 Å longer than the corresponding bond in the four-membered ring. However, like the bond in singlet cyclopropyne, it is still shorter than the prototype C-C distance, and is readily classified as a single bond. The multiple bond is 1.276 Å, significantly shorter (0.047 Å) than the multiple bond of triplet cyclobutyne, indeed even shorter than the double bond of cyclopropene,²² 1.296 Å. The bond lies slightly closer in length to that found in ethylene rather than acetylene, and it is best called a strong double (rather than a weak triple) bond.

Consideration of the harmonic vibrational frequencies (Table II) further elucidates the nature of these bonds. First we note that the multiple bond stretching frequencies of both 1A_1 and 3B_2 cyclopropyne are ~7% higher than their cyclobutyne analogues; each bond is in this sense stronger as well as shorter in the smaller of the two rings. Secondly, the triple bond stretching frequency of 2050 cm^{-1} in singlet cyclopropyne compares well with some experimentally observed triple bond frequencies in similar systems. Cyclooctyne,⁵ for example, has an observed C≡C frequency of 2210 cm^{-1} , while 3,3,7,7-tetramethylcycloheptyne²³ has

one of 2180 cm^{-1} ; more recently, Chapman⁶ has tentatively proposed the IR band at 1930 cm^{-1} as the C=C stretching frequency of acenaphthyne:



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Even with an empirical correction of 12% to the predicted SCF frequencies,^{24,25} the resulting value of 1804 cm^{-1} is not at all unreasonable for a triple bond. Finally, it is interesting to note that the double bond stretching frequency of 3B_2 cyclopropyne (1920 cm^{-1}) is very close to the triple bond stretch of 1A_1 cyclobutyne (1911 cm^{-1}). Even after employing the 12% correction, the resulting frequency of 1689 cm^{-1} is still reasonably strong, as compared to a value of 1566 cm^{-1} for cyclobutene,²⁶ or 1656 cm^{-1} in cyclopropene.²⁷

Perhaps the most notable feature of the predicted harmonic vibrational frequencies is the presence of a single imaginary normal mode for the 1A_1 state. The 3B_2 state is therefore a relative minimum on the energy surface, while the singlet is a transition state, consistent with our earlier prediction.¹⁰ The normal mode with the imaginary frequency may be labeled ring opening or C-C asymmetric stretch; motion in this direction presumably leads to the formation of propadienylidene, $\text{CH}_2=\text{C}=\text{C}:$, which is predicted to lie about 40 kcal below cyclopropyne on the energy surface.²⁸

By comparison, both triplet and singlet cyclobutyne are relative minima on their surfaces. In terms of individual bonds, however, the smaller ring would at first appear more "stable". All the bond lengths are significantly shorter for the 1A_1 state of cyclopropyne, and both the C≡C stretch and C-C symmetric stretch vibrational frequencies are higher. The main difference lies in the ring bond angles, which are

dictated by the molecular symmetry and the short carbon-carbon bond lengths. The shorter bonds of the smaller ring force a bond angle of 66° , while those of the larger ring require an angle of only 95° , not quite so far from the angle of 180° normally associated with triple bonds. The inherent instability of singlet cyclopropyne lies in its unattainably small bond angle. Indeed, the imaginary frequency indicates that the molecular energy is at a maximum, decreasing with a change in this bond angle.

Concluding Remarks

Our earlier work on cyclopropyne has been significantly extended in this paper. In particular, the calculation of force constants has shown unambiguously that the ground (1A_1) state of cyclopropyne is a transition state rather than a relative minimum. It has also been shown that the triple bond in this system is fairly short and strong, more so than the comparable bond in singlet cyclobutyne. Despite the apparent strength of the bond, the acute C-C \equiv C bond angle (66°) is too small to allow the incorporation of this bond into a stable ring. While the 3B_2 state does represent a relative minimum and contains a fairly strong bond, this species is best represented as a diradical, and contains only a double bond. This supports our earlier conclusion^{9,10} that cyclopropyne does not exist (or, more specifically, that it is not possible to incorporate a triple bond into an unsubstituted three-membered ring), and cyclobutyne is the smallest stable cycloalkyne.

Acknowledgments

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Table I. Total energies in hartrees and relative energies in kcal/mole for the lowest singlet and triplet electronic states of cyclopropyne.

<u>Level of Theory</u>	<u>Number of Configurations</u>	<u>E(hartrees)</u>	<u>Relative Energy(kcal)</u>
DZ TCSCF (1A_1)	2	-114.46490	0.0
DZ SCF (2B_2)	1	-114.45179	8.2
DZ CI (1A_1)	5724	-114.70296	0.0
DZ CI (3B_2)	3816	-114.69290	6.3
DZ+d TCSCF (1A_1)	2	-114.53855	0.0
DZ+d SCF (3B_2)	1	-114.51936	12.0
DZ+d CI (1A_1)	19331	-114.86497	0.0
DZ+d CI (3B_2)	12582	-114.84805	10.6

Table II. Predicted vibrational frequencies (in cm^{-1}) for the lowest singlet and triplet electronic states of cyclopropyne.

Description	1A_1		3B_2	
	DZ+d	DZ	DZ+d	DZ
asymmetric H str. B_1	3366	3395	3356	3396
symmetric H str. A_1	3287	3304	3273	3298
$C\equiv C$ (or $C=C$) str. A_1	2049	1972	1920	1840
CH_2 scissor A_1	168 ^o	167 ^o	1660	1652
CH_2 wag B_2	1246	1250	1151	1173
ring expansion ^a A_1	1181	1122	1111	1039
CH_2 rock B_1	1167	1146	1180	1172
ring torsion A_2	435	604	903	901
ring opening ^b B_2	620i	58i	79	702

^aMay also be called symmetric C-C stretch.

^bMay also be called asymmetric C-C stretch.

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Figure Captions

Figure 1. Theoretical structures for the lowest singlet and triplet electronic states of cyclopropyne. Singlet structures were obtained at the two-configuration self-consistent-field (TCSCF) level of theory. Triplet structures were determined via singlet configuration restricted Hartree-Fock (RHF) procedures. The abbreviations DZ and DZ+d stand for "double zeta" and "double zeta plus d function" basis sets. All bond distances are given in Å.

Figure 2. Predictions for cyclobutyne completely analogous to those for cyclopropyne in Figure 1.

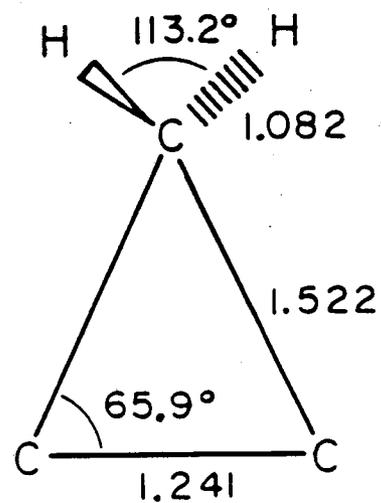
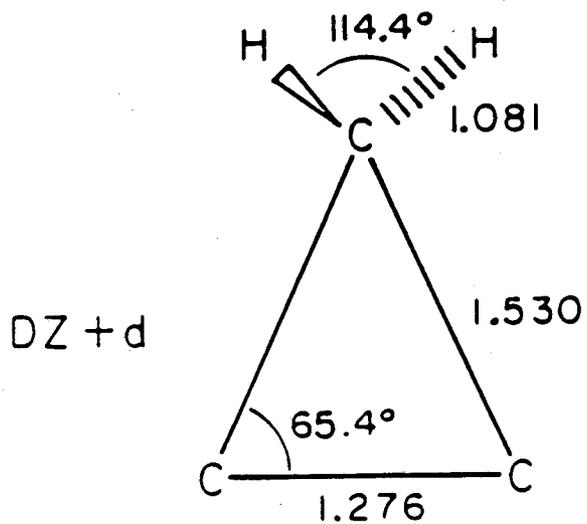
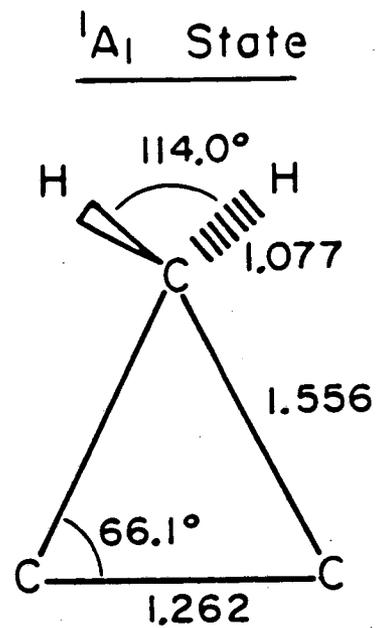
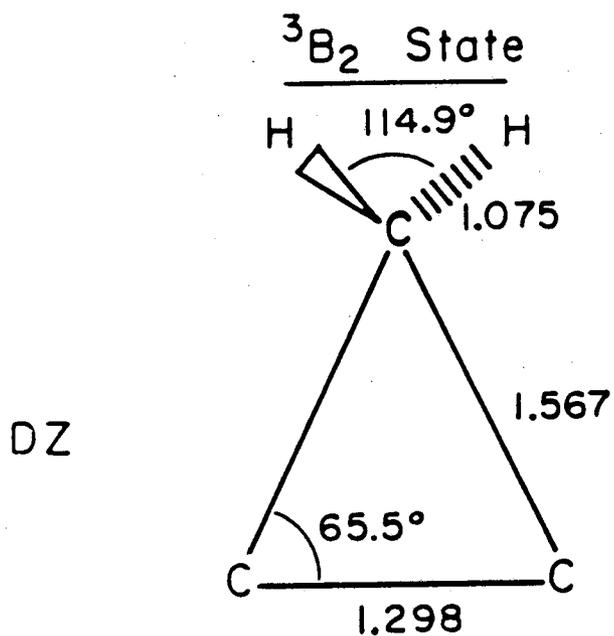
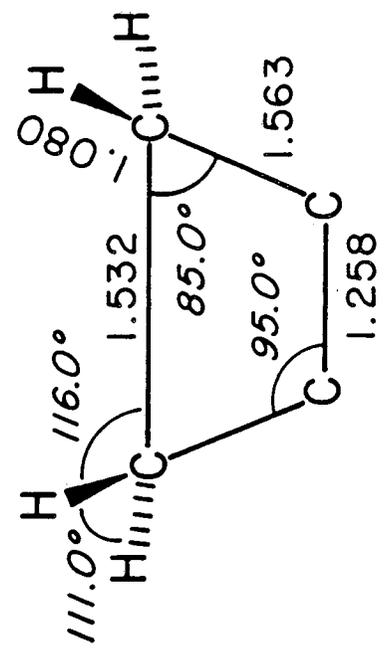
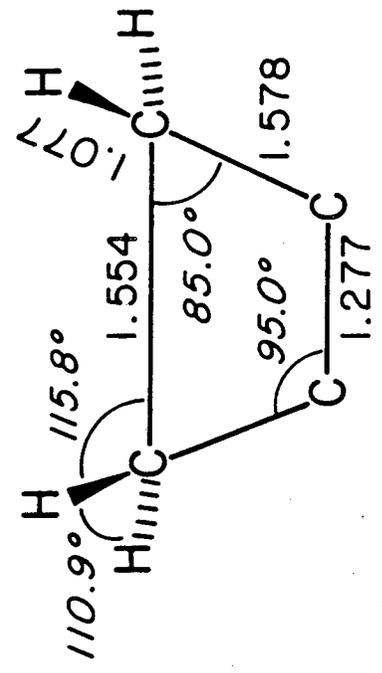
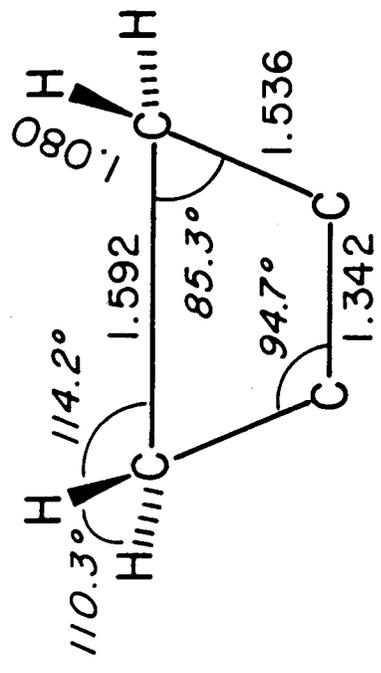


Figure 1

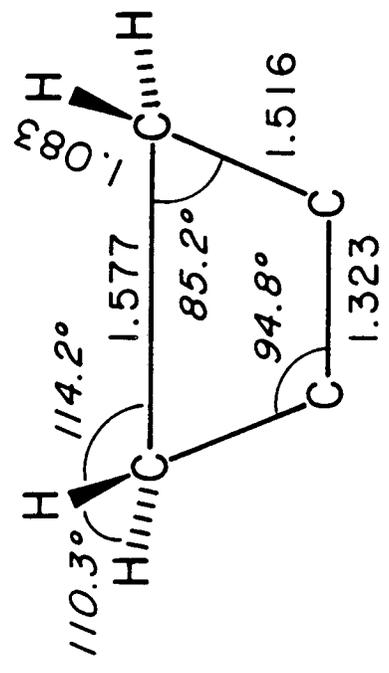
¹A₁ State



³B₂ State



DZ



DZ + d

Figure 2

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