

# Theoretical Study of Cyclopropene and its $C_3H_4$ Isomers

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*Ab initio* SCF MO and CI calculations are reported for the three  $C_3H_4$  isomers cyclopropene, methylacetylene and allene. The closed shell nature of each of these molecules allows for a good theoretical comparison of their stabilities and ionization potentials by the SCF method. It is pointed out that cyclopropene differs from most 22 electron systems with a triatomic skeleton in that it possesses a non-linear equilibrium structure; this fact is related to its unusual ground state electronic configuration, which corresponds to a highly excited state in simple triatomics such as  $CO_2$  and  $N_3^-$ . The electronic spectrum and the methylene rotational barrier of cyclopropene are also investigated.

Es wird über Ergebnisse von *ab initio* SCF-MO- und CI-Berechnungen der drei  $C_3H_4$ -Isomere Cyclopropen, Methylacetylen und Allen berichtet. Da alle drei Moleküle "closed shell" Charakter besitzen, ist ein guter theoretischer Vergleich ihrer relativen Stabilität sowie ihrer Ionisierungspotentiale mit Hilfe von SCF-Rechnungen möglich. Weiterhin wird darauf hingewiesen, daß sich Cyclopropen von den meisten dreiatomigen Systemen (Wasserstoffe werden nicht gezählt) mit 22 Elektronen dadurch unterscheidet, daß seine schweren Atome nicht in einer linearen Kette angeordnet sind. Diese Tatsache steht im Zusammenhang mit seiner ungewöhnlichen Elektronenkonfiguration im Grundzustand, welche bei einfachen dreiatomigen Molekülen wie  $CO_2$  und  $N_3^-$  einem hoch angeregten Zustand entspricht. Das Elektronenspektrum sowie die Methylene-Rotationsbarriere von Cyclopropen werden ebenfalls untersucht.

Calculs *ab initio* SCF MO et CI pour les trois isomères  $C_3H_4$ ; cyclopropène, méthylacétylène et allène. Ces molécules étant à couches complètes, la méthode SCF permet une bonne comparaison de leurs stabilités et de leurs potentiels d'ionisation. On fait remarquer que le cyclopropène diffère de la plupart des systèmes à 22 électrons à squelette triatomique en ce qu'il présente une structure d'équilibre non linéaire; ce fait est relié à la configuration électronique particulière de l'état fondamental qui correspondrait à un état hautement excité dans des molécules triatomiques simples comme  $CO_2$  et  $N_3^-$ . Le spectre électronique et la barrière rotationnelle du méthylène dans le cyclopropène ont aussi été étudiés.

## 1. Introduction

The three molecules cyclopropene, allene and methylacetylene, with their common  $C_3H_4$  formula, represent the simplest isomeric family among commonly occurring hydrocarbons and therefore would appear to be a fruitful object of investigation for a theoretical study of the *general* phenomenon of molecular isomerism. The fact that each of the three systems is characterized by a closed shell electronic configuration indicates that all of them should be treated on an approximately equal footing by the *ab initio* closed shell SCF method; calculations at this level can thus be expected to lead to a realistic comparison of the properties of these molecules necessary for a meaningful study of isomerism.

Perhaps the first aspect of the behaviour of the  $C_3H_4$  systems which should be analyzed is their molecular geometry since ultimately this is the basis on which they can be distinguished from one another. On this score cyclopropene seems to be the most interesting since it is the only one of the three isomers which does not possess the linear skeletal (CCC) equilibrium geometry characteristic of every known simple triatomic which is isoelectronic with them (for example,  $CO_2$  and azide ion  $N_3^-$ ). Thus the study of cyclopropene should lead to some further insight into the relationship originally discussed by Mulliken [1] and Walsh [2] between the structure of a molecule and the number of electrons it possesses. For this reason and also because in general less is known experimentally about cyclopropene, the present study of the  $C_3H_4$  isomers will place special emphasis on this molecule.

## 2. Geometry of the $C_3H_4$ Isomers

### *Arrangement of the Hydrogens*

Study of the geometry of hydrocarbons is, of course, complicated by the presence of hydrogen atoms, and since in the present case their position relative to the carbon nuclei uniquely determines the identity of the three  $C_3H_4$  isomers, this aspect of the geometrical behaviour of these systems is quite important. Furthermore, even though such identification can be accomplished strictly on

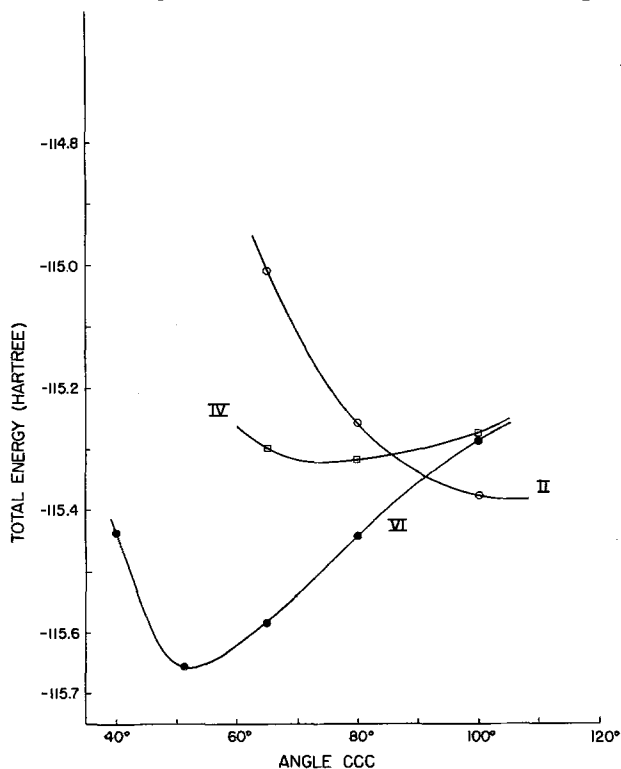


Fig. 1a. Angular potential curves for three different  ${}^1A_1$  SCF states of cyclopropene in its antiplanar  $CH_2$  conformation (Electronic configuration of each of these states is given in Table 2)

the basis of how many hydrogens are attached to each carbon, the relative position the lighter atoms assume with respect to one another also plays a critical role in determining the overall stability of these compounds. Allene, for example, is quite sensitive to the conformation of its terminal methylene groups, strongly preferring the antiplanar arrangement; the resulting potential barrier to internal rotation of the allene hydrogens has been studied in detail previously [3] by *ab initio* techniques.

In methylacetylene with its one acetylenic and three methyl-hydrogens no such barrier phenomenon exists and thus the study of their arrangement in this molecule seems less important, but in cyclopropene the situation becomes critical again because of the possibility of rotating its central CH<sub>2</sub> group relative to the CCC molecular plane. In order to investigate this particular rotational barrier two series of *ab initio* SCF calculations have been carried out, one for which the methylene group is in the CCC plane and one for which it is rotated 90° out of this plane. For each conformation the CCC angle opposite the double bond of cyclopropene is varied systematically from 49 to 100 deg to study the relationship between rotation of the methylene group and bending of the C<sub>3</sub> skeleton of the molecule.

The basis set employed for these calculations consists of gaussian expansions of near Hartree-Fock AO's (lobe functions) and is the same as that used earlier

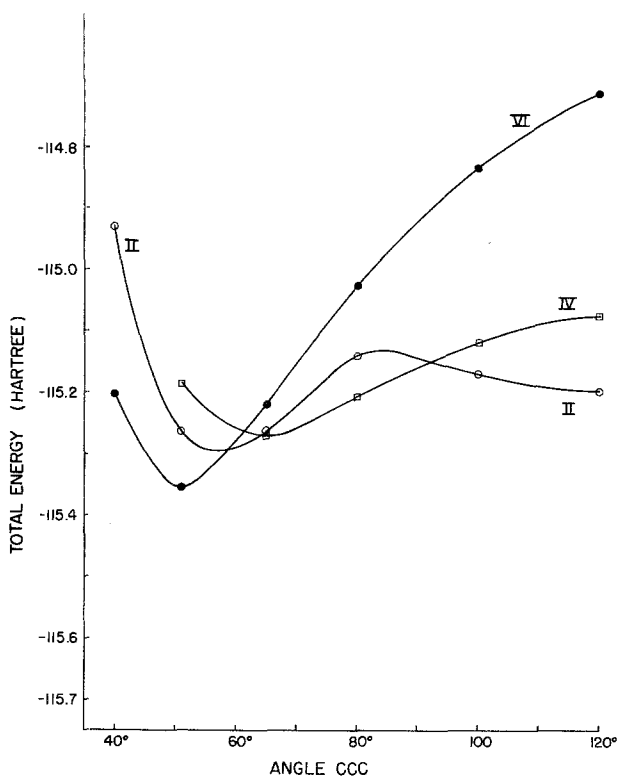


Fig. 1 b. Angular potential curves for three different <sup>1</sup>A<sub>1</sub> SCF states of cyclopropene in its planar CH<sub>2</sub> conformation

in the treatment of allene [3]. All geometrical parameters except those explicitly varied in these calculations are those found experimentally by Kasai *et al.* [4] (C–C = 1.515 Å, vinyl C–H = 1.070 Å, methylene C–H = 1.087 Å,  $\angle$  HCH =  $114^\circ 42'$ ,  $\angle$  HC–C =  $145^\circ 29'$ ); for each geometry considered the point group of the molecule is  $C_{2v}$ . SCF solutions for ground and several closed shell excited states are obtained in each case and the resulting angular potential curves are given in Fig. 1 a and b respectively for the antiplanar and planar conformations.

Comparison of these two figures shows that by far the lowest energy occurs for the antiplanar arrangement of hydrogens, in agreement with experiment and also with the theoretical inference from VB theory that there should be tetrahedral hybridization at the central carbon atom. The barrier to rotation into the planar form of cyclopropene is exceptionally large (189 kcal/mole), more than twice as great, for example, as is calculated for the rotational barrier of allene at the same level of treatment (82 kcal/mole, SCF value). The magnitude of the barrier gives a quantitative indication of the resistance of the system toward placing all four single bonds about the central carbon in one plane.

#### *Skeletal Bond Angles and Electronic Configurations*

In both methylene conformations the calculations find the expected small equilibrium CCC angle for cyclopropene; this structure is quite different from the linear arrangement exhibited by the other  $C_3H_4$  isomers and by all known iso-electronic triatomic molecules. Since the usual explanation for the fact that iso-electronic molecules generally have the same shape is based on the circumstance of their possessing the same ground state electronic configuration (which in turn determines the gross geometry of the systems), the clear indication is that cyclopropene prefers a different electronic configuration than either of its isomers. Ordinarily this point can be investigated quite effectively even without the aid of SCF calculations by carrying out a group theoretical analysis of the VB structure of the molecule in question; Tables 1a, b present the results of such an analysis for cyclopropene in its antiplanar and planar conformations respectively.

Table 1. Occupied molecular orbitals derived from group theoretical analysis of the VB description of cyclopropene with (a) antiplanar and (b) planar  $CH_2$  group

VB description	(a) occupied MO's	(b) occupied MO's
$3 \times 1s$	$a_1, a_1, b_2$	$a_1, a_1, b_2$
$3 \times$ CC single bonds	$a_1, a_1, b_2$	$a_1, a_1, b_2$
$4 \times$ CH bonds	$a_1, b_2, a_1, b_1$	$a_1, b_2, a_1, b_2$
$\pi$ bond	$b_1$	$b_1$
Total occupied:	$6 \times a_1, 3 \times b_2, 2 \times b_1$	$6 \times a_1, 4 \times b_2, 1 \times b_1$

In the preferred antiplanar arrangement the electronic configuration indicated by the VB analysis is the same as that found to be optimum in the SCF calculations. It is *not* the same, however, as that universally preferred by the other 22 electron molecules with triatomic skeletons (see Table 2); in cyclopropene the  $6a_1$  and  $2b_1$

MO's are doubly occupied in the place of the  $1\pi_g$  components ( $4b_2$  and  $1a_2$ ), invariably filled in the other isoelectronic systems<sup>1</sup>.

The SCF potential curves for each of the states described in Table 2 have been calculated previously for the 22 electron systems azide ion [5] N<sub>3</sub><sup>-</sup> and symmetric NON [6]. Examination of these data shows clearly that simple triatomics also prefer quite small internuclear angles when excited to the electronic configuration characterizing the ground state of cyclopropene (VI in Table 2). Similar comparisons can be made between the potential curves of the *excited* configurations in Fig. 1 a and the corresponding results for N<sub>3</sub><sup>-</sup> and NON; the only qualitative distinction to be drawn between these curves is that the potential minima for the cyclopropene states occur uniformly at angles approximately 20° smaller than for the corresponding states of the simple triatomics<sup>2</sup>. These data thus supply further evidence for the general conclusion that the electronic configuration a molecule assumes determines its overall shape.

The group theoretical analysis of the VB description of planar cyclopropene (Table 1 b) predicts a different electronic configuration (II in Table 2) than either of those discussed above; the orientation of the methylene group causes an exchange of a  $b_2$  MO for one of  $b_1$  symmetry in the occupied set relative to that of antiplanar cyclopropene. In this case, however, the SCF calculations do not lead to the ground state indicated by the VB structure but rather to the same one preferred in the antiplanar form (VI in Table 2), for which there seems to be no clear VB analog for the planar conformation of hydrogens. The fact that configuration II is not optimum for this arrangement, is thus another indication of the difficulties encountered whenever four carbon bonds are forced to lie in the same plane. The proximity of the three closed shell potential curves (especially II and VI) calculated for the planar molecule (Fig. 1 b) is in sharp contrast to what is observed in the antiplanar geometry (Fig. 1 a) and indicates that the true ground state in this case may be a triplet with one electron in both the  $4b_2$  and  $2b_1$  MO's.

Table 2. *Electronic configuration (C<sub>2v</sub> and D<sub>∞h</sub> notation) for different closed shell states of a 22 electron triatomic molecule*

C <sub>2v</sub> -symmetry		D <sub>∞h</sub> -symmetry
Electronic configuration		Electronic configuration
I [core] $1a_2^2 4b_2^2$ <sup>a</sup>	{ $6a_1^2 2b_1^2$ } <sup>c</sup>	[core*] $1\pi_g^4$
II [core] $4b_2^2 6a_1^2$	{ $1a_2^2 2b_1^2$ }	[core*] $1\pi_g^2 2\pi_u^2$
III [core] $1a_2^2 2b_1^2$	{ $4b_2^2 6a_1^2$ }	[core*] $1\pi_g^2 2\pi_u^2$
IV [core] $1a_2^2 6a_1^2$	{ $4b_2^2 2b_1^2$ }	[core*] $1\pi_g^2 2\pi_u^2$
V [core] $4b_2^2 2b_1^2$	{ $1a_2^2 6a_1^2$ }	[core*] $1\pi_g^2 2\pi_u^2$
VI [core] $6a_1^2 2b_1^2$ <sup>b</sup>	{ $1a_2^2 4b_2^2$ }	[core*] $2\pi_u^4$
[core] = $1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 4a_1^2 1b_1^2 5a_1^2 3b_2^2$		
[core*] = $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 3\sigma_g^2 2\sigma_u^2 1\pi_u^4 4\sigma_g^2 3\sigma_u^2$		

<sup>a</sup> Usual ground state of 22 electron triatomics (linear equilibrium geometry).

<sup>b</sup> Cyclopropene ground state.

<sup>c</sup> Shorthand notation used previously in Refs. [5, 6].

<sup>1</sup> In allene and methylacetylene the C<sub>2v</sub> notation is only approximate, of course, in such cases identification of the MO's is based upon their nodal properties.

<sup>2</sup> The latter difference is most likely caused by the greater diffusion of charge out of the triatomic ring for the hydrocarbon (to the hydrogen atoms).

The *shapes* of the potential curves in Fig. 1b are also interesting. Comparison with those of the antiplanar molecule finds the usual similarity between potential curves of corresponding states for configurations IV and VI but not for II (Table 2), the VB ground state curve; the latter shows a double minimum for planar cyclopropene not duplicated in the corresponding curves for simple triatomics. This exceptional behaviour can be understood by again referring to Table 1b; in the planar molecule the  $4b_2$  is largely CH bonding, a fact which distinguishes it markedly from the corresponding MO in antiplanar cyclopropene (obviously also in simple triatomics). As a result this  $4b_2$  orbital exhibits a distinctive angular behaviour, being much less resistant to a decrease in internuclear angle than any of its counterparts in other systems. Consequently planar states which occupy the  $4b_2$  (II for example) are characterized by potential curves which are radically different from those ordinarily observed for these electronic configurations. The double minimum shown by II in Fig. 1b thus emphasizes that the relationship between electronic configuration and molecular shape holds in more complicated systems only as long as the angular behaviour of the individual MO's is not altered relative to that found for the parent family of molecules.

### 3. $C_3H_4$ Isomers at Equilibrium

#### *Stability*

Despite the differences in their electronic configurations all three  $C_3H_4$  isomers are closed shell systems at equilibrium and therefore the SCF method should be capable of treating all of them at approximately the same level. The calculations already discussed for allene [3] and cyclopropene were thus supplemented by one employing an analogous basis set for methylacetylene in its experimental geometry [7] in order to effect a theoretical comparison of these systems; on the basis of previous calculations [8] for  $C_2H_2$ , however, the scale factor for the acetylenic hydrogen of this isomer was increased to  $2.40^{\frac{1}{2}}$  relative to the value of  $2.0^{\frac{1}{2}}$  assumed elsewhere for H AO's in the treatment of these molecules. Total, kinetic and orbital energies for this calculation and the analogous data for cyclopropene (fixed group basis) are given in Table 3a while those for allene are contained in an earlier reference [3].

In addition a second series of calculations was carried out for the three molecules, again with each of them in their respective experimental nuclear geometries, using a more flexible basis in which the carbon  $2s$  and  $2p$  AO's of the original set are each decomposed into two parts; this procedure increases the number of free coefficients in the SCF calculations from 22 to 34 without changing the total number of individual gaussians in the basis set (50 of  $s$  and 45 of  $p$  type). Total, kinetic and orbital energies for these three calculations are given in Table 3b; as a result of this improvement in the treatment substantially better agreement with the virial theorem is obtained and an average energy lowering of about 3 eV is effected.

Relative stabilities of the three isomers determined from the above calculations are compared in Table 4 with the corresponding experimental data and also with the semiempirical results of Dewar and Klopman [9] and Baird and Dewar [10].

Table 3a. Total energy  $E_T$ , kinetic energy  $E_k$  and orbital energies for the ground states of methylacetylene and cyclopropene (in their experimental nuclear geometries) obtained from the fixed group SCF treatment. Throughout this paper, unless otherwise specified, all energy values are given in hartree units

Methylacetylene		Cyclopropene	
$1a_1$	- 11.3964	$1a_1$	- 11.3748
$2a_1$	- 11.3560	$1b_2$	- 11.3729
$3a_1$	- 11.3292	$2a_1$	- 11.3320
$4a_1$	- 1.0845	$3a_1$	- 1.2056
$5a_1$	- 0.9900	$4a_1$	- 0.8561
$6a_1$	- 0.7493	$2b_2$	- 0.7947
$7a_1$	- 0.6511	$5a_1$	- 0.7179
$1e(1\pi_u)$	- 0.6151	$1b_1$	- 0.6347
$2e(1\pi_g)$	- 0.4317	$6a_1$	- 0.5327
		$3b_2$	- 0.4663
		$2b_1$	- 0.4012
$3e(2\pi_u)$	0.2417	$1a_2$	0.1712
		$4b_2$	0.3672
$E_T$	- 115.7122		- 115.6561
$-E_k/E_T$	0.9910		0.9934

Table 3b. Total energy  $E_T$ , kinetic energy  $E_k$  and orbital energies for the ground states of methylacetylene, allene and cyclopropene (in their experimental nuclear geometries) obtained from the extended basis set SCF treatment

Methylacetylene		Allene		Cyclopropene	
$1a_1$	- 11.2497	$1a_1$	- 11.2790	$1a_1$	- 11.2544
$2a_1$	- 11.2475	$1b_1$	- 11.2407	$1b_2$	- 11.2523
$3a_1$	- 11.2266	$2a_1$	- 11.2406	$2a_1$	- 11.2401
$4a_1$	- 1.0586	$3a_1$	- 1.0786	$3a_1$	- 1.1690
$5a_1$	- 0.9588	$2b_1$	- 0.9631	$4a_1$	- 0.8280
$6a_1$	- 0.7148	$4a_1$	- 0.7112	$2b_2$	- 0.7641
$7a_1$	- 0.6155	$3b_1$	- 0.6238	$5a_1$	- 0.6827
$1e(1\pi_u)$	- 0.5864	$1e(1\pi_u)$	- 0.6135	$1b_1$	- 0.6022
$2e(1\pi_g)$	- 0.3810	$2e(1\pi_g)$	- 0.3736	$6a_1$	- 0.4912
				$3b_2$	- 0.4190
				$2b_1$	- 0.3523
$3e(2\pi_u)$	0.2126	$3e(2\pi_u)$	0.1676	$1a_2$	0.1502
				$4b_2$	0.2452
$E_T$	- 115.8177		- 115.8204		- 115.7635
$-E_k/E_T$	0.99995		1.0001		1.0009

The initial (fixed group) series of SCF calculations finds the same order of stabilities as that observed experimentally but it overestimates the respective energy differences by from 7 to 13 kcal/mole. The extended treatment leads to a greater lowering in total energy for allene than for the other isomers and actually finds it to be slightly more stable than methylacetylene; the total error relative to experiment is only 3.3 kcal in this case, however, so that the better calculations do lead to a more accurate picture of the stabilities of these molecules. Each of these discrepancies, in turn, is at least an order of magnitude smaller than calculated

for the heats of atomization (the error in the methylacetylene heat of atomization, for example, is 190 kcal), thereby emphasizing that the SCF method can be usefully applied to energy comparisons as long as the systems being considered are all closed shell species<sup>3</sup>.

Table 4. Total energy (kcal/mole) of the ground states of allene and cyclopropene, referenced to the methylacetylene ground state energy, obtained by different methods. (The experimental heat of atomization for methylacetylene is 676.8 kcal/mole)

	Experimental <sup>a</sup>	Fixed group treatment	Extended treatment	B, D, K <sup>a</sup>
Methylacetylene	0.0	0.0	0.0	0.0
Allene	1.6	9.0	- 1.7	7.2
Cyclopropene	22.3	35.2	34.0	44.8

<sup>a</sup> Ref. [9, 10] and references therein for experimental data.

### Ionization Potentials

The closed shell nature of the C<sub>3</sub>H<sub>4</sub> isomers should also allow reliable comparison of their ionization potentials by the SCF method. Table 5 presents calculated values (Koopmans' Theorem) for the minimum ionization potentials of these systems (experimental geometries) along with the best experimental data available [11]. The order of I.P.'s is the same in the two sets of SCF calculations and agrees with that found experimentally; for these systems the relative order of ionization potentials rather closely parallels that of their binding energies. The fixed group calculations overestimate all the minimum I.P.'s by from 1.0 to 1.5 eV while the extended treatment obtains almost quantitative agreement with experiment, especially for allene and methylacetylene<sup>4</sup>.

Table 5. Minimum ionization potentials (eV) of several compounds obtained by different treatments

	Experimental <sup>a</sup>	Fixed group treatment	Extended treatment
Methylacetylene	10.36	11.75	10.37
Allene	10.19	11.46	10.17
Cyclopropene	9.95	10.92	9.59
Acetylene	11.40	12.96	11.24

<sup>a</sup> Ref. [11].

<sup>3</sup> One might go somewhat further and argue that the comparison will be even more reliable for systems with the same electronic configuration; such as analysis is substantiated by the data of Table 4 and seems intuitively reasonable in this case since one expects cyclopropene to have more correlation energy than either of its isomers because it possesses a much more compact structure.

<sup>4</sup> Of the experimental data in Table 5 the least reliable is the cyclopropene I.P.; only one determination is reported and this by the electron impact method, which is believed to overestimate the corresponding quantity in cyclopropane by from 0.2 to 0.5 eV.



The ionization potential of methylacetylene is also interesting in comparison with that of acetylene. Experimentally the methyl substituent lowers the minimum I.P. by 1.04 eV; the present calculations find lowerings of 1.21 and 0.87 eV respectively for the fixed group and extended treatments, again in good agreement with experiment. Qualitatively this result has been attributed to the electron donating properties of the methyl group relative to the hydrogen atom, or alternatively to the hyperconjugative effects of the methyl hydrogens. In the present context of MO calculations, however, the most direct explanation is that the highest occupied MO in methylacetylene is antibonding between the central and methyl carbons (a situation which arises because this is the second most stable *e* MO, the first corresponding in the main to the CH bonds of the methyl group); thus it is less stable than the analogous acetylene MO, which is, of course, non-bonding with both hydrogens.

#### 4. Spectrum and Angular Potential Curves of Cyclopropene

##### *Ground State and CI*

A polynomial fit for the SCF ground state potential curve of cyclopropene (Fig. 1a) leads to a calculated equilibrium angle of 53.4°, compared to the experimental value [4] of 50.8°; thus the CC double bond length is overestimated by 0.06 Å, a result which is consistent with previous experience with gaussian fixed group basis sets (the overestimation is generally between 0.05 and 0.10 Å). Such calculations have been most accurate for predicting equilibrium angles for systems whose terminal atoms are separated by distances considerably greater than normal bond lengths.

In addition to the SCF calculations a CI treatment was carried out for cyclopropene in which the SCF MO's at each angle are used to construct the necessary determinantal wavefunctions. The main benefit accruing from this additional work is the comparison it allows among the potential curves of the ground and excited states of the molecule, thereby initiating a study of its electronic spectrum, a subject which has received only scant attention experimentally.

In the CI calculations for the antiplanar hydrogen conformation a fixed core of seven MO's is retained at all angles and excitations from the  $1b_1$ ,  $6a_1$ ,  $2b_1$  and  $3b_2$  to the  $1a_2$ ,  $4b_2$ ,  $7a_1$  and  $5b_2$  MO's are considered; details concerning the specific CI techniques employed can be found elsewhere [12]. All configurations corresponding to single and double excitations among these valence orbitals are taken into account in addition to a sufficient number of triple excitation species to achieve the limit to which such a treatment can be carried, both for ground and low lying excited states. Effectively this prescription leads to secular equations for each symmetry type which are approximately  $100 \times 100$  (smaller order for quintuplet secular equation). Potential curves for ground and low lying excited states resulting from this calculation along with that of the  $^1A_1$  SCF ground state are given in Fig. 2.

As a result of the CI the ground state equilibrium angle of cyclopropene increases still further beyond the experimental value to 54.9°. This result is to

be expected from the fact that CI substitutes the antibonding character (with respect to the CC double bond) of the  $1a_2$  and  $4b_2$  MO's for the bonding tendencies of the  $6a_1$  and  $2b_1$  (Fig. 3). Examination of the angular force constants determined from the two calculations (Table 6) is consistent with this finding, showing the CI value to be significantly lower than that of the SCF treatment; conversion of these

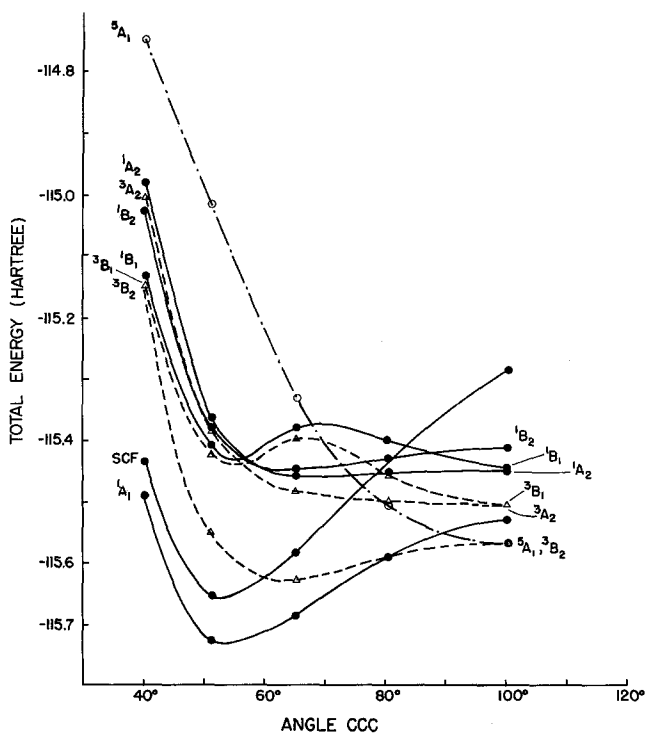


Fig. 2. Angular potential curves for the low lying states of cyclopropene (antiplanar  $\text{CH}_2$  group) obtained from the fixed group CI treatment

results to stretching force constants yields values of 13.2 and 10.9  $\text{mdyn}/\text{\AA}$  respectively, compared to a measured value of 9.138  $\text{mdyn}/\text{\AA}$  [13, 14]. Experimentally cyclopropene is found to have a slightly smaller C=C stretching frequency than is observed for a normal double bond (9.5–9.9  $\text{mdyn}/\text{\AA}$ ) in a straight chain molecule.

#### Excited States

The CI calculations find the lowest excited state of cyclopropene to be the  $^3B_2$  which results primarily from the  $2b_1 \rightarrow 1a_2$  excitation, a typical  $\pi \rightarrow \pi^*$  species, localized to a great extent in the CC double bond. The equilibrium angle of this state is significantly larger than that of the ground state because of the effect of the electron transfer from the  $1a_2$  to the  $2b_1$  MO (see Fig. 3); it should possess an equilibrium geometry roughly equal to that of cyclopropane, with all three CC bonds of approximately the same length.

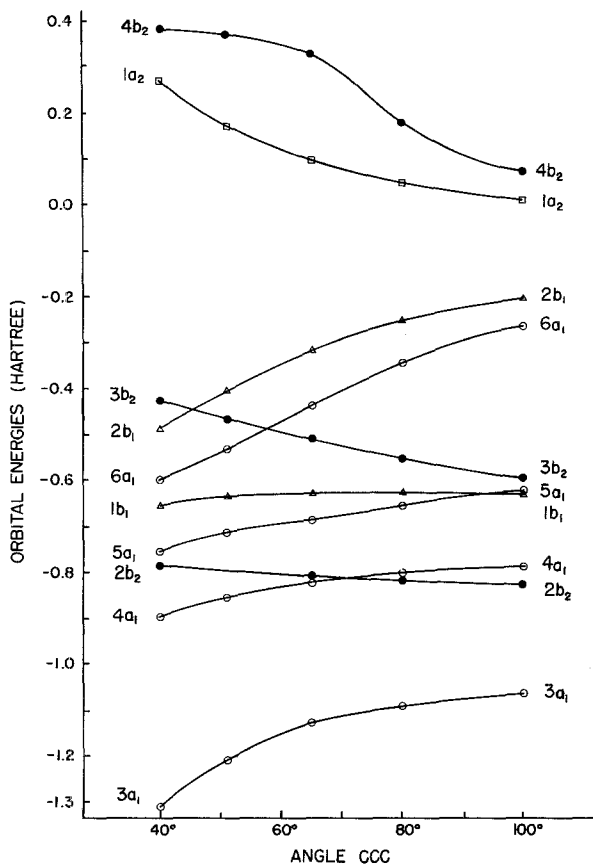


Fig. 3. SCF orbital energies for the ground state of cyclopropene (antiplanar CH<sub>2</sub> group) as a function of the CCC angle

Table 6. Equilibrium angles (deg.) and bending force constants ( $10^{-11}$  erg/rad<sup>2</sup>) for several states of cyclopropene (CI values unless otherwise indicated)

State	$\theta_e$	$k_\theta$
Planar CH <sub>2</sub> -group:		
<sup>1</sup> A <sub>1</sub> (SCF, Config. VI)	50.3	29.6
Antiplanar CH <sub>2</sub> -group:		
<sup>1</sup> A <sub>1</sub> (SCF, Config. VI)	53.4	24.1
<sup>1</sup> A <sub>1</sub>	54.9	19.7
<sup>3</sup> B <sub>2</sub>	62.2	10.8
<sup>1</sup> B <sub>2</sub>	63.0	7.7
<sup>1</sup> A <sub>2</sub>	70.0	4.9
<sup>1</sup> B <sub>1</sub>	55.4	22.0

The next lowest triplet corresponds to a  $2b_1 \rightarrow 4b_2$  excitation (<sup>3</sup>A<sub>2</sub>) and possesses an even larger equilibrium angle than does the <sup>3</sup>B<sub>2</sub> state, due to the fact that the 4b<sub>2</sub> MO is much more antibonding than the 1a<sub>2</sub> in antiplanar cyclopropene (at least above 60°; see Fig. 3). The <sup>5</sup>A<sub>1</sub> state also appears to be important at large angles, with an energy minimum occurring above 100°; at such angles this

quintuplet apparently becomes the ground state of cyclopropene. In general the great majority of low lying excited species of the molecule are calculated to have larger equilibrium angles than the ground state ( ${}^1A_1$ ), indicating once again that the electronic configuration of the latter allows approximately the maximum differential of bonding versus antibonding character between terminal atoms.

Vertical excitation energies calculated from the CI results (at the cyclopropene *experimental* equilibrium geometry) are given in Table 7; also contained in this table are analogous data obtained from a CI treatment based on the MO's of the extended SCF calculation of cyclopropene. The latter values can be expected to be somewhat more accurate since the larger basis set should lead to a more reliable representation of the virtual MO's populated in the excited configurations. Perhaps the most surprising observation from this table is the result that the lowest energy fully allowed singlet-singlet transition involves the  ${}^1B_1$  state (corresponding to a  $3b_2 \rightarrow 1a_2$  excitation), not the  ${}^1B_2$  species associated with the usual  $\pi \rightarrow \pi^*$  transition. The potential curves of Fig. 2 indicate, however, that the electronic spectrum of cyclopropene is more complicated than would appear from Table 7 and suggest that it probably cannot be explained satisfactorily unless the possibility of non-vertical transition is taken into account.

Table 7. Vertical excitation energies ( $eV$ ) from the ground state of cyclopropene (antiplanar  $CH_2$  group, *experimental geometry*) obtained from two different CI treatments

	Extended treatment	Fixed group treatment
${}^1A_1$	0.00	0.00
${}^3B_2$	4.57	4.76
${}^3B_1$	7.51	8.19
${}^1B_1$	7.87	8.56
${}^1B_2$	8.24	9.25( ${}^3A_2$ )
${}^3A_2$	8.81	9.41( ${}^1B_2$ )
${}^1A_2$	9.17	9.82
$2{}^3A_2$	9.50	11.02( ${}^3A_1$ )
$2{}^3B_1$	9.92	11.39( $2{}^3A_2$ )
$2{}^1A_2$	9.94	11.80
${}^3A_1$	10.17	13.05( $2{}^3B_2$ )

Table 8. Vertical excitation energies ( $eV$ ) from the  ${}^3A_2$  planar cyclopropene ground state calculated via a fixed group CI treatment

${}^3A_2$	0.00	$2{}^1A_1$	3.68
${}^1A_2$	0.18	${}^1B_1$	4.16
${}^1A_1$	0.34	${}^5B_1$	6.27
${}^3B_2$	1.01	$2{}^3B_1$	6.67
${}^1B_2$	2.71	$3{}^1A_1$	7.32
${}^3B_1$	2.95		

Finally, a CI calculation was carried out for planar cyclopropene ( $\sphericalangle$  CCC =  $50.8^\circ$ ) using the fixed group MO basis in order to more closely study the relationship between ground and excited states in this conformation. The resulting vertical excitation energies are given in Table 8. As expected from Fig. 1b the ground state in this geometry is calculated to be a triplet ( ${}^3A_2$ ) whose major

contributing electronic configuration singly occupies both the  $2b_1$  and the  $4b_2$  MO's. The 0-0 energy difference between this state of planar cyclopropene and the ground state of the antiplanar conformation (182.3 kcal/mole) is still quite large, only slightly less than the closed shell SCF value for this barrier given in Section 2.

## 5. Conclusion

The reason that cyclopropene has a non-linear skeletal geometry in contrast to other 22 electron molecules, particularly its isomers methylacetylene and allene, is that its ground state electronic configuration is markedly different from that of the others; the potential curves exhibited by the other systems when excited to this electronic configuration are in fact quite similar to that of the cyclopropene ground state, with minima at small internuclear angles. From a broader point of view this result shows that the correspondence between electronic configuration and geometry of a molecule can be carried over to more complicated systems than originally considered by Mulliken and Walsh. In the generalized form of this relationship, however, one must allow for the possibility that the hydrogen atoms of a given system may cause it to assume a ground state electronic configuration which differs from that of its isoelectronic counterparts in a parent family of molecules not containing hydrogen. In order to make the extension complete then, all that is necessary is to explain and predict how the position of hydrogen atoms in a system affects the relative stability of its MO's and therefore ultimately determines its ground state electronic configuration.

In the case of the C<sub>3</sub>H<sub>4</sub> isomers discussed in this paper, for which the appropriate parent family consists of the simple triatomic molecules, such an analysis is not difficult. The valence orbitals in these systems can be conveniently divided into two distinct categories according to whether the majority of their charge distribution is found at the central or the terminal positions of the molecule; the  $4b_2$  and  $1a_2$  MO's ( $1\pi_g$ ), with their nodal planes through the central atom, obviously fall in the second category while the  $6a_1$  and  $2b_1$  ( $2\pi_u$ ) belong to the first. Addition of a hydrogen atom to triatomic molecules can be expected to produce a relative increase in stability for the valence MO's with the greatest charge distribution at the heavy atom to which it is attached.

In both methylacetylene and allene, all of whose hydrogens are found at the end atom positions of the C<sub>3</sub> skeleton, the  $4b_2$  and  $1a_2$  MO's are thus definitely favoured over the  $6a_1$  and  $2b_1$  (especially since the  $4b_2$  and  $1a_2$  are ordinarily preferred over the  $6a_1$  and  $2b_1$  even without the added influence of end atom hydrogens) and are therefore occupied in the ground states of these systems. Since this is the same electronic configuration favoured by all the 22 electron simple triatomics (configuration I of Table 2) one is led correctly to predict a linear skeletal geometry for each of these compounds.

On the other hand in cyclopropene, with two central atom hydrogens and only one at each "terminal" carbon, the *other* category of MO's is relatively stabilized by the hydrogen participation. It is thus reasonable that occupation of the MO's in the central atom category is preferred ( $6a_1$  and  $2b_1$ ) and as a result that configuration VI of Table 2 is the cyclopropene ground state. According to the usual theory such an electronic configuration implies the known small equilibrium

angle of cyclopropene because both of the occupied valence MO's are strongly bonding (especially the  $6a_1$ ) between the end atoms and the competing antibonding character of the  $4b_2$  and  $1a_2$  is excluded.

Completely analogous remarks hold for 24 electron systems, for which the common equilibrium angle is approximately  $120^\circ$  (two end atom MO's and one of the central atom category are occupied in the corresponding ground state electronic configuration), with  $O_3$ ,  $NO_2^-$ ,  $HCOO^-$  and propene  $C_3H_6$  satisfying this description. Cyclopropane, which has a greater number of hydrogen atoms at its *central* carbon than does isomeric propene, does not follow this pattern, however; instead it prefers an electronic configuration which occupies two central atom MO's ( $6a_1$  and  $2b_1$ ) and only one of the end atom variety. As a result it possesses a ground state equilibrium geometry with an unusually small internuclear angle for a member of this isoelectronic family.

In summary it can be said that while the addition of hydrogens complicates the original theory of Mulliken and Walsh by causing a reordering of orbital stabilities relative to their arrangement in some parent system (without hydrogens), it does not alter its simple fundamental postulate, namely that the overall shape of a molecule is determined first and foremost by the electronic configuration it assumes. Hydrogens can lead to a skeletal geometry which is different from that of an isoelectronic molecule not containing hydrogen by causing a different electronic configuration to be optimum for the more complicated systems.

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