

that the other, closed-shell, phenyl orbitals are included essentially unchanged in the C_6H_5F orbital space. The situation is somewhat different for the C_6H_5F CO where five SCF MO's have coefficients larger than 0.1; this indicates that the bonding orbital of eq 6 is distributed over several SCF canonical MO's. The $6a_1$ SCF MO makes the largest contribution, 65%, to the CO. This deep MO with SCF $\epsilon = -45.2$ eV has considerable C s-p and F s-p character; it is clearly a phenyl-F bonding orbital, and this is the reason for the large ϵ . However, the $9a_1$ to $11a_1$, and the $13a_1$ SCF MO's also make large contributions to this C_6H_5F CO: 6%, 10%, 14%, and 3.5%, respectively.

We consider next the CO λ 's of π (b_1) symmetry. The $C_6H_5X-C_6H_5$ λ 's are large, 0.997 or 0.998, showing that the phenyl fragment orbitals are, with only very small changes, included in the C_6H_5X space. The C_6H_5X-X λ 's are somewhat smaller than 1.0; this corresponds to donation of charge from the substituent π lone pair into the empty, unoccupied, phenyl π MO's. From the CO λ 's, the order of this donation is $NH_2 > OH > F$ which is consistent with the order given by the populations in Table IV.

The smallest CO values for the b_2 and a_2 symmetries are very near 1; the smallest is 0.996 for the b_2 symmetry of C_6H_5F-F . This is conclusive evidence that the fragment orbitals in these symmetries are essentially unchanged and uninvolved in the bonding.

IV. Conclusions

Differences in bonding properties of species such as those considered in the present study are most likely to be important in order to describe and understand differences in reactivity. In

the present work, we have shown that a corresponding orbital analysis provides a useful description of the bonding. The corresponding orbital eigenvalues show that, at most, one corresponding orbital per symmetry is involved in the bonding. This is different from the SCF canonical orbitals where the bonding character may be distributed over several MO's. The smallest, nonzero CO eigenvalues also show the trends in the bonding for this series of substituted benzenes. The strongest bonding is in the $a_1(\sigma)$ space where the phenyl to substituent charge transfer is in the order $C_6H_5F \gtrsim C_6H_5OH > C_6H_5NH_2$. The bonding in the $b_1(\pi)$ space is weaker and the substituent to phenyl charge donation is in the order $C_6H_5NH_2 > C_6H_5OH > C_6H_5F$. These trends are consistent with those obtained from other studies,^{9,12} and we emphasize the utility of the trends given by the CO eigenvalues. It is relevant to point out that the corresponding orbitals and eigenvalues are well defined and stable to increase in the size of the basis set used to describe the MO's. This is in sharp contrast to a population analysis which is increasingly ill defined for larger basis sets. The approach that we have presented for corresponding orbitals between a subunit and the total, composite, system does not require difficult calculations and can be evaluated in a straightforward fashion.

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Registry No. $C_6H_5NH_2$, 62-53-3; C_6H_5OH , 108-95-2; C_6H_5F , 462-06-6.

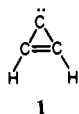
Toward the Laboratory Identification of Cyclopropenylidene

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Abstract: Nonempirical molecular electronic structure theory has been used to predict the geometries and energetics of the lowest singlet and triplet states of $\dot{C}-HC=CH$. The closed-shell singlet ground state is predicted to lie about 70 kcal/mol below the lowest triplet state. Actually there are two low-lying triplet states, 3B_1 and 3A_2 , which lie very close energetically. Ground-state cyclopropenylidene is predicted to have a dipole moment $\mu \sim 3.4$ D, making it a very nucleophilic carbene. Vibrational frequencies are predicted for all three low-lying electronic states at the double- ζ plus polarization (DZ+P) self-consistent-field (SCF) or two-configuration (TC) SCF levels of theory. A comparison of the predicted harmonic frequencies of singlet cyclopropenylidene and cyclopropene at the SCF level of theory is made. These predictions should assist in the identification of cyclopropenylidene from matrix-isolation infrared spectroscopy.

For the past two decades cyclopropenylidene and some of its derivatives have elicited much theoretical¹⁻⁷ and experimental⁸⁻¹² interest. The motivations behind these investigations have



basically fallen into two categories. First, several studies have centered around the determination of the ground-state electronic structure of cyclopropenylidene. Theory^{13,14} and experiment^{15,16} are now in concurrence that methylene has a triplet ground state with a singlet-triplet energy difference, $\Delta E(S-T)$, of about 9 kcal/mol. However, CH_2 is the exception and numerous carbenes which have a singlet ground-state electronic structure have been

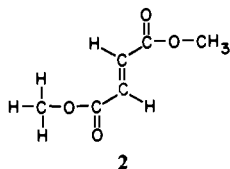
observed.¹⁷ The primary factor which must be considered when comparing the energies of the singlet and triplet states is the

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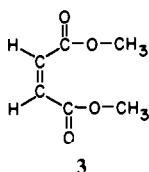
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relative stability of the σ -type orbital and the p-type orbital on the divalent carbon.^{4,17} Essentially, a triplet carbene has the configuration σp whereas the singlet is σ^2 . So, in effect, if the substituents on the divalent carbon tend to raise the energy of the p-orbital or lower the energy of the σ -orbital, then a singlet ground state will usually be preferred. Those substituent effects which will lead to a singlet carbene fall into inductive¹⁸ and resonance¹⁹ considerations. Specifically, for cyclopropenylidene, the inductive effect is directly related to the bond angle¹⁸ of the divalent carbon whereas the resonance effect is dependent upon the ability of the substituent to back-donate π -electrons.¹⁹ Thus, structural considerations favor the singlet state due to the small bond angle at the carbene center^{13,18} which causes the σ -orbital to be lowered in energy with an increased amount of s character. Also, it is easily seen that for a singlet configuration the ring will contain $4n + 2$ ($n = 0$) π -electrons and is expected to be aromatically stabilized.²⁰ In other words, the p-type orbital on the divalent carbon is raised in energy when mixing with the π -orbital of the ethylene substituent. Not surprisingly then, every investigation concerning the ground-state electron configuration has shown cyclopropenylidene and its derivatives to behave according to a singlet structure. Some of the theoretical studies^{1-3,5} have also investigated the singlet-triplet energy difference and have predicted it to be quite substantial, on the order of 50 kcal/mol or higher.

As a result of the added π -electron density at the divalent carbon, cyclopropenylidene is expected to be a rather nucleophilic carbene, and this expected property of cyclopropenylidene and its derivatives has led to a second category of studies. Generally, carbenes exhibit both electrophilic and nucleophilic character,²¹ although singlet carbenes tend to show an increased degree of nucleophilicity. Moreover, diphenylcyclopropenylidene has been shown to be very selective in reacting with olefins,¹¹ only reacting with electrophilic-type olefins such as dimethyl fumarate.



However, in its reactions with dimethyl fumarate and dimethyl maleate,



the same spiro-pentene is isolated, which tends to favor a two-step nonstereospecific addition across the double bond. In the past, two step mechanisms such as this were thought to be due to triplet carbene additions.¹¹ However, if one considers that diphenylcyclopropenylidene only reacts with electrophilic olefins then, for an intermediate, the negative polarization on the olefinic carbon will necessarily be resonance stabilized by an electron-withdrawing

group and the positive polarization is delocalized throughout the cyclopropenyl ring.¹¹ Hence a two-step process is not at all unreasonable.

This interpretation of the reactions of diphenylcyclopropenylidene tends to indicate that it is a very nucleophilic carbene, and indeed every theoretical study of the electron density at the carbene center of cyclopropenylidene and its derivatives has revealed a large partial negative charge.^{3,4,12} Furthermore, in a theoretical determination of the electrophilic selectivity of singlet carbenes, cyclopropenylidene was shown to have an extremely high selectivity index.⁷

Interestingly enough, in considering the overall stability of cyclopropenylidene and its derivatives it is apparent that π -electron withdrawing substituents should destabilize the isolated cyclic carbene,²² which would imply that cyclopropenylidene should be more easily observed than its diphenyl derivative. However, this line of reasoning ignores the effective shielding of the molecule by the bulky phenyl groups. Nevertheless, diaminocyclopropenylidene¹² has been synthesized, and the unsubstituted compound might be intermediate in stability between these two substituted compounds. Yet the parent cyclopropenylidene has not been observed to date. Therefore, with encouragement from Hoffmann and Maier,²³ it is in the hope of aiding in the identification of cyclopropenylidene that we have undertaken this theoretical project. Here we report for the first time *ab initio* predictions for the harmonic vibrational frequencies as well as structures, energies, and dipole moments of singlet (1A_1) and triplet (3B_1 and 3A_2) cyclopropenylidene. The dependence of these properties on the electron configurations included in the zeroth-order wave functions is investigated in a qualitative sense, and it is found that the dipole moment of the singlet ground state is more dependent than are the vibrational frequencies. The singlet-triplet energy difference is determined for the two different triplet surfaces relative to the ground-state singlet surface. The stability of the cyclopropenylidene molecule relative to dissociation to acetylene plus carbon is discussed. Finally, in order to judge the reliability of the theoretical predictions for the modes in the energetically lower end of the infrared spectrum (500 to 1600 cm^{-1}), results of an analysis of the infrared intensities and harmonic frequencies for the ground state of cyclopropenylidene and for cyclopropene are compared.

Theoretical Approach

Two basis sets were employed in the theoretical investigations reported here. The first is the basis suggested by Huzinaga²⁴ and later contracted by Dunning²⁵ and is commonly referred to as a double- ζ (DZ) basis. It is designated by C(9s 5p/4s 2p) and H(4s/2s) for carbon and hydrogen, respectively. The hydrogen s functions were scaled by a factor of 1.2. The second basis was constituted by adding polarization functions and is called a double- ζ plus polarization (DZ+P) basis. It is specified by C-(9s 5p 1d/4s 2p 1d) and H(4s 1p/2s 1p). The polarization function orbital exponents used were²⁶ $\alpha_d(\text{C}) = 0.75$ and $\alpha_p(\text{H}) = 0.75$.

Two separate triplet electronic states, 3B_1 and 3A_2 , were studied at the self-consistent-field (SCF) level of theory, as well as the corresponding singlets at the two-configuration self-consistent-field (TCSCF) level of theory. With the a_1 and b_2 irreducible representations representing the in-plane symmetries, the triplet electron configurations are

$$1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 4a_1^2 5a_1^2 1b_1^2 3b_2^2 6a_1 2b_1 \quad ^3B_1 \quad (1)$$

and

$$1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 4a_1^2 5a_1^2 1b_1^2 3b_2^2 6a_1 1a_2 \quad ^3A_2 \quad (2)$$

The fact that both of these triplet states are low lying suggests

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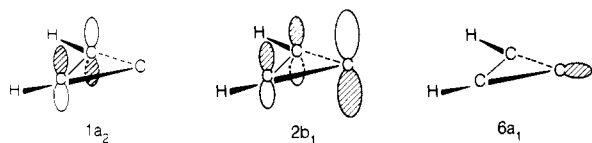
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Chart 1. Qualitative Drawings of the Main Contributions to the $6a_1$, $1a_2$, and $2b_1$ Molecular Orbitals

two possible TCSCF descriptions for the singlet ground state of cyclopropenylidene

$$C_1(1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 4a_1^2 5a_1^2 1b_1^2 3b_2^2 6a_1^2) + C_2(1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 4a_1^2 5a_1^2 1b_1^2 3b_2^2 2b_1^2) \quad {}^1A_1 \quad (3)$$

and

$$C_1'(1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 4a_1^2 5a_1^2 1b_1^2 3b_2^2 6a_1^2) + C_2'(1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 4a_1^2 5a_1^2 1b_1^2 3b_2^2 1a_2^2) \quad {}^1A_1 \quad (4)$$

Hereafter these two wave functions will be referred to as TCSCF I and TCSCF II. The atomic orbitals which make the largest contribution to the $6a_1$, $2b_1$, and $1a_2$ molecular orbitals are shown in Chart 1.

Stationary points on the respective potential energy surfaces were converged upon precisely by using analytic gradient methods²⁷ and a C_{2v} symmetry constraint. The harmonic vibrational frequencies of each stationary point were then determined by diagonalizing the analytic energy second derivative^{28,29} matrix. In the case of the DZ+P triplets the hessian or second derivative matrix was obtained by finite differences of analytic gradients.

In an attempt to establish more reliably $\Delta E(S-T)$, configuration interaction (CI) was performed at the SCF and TCSCF optimum geometries. The CI wave functions included all interacting singly and doubly excited configurations (CISD) relative to both references for the two separate descriptions of the singlet ground state. The Hartree-Fock interacting space^{30,31} of single and double excitations was included for the two triplet states. All three doubly occupied carbon core 1s-like molecular orbitals were frozen and the corresponding three virtuals deleted for the CISD determinations. This amounted to 16832 configurations for the DZ+P 3B_1 state, 16822 for the DZ+P 3A_2 state, 26522 for the DZ+P singlet wave function I, and 26521 for the DZ+P singlet wave function II.

The stability of the cyclopropenylidene molecule with respect to dissociated products was judged by CISD descriptions of ground-state acetylene plus 3P C at essentially infinite separation, again with the aforementioned 3 frozen and 3 deleted orbitals. Acetylene plus carbon was chosen for comparison based on the thermochemical data (of all possible combinations), which indicate that $C + HCCH$ lies lowest energetically among possible fragmentation products.

Lastly, after analyzing the vibrational frequencies of the ground-state singlet obtained from the two TCSCF descriptions it became evident that a better qualitative understanding of the behavior of theoretical predictions in the 500 to 1600 cm^{-1} region of infrared frequencies was needed. In other words, it is well-known that for heavy atom-hydrogen atom stretches theoretical predictions at the harmonic SCF level of theory are roughly 10–15% too high.³² However, this generally encompasses the 1800 to 4000 cm^{-1} region (A-H stretches) of the infrared spectrum. A general rule as such for the more complicated normal modes has not been well established and especially for ring compounds where theoretical predictions lower than the experimental value have been obtained.³³ Therefore, we found it desirable to perform analytic second derivative analyses on optimized SCF geometries

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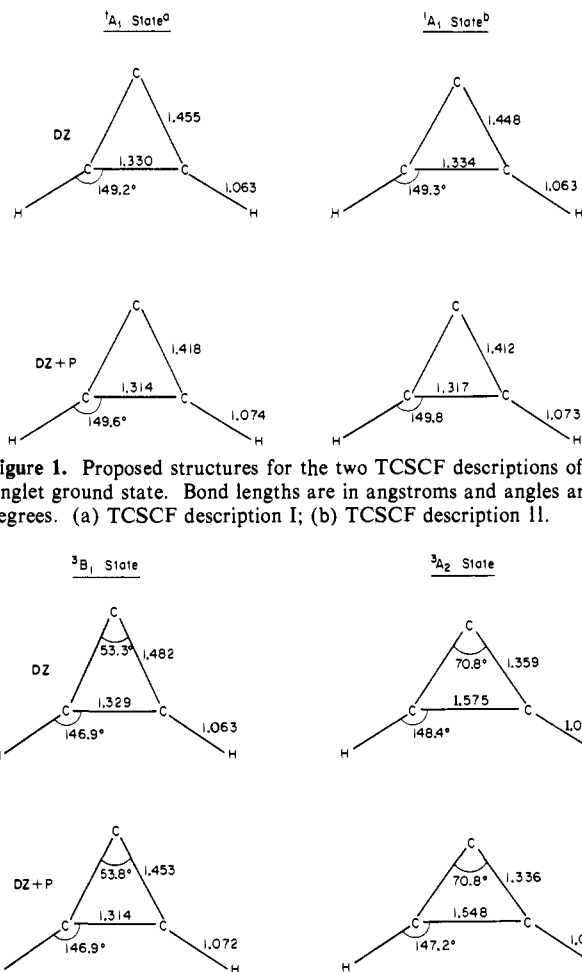


Figure 1. Proposed structures for the two TCSCF descriptions of the singlet ground state. Bond lengths are in angstroms and angles are in degrees. (a) TCSCF description I; (b) TCSCF description II.

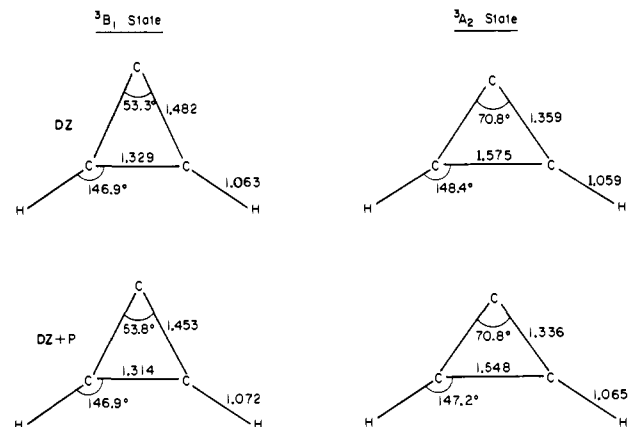


Figure 2. Proposed structures for the two triplet states investigated. Bond lengths are in angstroms and angles are in degrees.

of singlet cyclopropenylidene and cyclopropene using the previously mentioned DZ and DZ+P basis sets. Also of help to experimentalists are predictions of the relative intensities of these normal modes, and so these are also reported for both compounds. These are determined theoretically as the square of the partial derivative of the dipole moment with respect to the normal coordinate evaluated at the equilibrium geometry.

Structures and Energetics

The DZ and DZ+P optimized geometries are given in Figure 1 for the two TCSCF descriptions of the singlet and Figure 2 for the two distinct triplet states. The discussion of the structures and energetics from the SCF description of cyclopropenylidene and cyclopropene will be left until the end of this section. In all cases it is seen that the polarization functions shorten the ring bond lengths considerably. For example, in the case of the TCSCF I singlet wave function, the distance between the two doubly bonded carbons $r(C=C)$ goes from 1.330 (DZ) to 1.314 Å (DZ+P). Similarly, the bond distance $r(C-C)$ is reduced from 1.455 (DZ) to 1.418 Å (DZ+P). The carbon-hydrogen bond length is not as appreciably affected, although it follows the trend of becoming longer with the addition of polarization functions.

In comparing the two singlet structures it is readily noticeable that in the case of TCSCF II $r(C=C)$ is slightly longer, while $r(C-C)$ is slightly shorter than the analogous quantities for TCSCF description I. This observation is independent of the basis set used. The other geometrical parameters are not affected by the choice of the second configuration in the two-configuration SCF wave functions.

The two triplet states are predicted to have rather different characteristics. Both of the carbon-carbon bond lengths, $r(C=C)$ and $r(C-C)$, change drastically between the 3B_1 and 3A_2 structures. The 3B_1 structure more nearly resembles the singlet

Table I. Total Energies in Hartrees and Singlet-Triplet Differences, $\Delta E(S-T)$, in kcal/mol for the Two Pairs of Wave Functions Investigated^a

ref wave function	SCF/TCSCF		CISD	
	<i>E</i> , hartree	$\Delta E(S-T)$, kcal/mol	<i>E</i> , hartree	$\Delta E(S-T)$, kcal/mol
DZ TCSCF I (¹ A ₁)	-114.56729	-57.0	-114.79196	-57.0
DZ (³ B ₁)	-114.47653		-114.70105	
DZ TCSCF II (¹ A ₁)	-114.55765	-58.6	-114.78828	-53.7
DZ (³ A ₂)	-114.46428		-114.70267	
DZ+P TCSCF I (¹ A ₁)	-114.65219	-69.9	-114.98102	-70.3
DZ+P (³ B ₁)	-114.54082		-114.86896	
DZ+P TCSCF II (¹ A ₁)	-114.63956	-66.1	-114.97689	-62.7
DZ+P (³ A ₂)	-114.53423		-114.87702	
DZ SCF (¹ A ₁)	-114.55655			
DZ+P SCF (¹ A ₁)	-114.63779			

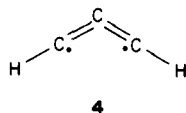
^a As noted from the total energies and as discussed in the text, TCSCF wave function I is preferable to II as a description of the ground state.

Table II. Configuration Mixing Coefficients for the Two Different TCSCF Descriptions of the Ground-State Singlet^a

	first configuration	second configuration
DZ TCSCF I	0.9920	-0.1259
DZ TCSCF II	0.9997	-0.0248
DZ+P TCSCF I	0.9910	-0.1336
DZ+P TCSCF II	0.9995	-0.0303

^a It is seen that TCSCF I provides a more complete description of the cyclopropenylidene ground state than does TCSCF II.

structures (except that $r(C-C)$ is longer), while the ³A₂ structure shows a considerable increase of the C-C-C angle as well as a shortening of the carbon-carbon single bond. Actually, these parameters change to such a degree that it might be better to view the ³A₂ structure as having two C=C double bonds



The other geometrical parameters change, but to a much lesser degree.

The SCF/TCSCF and CISD energies for the four wave functions investigated as well as the corresponding $\Delta E(S-T)$ values are given in Table I. Also the configuration mixing coefficients for the TCSCF descriptions of the singlet are given in Table II. As expected,¹⁻⁷ the ground electronic state is shown to be the closed-shell singlet. The calculated $\Delta E(S-T)$ values for the different basis sets agree most closely with the values reported by Baird and Taylor.² On the basis of experience,³⁴ the DZ+P basis set gives more reliable values for singlet-triplet splittings. It is encouraging that the SCF/TCSCF and CISD results (for a given basis set) based on the TCSCF I wave function agree to within 1 kcal/mol. Thus we can report with some degree of confidence that the difference in energy between the ground-state singlet and lowest lying SCF triplet (³B₁) is close to 70 kcal/mol, the value predicted with the larger DZ+P basis set.

The energy of TCSCF singlet wave function I is the lowest at all levels of theory. It is also apparent from the configuration mixing coefficients listed in Table II that the second configuration involved in singlet wave function I is more important than is the second configuration used in singlet wave function II. The dipole moments listed in Table III for all the wave functions studied indicate the importance of the $6a_1^2 \rightarrow 2b_1^2$ configuration. The singlet ground-state CISD dipole moment for TCSCF treatment I is 3.33 D (DZ+P) whereas that for TCSCF II is 3.48 D (DZ+P). The substantial difference between these two values seems to indicate the importance of the $6a_1^2 \rightarrow 2b_1^2$ configuration, especially considering the fact that the DZ+P CI prediction is

Table III. Predicted Dipole Moments in Debyes for the Cyclopropenylidene Wave Functions Studied^a

ref wave function	SCF/TCSCF, D	CISD, D
DZ TCSCF I (¹ A ₁)	3.30	3.40
DZ TCSCF II (¹ A ₁)	3.57	3.51
DZ (³ B ₁)	1.41	1.54
DZ (³ A ₂)	0.85	0.99
DZ+P TCSCF I (¹ A ₁)	3.32	3.33
DZ+P TCSCF II (¹ A ₁)	3.58	3.48
DZ+P (³ B ₁)	1.47	1.55
DZ+P (³ A ₂)	0.99	1.13
DZ SCF (¹ A ₁)	3.57	
DZ+P SCF (¹ A ₁)	3.58	

^a The carbene center contains a partial negative charge. Values reported are for the SCF/TCSCF optimum geometries.

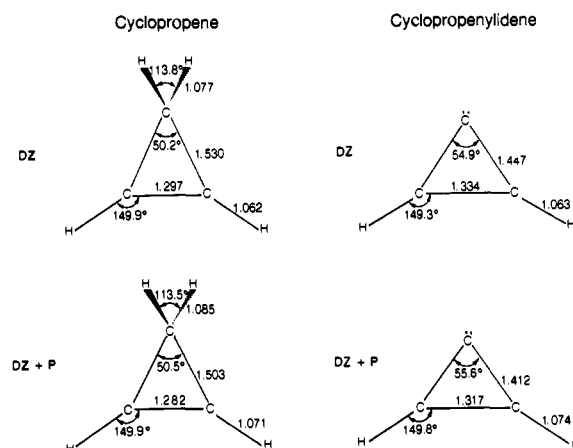


Figure 3. Proposed structures for the SCF description of singlet cyclopropenylidene and cyclopropene. Bond lengths are in angstroms and angles are in degrees.

so close to the TCSCF I value. The dipole moments reported for the singlet structures are near the value reported by Pople and co-workers.^{5a} Those listed for the triplet states confirm the importance of delocalization of the ring π -electrons to the carbene center with their much smaller magnitudes.

One very interesting result which should be noted is that the absolute energies of the two triplet states switch in order in going from the SCF to the CISD level of theory. The difference in energy between these two triplet states is never large and this precludes a definitive statement as to the precise value of the triplet-triplet energy separation. However, in view of the harmonic vibrational analysis the importance of this question is lessened.

The basis set effects for the structure of the SCF description of singlet cyclopropenylidene follow analogously the TCSCF tendencies as shown in Figure 3. Cyclopropene, however, shows the same shortening of the carbon-carbon bonds but to a lesser

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Table IV. Predicted Harmonic Vibrational Frequencies in cm^{-1} for the Two TCSCF (Two-Configuration Self-Consistent-Field) Descriptions of the Singlet Ground State of Cyclopropenylidene^a

approximate description	TCSCF I		TCSCF II	
	DZ	DZ+P	DZ	DZ+P
ν_1 sym CH str	A ₁ 3544	3458	3544	3461
ν_2 asym CH str	B ₁ 3500	3418	3500	3423
ν_3 C=C str	A ₁ 1707	1763	1699	1759
ν_4 sym C—C str + in-plane sym CH bend	A ₁ 1312	1400	1337	1419
ν_5 in-plane asym CH bend + asym C—C str	B ₁ 1180	1190	1179	1191
ν_6 out-of-plane, out-of-phase CH bend	A ₂ 1054	1064	1059	1071
ν_7 asym C—C str + in-plane asym CH bend	B ₁ 926	994	936	998
ν_8 in-plane sym CH bend + sym C—C str	A ₁ 995	982	996	984
ν_9 out-of-plane, in-phase CH bend	B ₂ 847	844	856	847

^aNote as discussed in the text that TCSCF wave function I should give the more reliable theoretical predictions.

Table V. Predicted Harmonic Vibrational Frequencies in cm^{-1} for the Lowest SCF Triplet State, 3B_1 , of Cyclopropenylidene

approximate description	DZ	DZ+P
ν_1 sym CH str	A ₁ 3549	3480
ν_2 asym CH str	B ₁ 3500	3434
ν_3 C=C str	A ₁ 1709	1749
ν_4 sym C—C str + in-plane sym CH bend	A ₁ 1286	1320
ν_5 in-plane asym CH bend + asym C—C str	B ₁ 1180	1155
ν_6 out-of-plane, out-of-phase CH bend	A ₂ 963	939
ν_7 asym C—C str + in-plane asym CH bend	B ₁ 867	914
ν_8 in-plane sym CH bend + sym C—C str	A ₁ 1026	1008
ν_9 out-of-plane, in-phase CH bend	B ₂ 691	633

extent, and instead of the carbon-hydrogen bonds lengthening they also shorten, as shown in Figure 3. The bond angles in both of these SCF descriptions are not appreciably affected when going from the DZ to DZ+P basis.

As required, the SCF description of singlet cyclopropenylidene gives a higher energy than either TCSCF description. The total energies for the DZ and DZ+P SCF descriptions of singlet cyclopropenylidene are listed in Table I. The dipole moment from each of these wave functions was determined, and these are listed in Table III. Notice that the DZ+P SCF dipole moment is 3.58 D which supports the earlier conclusion that the $6a_1^2 \rightarrow 2b_1^2$ configuration is important in the determination of the dipole moment. The TCSCF dipole moment with the same basis set is only 3.33 D.

The total energies determined for cyclopropene are -115.77411 and -115.84279 hartrees for the DZ and DZ+P basis sets, respectively.

Vibrational Frequencies

The harmonic vibrational frequencies for the two singlet TCSCF wave functions appear in Table IV and those for the triplets in Tables V (3B_1) and VI (3A_2). In performing a symmetry analysis of cyclopropenylidene there arise 4 normal modes of the totally symmetric irreducible representation, a_1 , 3 normal modes of b_1 symmetry, and one each of a_2 and b_2 symmetry, using the spectroscopic convention of assigning symmetries to the normal modes. The symmetry of each normal mode is indicated in the tables. Also, a general description of the vibrational motion is given. Again, the discussion comparing the SCF results of singlet cyclopropenylidene and cyclopropene will be reserved until the end of this section.

The harmonic vibrational frequencies for the two TCSCF ground-state descriptions are very similar for both the DZ and DZ+P basis sets. This was to be expected since the optimized structures do not vary significantly. Also, in going from the DZ to DZ+P basis set, the expected changes occur. For example, since the C=C bond length is shortened we would expect to see

Table VI. Predicted Harmonic Vibrational Frequencies in cm^{-1} for the Lowest 3A_2 State of Cyclopropenylidene

approximate description		DZ	DZ+P
ν_1	sym CH str	A ₁ 3597	3551
ν_2	asym CH str	B ₁ 3512	3473
ν_3	sym C=C str	A ₁ 1674	1730
ν_4	in-plane sym CH bend	A ₁ 964	930
ν_5	in-plane asym CH bend	B ₁ 982	963
ν_6	out-of-plane, out-of-phase CH bend	A ₂ 533i	652i
ν_7	asym C=C str or ring opening	B ₁ 3178i	2057i
ν_8	sym C—C str	A ₁ 791	846
ν_9	out-of-plane, in-phase CH bend	B ₂ 485i	573i

Table VII. Predicted Harmonic Frequencies and IR intensities for the 1A_1 Ground State of Cyclopropenylidene at the SCF Level of Theory

approximate description	freq, cm^{-1}		IR intensity, $(D^2/\text{\AA}^2)/\text{amu}$	
	DZ	DZ+P	DZ	DZ+P
ν_1 sym CH str	A ₁ 3544	3457	0.01	0.01
ν_2 asym CH str	B ₁ 3500	3418	0.06	0.02
ν_3 C=C str	A ₁ 1700	1759	0.01	0.01
ν_4 sym C—C str + in-plane sym CH bend	A ₁ 1337	1419	2.27	1.56
ν_5 in-plane asym CH bend + asym C—C str	B ₁ 1180	1191	0.54	0.50
ν_6 out-of-plane, out-of-phase CH bend	A ₂ 1060	1071	0	0
ν_7 asym C—C str + in-plane asym CH bend	B ₁ 935	998	0.02	0.05
ν_8 in-plane sym CH bend + sym C—C str	A ₁ 996	983	0.28	0.48
ν_9 out-of-plane, in-phase CH bend	B ₂ 856	854	1.26	0.62

the analogous frequency become larger and it does, increasing from 1707 (DZ) to 1763 cm^{-1} (DZ+P) for TCSCF I. Also, the C-H stretching frequencies both become smaller, in agreement with the lengthening of the C-H bond with extension of the basis set.

Since the optimum structure of the 3B_1 state so closely resembles the TCSCF I singlet structure, it is expected that its frequencies would be very similar and indeed this is found to be true with a few noticeable exceptions. The ordering of the ν_6 - ν_8 frequencies is somewhat different, although their magnitudes are still reasonably close to those of TCSCF I. The second unique factor is the much smaller ν_9 , an out-of-plane vibrational frequency. For TCSCF I ν_9 is 844 cm^{-1} (DZ+P) whereas for the 3B_1 state $\nu_9 = 633 \text{ cm}^{-1}$ (DZ+P). It should also be noted that for the two singlet descriptions, ν_5 and ν_6 become larger when the basis set is increased from DZ to DZ+P but that for the 3B_1 state these quantities decrease with extension of the basis.

The harmonic vibrational analysis for the 3A_2 state is quite different, exhibiting *three* imaginary frequencies and thus revealing the 3A_2 structure to be a potential maximum with respect to three distinct nuclear degrees of freedom. The addition of polarization functions reduces the largest imaginary frequency drastically from 3178i (DZ) to 2057i cm^{-1} (DZ+P), and this is the only significant basis set effect seen. The largest imaginary frequency corresponds to breaking one of the two equivalent carbon-carbon bonds, most likely yielding propenediylidene. The other two imaginary frequencies correspond to out-of-plane normal modes and would probably lead to internal rotation about a single bond within the resulting compound.

Thus the 3A_2 state, although predicted to lie lower energetically than the 3B_1 state, will not be observable for cyclopropenylidene-like geometries since there is no 3A_2 stable equilibrium geometry in this region of the energy hypersurface. It is also of interest to note that the triplet isomer formed when breaking the ring in the manner specified above does not appear to lead to the W-shaped lowest energy triplet of C_3H_2 given by Pople and co-workers.⁵

Table VIII. Predicted Harmonic Frequencies and IR Intensities for the SCF Description of Cyclopropene and Experimentally Observed Fundamentals

	approximate description ^a	corresponding mode in cyclopropenylidene	obsd freq, ^b cm ⁻¹	freq, cm ⁻¹		IR intensity, (D ² /Å ²)/amu	
				DZ	DZ+P	DZ	DZ+P
ν_1	C—H sym str	(ν_1)	A ₁ 3152	3555	3482	0.00	0.01
ν_2	CH ₂ sym str		A ₁ 2909	3268	3212	1.77	1.96
ν_3	C=C str	(ν_3)	A ₁ 1653	1815	1853	0.63	0.63
ν_4	CH ₂ scissor		A ₁ 1483	1655	1638	0.00	0.04
ν_5	C—C sym str	(ν_4)	A ₁ 1105	1215	1246	0.03	0.01
ν_6	C—H bend; in plane	(ν_8)	A ₁ 905	1019	1003	0.19	0.10
ν_7	CH ₂ twist		A ₂ 996	1100	1094	0	0
ν_8	C—H bend; out of plane	(ν_6)	A ₂ 815	978	952	0	0
ν_9	C—H asym str	(ν_2)	B ₁ 3116	3499	3432	0.06	0.04
ν_{10}	CH ₂ wag		B ₁ 1043	1214	1178	0.88	0.94
ν_{11}	C—H bend; in plane	(ν_5)	B ₁ 1011	1174	1148	1.13	0.56
ν_{12}	C—C asym str	(ν_7)	B ₁ 769	826	873	0.57	0.61
ν_{13}	CH ₂ asym str		B ₂ 2995	3355	3282	1.63	1.52
ν_{14}	CH ₂ rock		B ₂ 1088	1191	1190	0.05	0.06
ν_{15}	C—H bend; out of plane	(ν_9)	B ₂ 569	723	678	3.58	2.54

^a From ref 36. ^b From ref 35.

The harmonic vibrational frequencies for the SCF description of singlet cyclopropenylidene and cyclopropene are given in Tables VII and VIII, respectively. Along with the frequencies, the infrared (IR) intensities for each mode are given. The normal modes of cyclopropenylidene are numbered according to the scheme used with the TCSCF descriptions, and in fact the frequencies themselves do not vary much from the TCSCF frequencies. The descriptions of the normal modes of cyclopropene and the experimental values are taken from ref 35 and 36, and the numbered modes in parentheses correspond to the analogous modes in cyclopropenylidene.

For cyclopropene, it is clearly shown that the theoretical harmonic frequencies are always larger than the observed experimental frequencies. In the lower end of the spectrum (the last 11 modes) theory is 12.9% too high for the DZ+P basis on average. Also, the DZ+P optimized structure agrees very well with the experimentally determined structure.³⁶ Thus, based on these results one may conclude that a DZ+P SCF description gives reasonable predictions for the small ring compound being considered here and so the predicted vibrational frequencies of cyclopropenylidene are probably about 10% too high.

One more interesting fact to be noticed is the relationship which exists between the predicted harmonic frequencies of cyclopropene and cyclopropenylidene. By comparing the optimized structures the relative magnitude of some modes should be easily predicted. For example, since the C—H bond length in cyclopropenylidene is longer than the corresponding bond length in cyclopropene, the corresponding C—H stretches would be expected to have higher harmonic frequencies for cyclopropene and indeed this is the case. Such qualitative arguments are in general true for all the in-plane modes of cyclopropenylidene with the possible exception of normal mode ν_5 . However, there are competing effects for this normal mode, and this result is easily understood.

Conclusions

To judge the relative stability of cyclopropenylidene CISD was performed on the most stable dissociation products, ground-state acetylene + ³P carbon. For the DZ+P basis this energy was determined to be -114.82509 hartrees with the DZ basis yielding -114.68998 hartrees. The corresponding energies with the

Davidson correction for unlinked clusters are -114.86017 and -114.71124 hartrees for the DZ+P and DZ basis sets, respectively. Comparing the DZ+P results to the lowest energy CISD singlet wave function I shows cyclopropenylidene to be 97.8 kcal/mol lower in energy without Davidson's correction and 101.5 kcal/mol with the correction. While ³P carbon plus ground-state acetylene are not the correct dissociation products for the singlet wave function I, this comparison does indicate that the production of cyclopropenylidene is feasible.

It is true, of course, that cyclopropenylidene will not have a very long lifetime due to its highly reactive nature. However, both diaminocyclopropenylidene and diphenylcyclopropenylidene have already been observed, and the parent cyclopropenylidene might be of nearly comparable stability. The most promising technique for the identification of $\text{C}=\text{HC}=\text{CH}$ in the near future is infrared matrix isolation spectroscopy, and we are hopeful that the experiments of Hoffmann and Maier²³ will prove successful in this regard.

It should be emphasized in closing that the most reliable theoretical predictions of the ground-state infrared spectrum of cyclopropenylidene are found in column two (DZ+P TCSCF I) of Table IV. Previous experience suggests³² that these harmonic vibrational frequencies should lie about 10% above the (to be) observed fundamentals.

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Registry No. Cyclopropenylidene, 16165-40-5; cyclopropene, 2781-85-3.

(37) **Note Added in Proof:** Subsequent to the submission of this paper, Professors Hoffmann and Maier were able to identify cyclopropenylidene via matrix isolation. It is encouraging that the vibrational frequencies and intensities predicted here played a significant role in their pioneering experimental study: H. P. Reisenauer, G. Maier, A. Riemann, and R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **23**, 641 (1984).

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