dimensional lattice and is not necessarily related to the optical transition frequencies. Such analysis is facilitated by the lack of rotation of the HMB in the lattice.[17]

C. Excitons. This complex also presents a problem which has been observed in other EDA complexes wherein the CT transition dipoles are collinear.[1,9] Simple exciton arguments lead to a prediction of a red shift and intensification of the CT band from its solution values. Indeed, this is observed in most cases (TCNQ–anthracene is a notable exception). If the total integrated intensities of the CT bands are used, a calculated (one-dimensional)[18] red shift of only 710 cm^{-1} from the solution CT peak is obtained which is less than the 1100-cm^{-1} shift which is observed. Tacit in this calculation is the assumption that the configurations and transitions observed in the crystal are directly related to those found in solution. The greatest deviations in energy would arise from the situation wherein the complexes in solution and the crystal possess quite different geometries. The fact that the solution and crystal CT transition intensities are similar offers, at best, weak support for the possibility that the geometries are similar.

V. Conclusions

The HMB–TCNE single crystal displays spectral structure in the visible which is attributed to three separate CT transitions which arise from the three different arrangements which are possible for a given HMB in the crystal stack. These configurations may be approximated by EDA complex trimers AA, AB, and BB which are expected to have slightly varying total energies as well as different CT transition frequencies. The spectra in the visible region form two distinct, structurally similar bands with a shoulder at higher energy which becomes a third transition upon deconvolution. These bands may be associated with $\bar{\nu}_{\mathrm{CT}}$ for the trimers.

The model of binary alloys may be applied to the EDA stack and relevant statistics, when applied to the intensity ratios, support the hypothesis of EDA triads in the crystal. The treatment can be further extended to estimate the energy difference of the AB-type complex from that of the AA or BB type.

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Electronic Structure of the Lowest $^1A_1$ and $^3B_1$ States of Cyclopropenylidene

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Abstract: Multiconfiguration self-consistent field calculations have been performed at several geometries on the lowest $^1A_1$ and $^3B_1$ states of cyclopropenylidene. The effects of hybridization and electron correlation are analyzed at the various geometries. These model prototype calculations reveal strong correlation effects in the aromatic singlet state as well as a singlet–triplet potential surface crossing which may play a role in the chemical reactivity of analogous chemical reactions involving insertion of singlet or triplet reagents into triple bonds. It is demonstrated that multiconfigurational wave functions are absolutely necessary to obtain a qualitative description of the two spin states of these unsaturated carbenes.

I. Introduction

Considerable theoretical and experimental interest has been devoted to the chemistry of saturated and unsaturated carbenes. Theoretical research in our laboratory[1] and theoretical and experimental work in other laboratories[1-5,13] has focused on the very important question of singlet–triplet energy differences of isolated carbenes. Indeed, postulation of one-step stereospecific addition of singlet carbenes and two-step nonstereospecific addition of triplet carbenes to olefins has played a dominant role in the experimental determination of the spin state of carbenoid intermediates.[3] In this report, we attempt to gain a fundamental understanding of a particular carbene reaction that appears to involve a nonstereospecific singlet addition of a cyclic carbene.[4] Diphenylcyclopropenylidene appears to insert into both dimethyl maleate and dimethyl fumarate to produce the same spiropentene, thereby suggesting a triplet-like mechanism. However, the carbene itself is gen-

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erated by an α-elimination process which tends to produce singlet carbenes. This anomalous behavior may be due to the cyclopropenyl moiety acting to stabilize a dipolar intermediate and thus facilitating a triplet-like two-step insertion. In addition to attempting to better understand the cyclopropenylidene moiety, we attempt to address the effects of configuration mixing on the aromatic nature of the singlet state of this species. Finally, we also consider the dissociation of this cyclic carbene into acetylene and (^{3}P or ^{1}D) carbon as a prototype study of singlet and triplet surface crossings involving insertions into triple bonds (as occur, for example, in H_2C + HCCH). Recently, Epiotis[18] and Salem[19] have examined the possibility that singlet–triplet surface transitions could provide a direct route to achieve insertion products in reactions which are orbitally forbidden when restricted to a single reaction surface. Such forbidden reactions include the singlet-state insertion of CH_2 into acetylene to yield cyclopropene and the addition of ^{1}D carbon atom to acetylene to give cyclopropenylidene. In fact, the above-mentioned anomalous insertion of (presumably) singlet cyclopropenylidene into double bonds to give triplet-like products could be the result of such a surface crossing. In an attempt to gain knowledge about the electronic structure factors that govern these surface crossing situations, we have examined the energies of the lowest singlet and triplet states of the cyclopropenylidene → acetylene + (^{3}P or ^{1}D)C "reaction".

Our investigation deals with the prototype system, cyclopropenylidene, because this molecule is small enough to allow reliable theoretical calculations to be performed while still maintaining the essential features necessary to allow chemical insight to be gained. Single configuration ab initio calculations indicate that the multiplicity of the ground state is singlet and that cyclopropenylidene is the most stable of the C_3H_2 geometrical isomers.[5] Previous calculations[1] indicate that, for linear unsaturated carbenes, singlet spin states tend to be more correlated than the corresponding triplet states. This singlet correlation is due predominantly to a single correlation configuration. As was shown in earlier work for linear carbenes, for methylene, and, as we demonstrate below, for cyclopropenylidene, this configuration mixing is absolutely essential in order to obtain a qualitatively correct picture of the lowest singlet and triplet potential energy surfaces (including their crossings, dissociation barriers, and asymptotic states) of the systems (e.g., H_2C: + HCCH, H_2CCC: + R_2CCR_2) for which cyclopropenylidene is being used as a prototype. Single-configuration wave functions (e.g., SCF) simply are not adequate in these cases.

Since cyclopropenylidene is isoelectronic with the aromatic cyclopropyl cation, qualitative molecular orbital theory argues that the correlation configuration involving promotion of the carbene electron pair into the system will not be as important in this cyclic carbene since this configuration does not possess the aromatic stability of the dominant configuration. The analysis of the role of aromaticity in determining the amplitudes of such electronic configurations is one of the novel goals of this study.

In order to properly describe the dissociation of the lowest singlet and triplet states and to measure the effects of orbital hybridization and correlation on these state energies, the present work makes use of the multiconfiguration self-consistent-field (MCSCF) and configuration interaction (CI) approaches. The advantages of this approach lie in the quantitative results that the CI procedure is capable of achieving, along with the simplicity of the form of the MCSCF wave function. Within C_{2v} spatial symmetry, the lowest $^1A_1$ and $^3B_1$ states are studied at various distorted geometries. These correlated calculations show that the singlet state is energetically lower than the triplet near the singlet equilibrium geometry but that the triplet becomes lower at distorted geometries.

Because of the relatively small atomic orbital basis sets employed, the accuracy of the potential surfaces generated is not expected to be high. However, by properly including that configuration mixing which is essential to a correct description of the lowest singlet and triplet states, we are able to gain a good qualitative description of the nature of the potential curve crossings which arise. As we argue in the text, the behavior of these potential curves may have much to do with insertion reactions involving triplet or singlet reagents and triple bonds.

A brief program description is given in section II for the procedures and techniques used in this study. Results and discussions for the $^1A_1$ and $^3B_1$ states of cyclopropenylidene are given in section III. Our conclusions are presented in section IV.

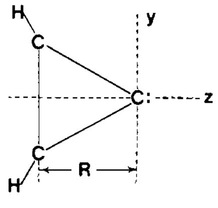
II. Quantum Chemical Methods

We have recently developed quantum chemical computer programs which perform orbital and configuration mixing optimization, including configuration selection, using procedures that have been implemented and separately reported by other researchers.[7-10] In our MCSCF program, orbital optimization is achieved by a procedure based on the direct annihilation of Hamiltonian matrix elements between the MCSCF reference space and its single excitations as defined by the generalized Brillouin theorem.[6] The variationally calculated mixing coefficients of the super-CI secular equations then define the orbital correction coefficients.[7] As pointed out by Dalgaard and Jørgensen,[8] this method is one of the most effective procedures for the determination of optimal orbitals. It has been shown[9] that the procedure displays second-order convergence properties and our experience to date confirms that approximate second-order convergence can be expected in practice. Moreover, we have also had good success in using this MCSCF method on excited states which are of the same symmetry as lower states.[10] For our calculations using the small (4s,2p-C/2s-H) contracted Gaussian basis (34 basis functions total) for the $^1A_1$ and $^3B_1$ states of cyclopropenylidene, which has 20 electrons, we find that convergence takes three to six MCSCF iterations if we begin with the canonical SCF orbitals of the singlet state.

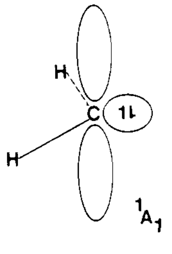
One- and two-electron integral generation over the symmetry adapted basis required 10–12 min using the MOLECULE program.[11] SCF calculations required 7–10 min at the various geometries using the GRNFNC program.[12] Each MCSCF iteration requires 4–9 min depending on the number of configurations and the number of molecular orbitals occupied. The partial two-electron integral transformation required in each MCSCF iteration accounts for 50–75% of this time, the remainder being devoted to matrix element construction and diagonalization within the iteration. These reported times are for the University of Utah College of Science DEC system 20/40 computer and for the 34 basis function cyclopropenylidene calculations using C_{2v} geometry.

III. Results and Discussion

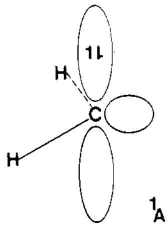
Adopting the geometry convention used previously for C_{2v} carbene investigations, the planar cyclopropenylidene is defined to lie in the yz plane with the z axis passing through the carbene carbon and between the carbon atoms of the C_2H_2 fragment. With this convention, s and p_z basis functions on the carbene carbon have a_1 spatial symmetry. p_y basis functions



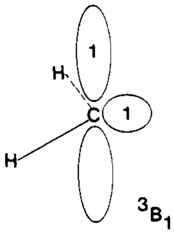
on the carbene carbon have b_2 symmetry and p_x basis functions on the carbene carbon have b_1 symmetry. The odd combination of p_x basis functions on the C_2H_2 fragment has a_2 symmetry as would a d_{xy} orbital on the carbene carbon. Previous carbene investigations indicate that at least two configurations are required to describe the lowest $^1A_1$ states. We reproduce the simple molecular orbital picture of these two configurations below for methylene along with the dominant $^3B_1$ configuration (the configurations are analogous for cyclopropenylidene). Configuration B (and the configuration analogous to B in other singlet carbenes) is referred to as the $a_1{}^2 \rightarrow b_1{}^2$ configuration. For methylene, the mixing coefficients for these configurations, C_A and C_B, approximately satisfy $C_A{}^2 + C_B{}^2 = 1$. For example, $C_A = 0.9617$, $C_B = 0.1943$ in a CI study of methylene by O'Neil, Schaefer, and Bender.[13]



A



B



C

Previous studies of linear unsaturated carbenes indicate that the singlet states are more correlated than the corresponding triplets[1] and that, at least for the singlet state, configuration mixing is essential for a proper description of the wave function. That is, when correlation is introduced into both calculations, the electronic energies of the singlet states are usually lowered more than the electronic energy of the triplet states. These earlier studies also indicate that basis set improvement tends to preferentially lower singlet electronic energies more than triplet energies. These improvements usually take the form of addition of polarization functions on the carbon centers. The importance of basis flexibility can be seen in the single determinant description of the linear carbene H_2CCC where the state ordering is actually reversed using basis sets without polarization functions.[1] Although it is essential to address these questions concerning optimal basis set choices if one is interested in obtaining an accurate description of the lowest singlet and triplet states, we believe that even the double-ζ quality basis used here gives the qualitatively correct picture which we seek in this work.

The present calculations indicate that, near the singlet state's equilibrium geometry, the $^1A_1$ state is lower in energy than the $^3B_1$ state. These calculations include treatment of configuration mixing for both the singlet and triplet states. The basis set used in the present study is the Dunning (4s2p-C/2s-H) contraction[14] of Huzinaga's (9s4p-C/4s-H) primitive Gaussian basis.[15] Since we find with this basis that the singlet is lower than the triplet and since basis flexibility tends to preferentially stabilize carbene singlet states, we expect that any improvements of the basis will not reverse our state orderings, although improvements may change the numerical values of the energy differences reported.

After noting that cyclopropenylidene is isoelectronic with the cyclopropyl cation, qualitative molecular orbital theory would indicate that similar aromatic stability should arise in cyclopropenylidene. That is, singlet cyclopropenylidene is aromatic in the sense that its π electrons satisfy the "$4n + 2$" rule. This would be expected to decrease the importance of the antiaromatic $a_1{}^2 \rightarrow b_1{}^2$ configuration in the singlet state. Thus the singlet might be less correlated than previously studied singlet unsaturated carbenes for which this $a_1{}^2 \rightarrow b_1{}^2$ configuration is the dominant correlation configuration. On the other hand, the triplet might be more correlated than for analogous noncyclic carbenes owing to the interaction of the dominant triplet configuration, which has three electrons in the b_1 orbitals, with low-energy configurations which involve excitations from these orbitals and which restore the $4n + 2$ π occupancy.

SCF, MCSCF, and CI calculations have been performed on the $^1A_1$ and $^3B_1$ states at various geometries using the above basis. Distortions away from the singlet equilibrium geometry (R_{eq}) involving increasing the distance between the carbene carbon and the HCCH fragment while preserving C_{2v} symmetry have been considered. The resulting SCF calculations show the singlet state to be lower than the triplet by 52 kcal/mol at R_{eq}. At large separation, the dissociation products are acetylene and a carbon atom. The ground state of the carbon atom is a triplet, ^3P, and is more stable than the ^1D carbon atom by 35 kcal/mol.[16] Thus, there must be a $^1A_1 - {}^3B_1$ curve crossing along this C_{2v} distortion path.

Because there are many geometrical degrees of freedom for this molecule, compromises had to be made in the constrained geometry optimization along the above-described "reaction path". Ideally one would like to optimize the geometry at every point along the path with a very large basis and at the CI or perhaps MCSCF level of calculation. Our compromise consisted of calculating an approximate reaction path in two steps, both of which involved the small (4s,2p-C/2s-H) contracted basis mentioned earlier. In the first approximation, we began with a previously reported equilibrium geometry for the singlet state[5] and explored small geometrical distortions around this point to locate the true (within our basis) geometry. The SCF optimized geometry thus obtained was essentially identical with that reported by Hehre et al.[5] Next, the carbene carbon was moved away from its equilibrium distance, keeping the internal geometry of the HCCH moiety fixed, until it appeared that all bonds to this atom had broken. Fragmentation seemed to be complete at about 10 bohr away from the equilibrium distance (R_{eq}). SCF and CI calculations were performed at several points along this (very constrained) reaction path in order to determine which electronic configurations seemed to be most important. The $a_1{}^2 \rightarrow b_1{}^2$ configuration was found to not be the most important singlet excitation for correlation of the $^1A_1$ state at R_{eq} using the original SCF orbitals, and a configuration curve crossing was observed near $R_{eq} + 1.5$ bohr in the $^3B_1$ state.

Having then used the very constrained geometry simply to determine the most important configurations of the singlet and triplet states, we proceeded to better optimize the geometry of the HCCH fragment at the approximate singlet–triplet potential curve crossing point ($R_{eq} + 2.0$ bohr) found from the above reaction path. Since we knew of no reasonable geometry for this distorted conformation, we decided to optimize the energy by first using a semiempirical SCF procedure and then following this by a more precise ab initio optimization. This was accomplished in a rather straightforward manner using the MNDO program of Dewar[17] which has the capability of doing either full or constrained geometry optimizations. Using this semiempirical SCF prediction of the minimum energy (as far as the HCCH moiety is concerned) conformation at this distorted geometry as an initial guess, the singlet state geometry was then optimized at the ab initio SCF level again using our small basis and within C_{2v} spatial symmetry. It should be mentioned that the semiempirical procedure predicts C_{2v} symmetry at all points at which optimizations were performed ($R_{eq} \leq R \leq R_{eq} + 2.0$). The singlet geometry was also optimized at $R_{eq} + 10.0$ bohr at the ab initio SCF level subject to the constraint that the acetylene was linear. That is, only the C≡C triple bond distance and the C—H single bond distances were optimized. From these three SCF-optimized geometries, other geometries were either interpolated or approximated with

Table I

E(6-MC)	R_{eq}	R_{eq} + 1.0	R_{eq} + 2.0	R_{eq} + 10.0
$^1A_1$	−114.5900	−114.5000	−114.4444	−114.4259
configuration	mixing coefficient			
(1)	0.9843	0.9744	0.9771	0.7075
(2)	−0.0110	−0.0430	−0.1161	−0.7068
(3)	−0.1210	−0.0242	−0.1377	−1.52*E* − 6
(4)	−0.0815	−0.1426	−0.0866	−2.54*E* − 4
(5)	−0.0699	−0.0896	0.0108	−2.51*E* − 6
(6)	−0.0691	0.1407	−0.0716	2.90*E* − 4

(1): (1-5) a_1^2, $6a_1^2$, $1b_2^2$, $2b_2^2$, $3b_2^2$, $1b_1^2$
(2): (1-5) a_1^2, $6a_1^2$, $1b_2^2$, $2b_2^2$, $1b_1^2$, $2b_1^2$
(3): (1-5) a_1^2, $1b_2^2$, $2b_2^2$, $3b_2^2$, $1b_1^2$, $2b_1^2$
(4): (1-5) a_1^2, $6a_1^2$, $1b_2^2$, $2b_2^2$, $4b_2^2$, $1b_1^2$
(5): (1-5) a_1^2, $6a_1$, $7a_1$, $1b_2^2$, $2b_2^2$, $3b_2^2$, $1b_1$, $2b_1$
(6): (1-5) a_1^2, $6a_1$, $7a_1$, $1b_2^2$, $2b_2^2$, $3b_2$, $4b_2$, $1b_1^2$

the semiempirical MNDO SCF procedure. The resultant "internal geometry" optimized singlet and triplet MCSCF potential curves are shown in Figure 1. It should be noted that in Figure 1 the two configurations necessary to properly describe the ^{1}D carbon atom have been included. Hence, these potential curves dissociate correctly to singlet acetylene and ^{3}P or ^{1}D carbon atom.

The six most important configurations for the singlet state are listed in Table I along with their expansion coefficients in the six configuration (6-MC) MCSCF wave function at R_{eq}, R_{eq} + 1.0, R_{eq} + 10.0 bohr. The first configuration is the SCF configuration which remains dominant throughout the distortion path. The second configuration is the $b_2^2 \rightarrow b_1^2$ configuration that is necessary to properly describe the ^{1}D carbon atom and to break the two σ bonds. This configuration does not contribute significantly to the molecular correlation as can be seen from its R_{eq} expansion coefficient, which varies from −0.707 at R_{eq} + 10.0 to −0.116 at R_{eq} + 2.0 to only −0.043 at R_{eq} + 1.0. This trend arises primarily because the b_2 orbital on the carbene carbon interacts quite differently than the b_1 orbital on the carbene carbon with the corresponding orbitals of the C_2H_2 fragment. In the first (SCF) configuration in which it is occupied, the carbene carbon b_2 orbital interacts quite strongly with what is essentially the occupied carbon–carbon $2\sigma^*$ orbital of HCCH and the unoccupied π^* orbital of the acetylene, with both of the resulting occupied orbitals being delocalized over all three carbon centers at R_{eq}. The b_1 orbital, on the other hand, interacts only with the orbital of acetylene in order to delocalize the acetylene electrons. In the second configuration, however, when this b_1 orbital is occupied and when the geometry is near the equilibrium geometry, there are 4 π electrons. Hence, this configuration acquires antiaromatic character at small distortions, which raises its energy significantly. Thus, it appears that the b_2 orbital on the carbene carbon has a strong covalent interaction with the HCCH fragment whereas the b_1 orbital on the carbene carbon prefers to have a small electron-accepting effect. As the interaction decreases with larger separations, the configurations involving the b_1 and b_2 orbitals on the carbene carbon become degenerate as can be inferred from their expansion coefficients at R_{eq} + 10.0.

The next configuration listed in Table I is the $a_1^2 \rightarrow b_1^2$ excitation that has been found to be important in the previous carbene studies. The fourth configuration in Table I, which is a $b_2^2 \rightarrow b_2^2$ excitation from the SCF configuration, is a result of the strong interaction of the carbene carbon b_2 orbital with the acetylene b_2 orbital mentioned above. The occupied b_2 molecular orbital has large contributions from not only the carbene carbon but also from what is a π^* orbital on the C_2H_2 fragment. The unoccupied b_2 molecular orbital, however, has an additional nodal surface between the carbene carbon and the C_2H_2 fragment. Thus, this $b_2^2 \rightarrow b_2^2$ configuration can be thought of as a "radial correlation" type configuration that is allowing the electrons to become spatially separated onto the different fragments thus breaking the σ bonds. The last two configurations included in the 6-MC calculation were the next most important configurations near R_{eq}. Although never dominant along the reaction path, these two configurations increase in importance at slightly distorted geometries, reach their maximum importance around R_{eq} + 1.0, and then decrease in importance past R_{eq} + 2.0. The final six-configuration wave function yields a singlet dissociation energy of 103 kcal/mol and a singlet–triplet crossing at 94 kcal/mol above the singlet R_{eq} energy.

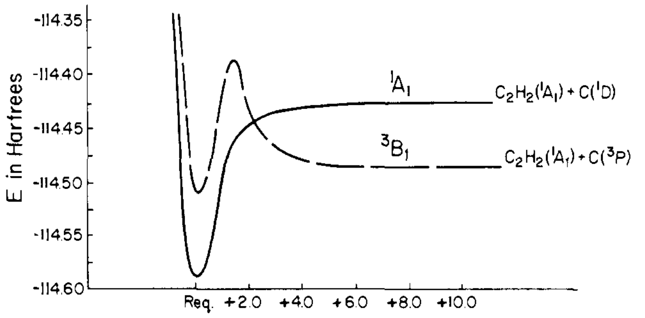


Figure 1. Lowest 6-MC $^1A_1$ and 4-MC $^3B_1$ C_{2v} potential energy curves using optimized HCCH fragment geometry. For R_{eq}: r(C═C) = 2.483 bohr, r(C—C) = 2.725 bohr, r(C—H) = 2.037 bohr, ∠(HC═C) = 147.2°.

MCSCF calculations have also been performed on the $^3B_1$ state with up to four configurations. The dissociation products for this state are acetylene and ^{3}P carbon atom. Since there is only one carbon atom triplet state for the orbital occupancy corresponding to $1s^2$, $2s^2$, 2p, 2p′, only a single configuration is required for the correct dissociation products. The selection of essential correlation configurations for the triplet state was performed at R_{eq} and R_{eq} + 1.0 to ensure that all important configurations were included near the configuration crossing point found for this triplet state. The equilibrium triplet geometry was not optimized, however, so that the true triplet dissociation energy will be underestimated by the present calculations.

The configuration corresponding to the correct carbon atom dissociation is the first configuration listed in Table II. There is a configuration curve crossing at approximately R_{eq} + 1.5 bohr involving this configuration and the configuration which is dominant near R_{eq}. The major configuration near R_{eq} is the $a_1 \rightarrow b_1$ single excitation from the dominant singlet configuration, as is expected from the previous carbene calculations, and is the second configuration listed in Table II. The third triplet configuration corresponds to the correlation that might be expected to be important from the qualitative considerations discussed earlier having to do with removing antiaromatic character from the $^3B_1$ state. The fourth triplet configuration included in the MCSCF wave function is again the result of the "radial correlation" within the occupied b_2 molecular orbital. This configuration is the $b_2^2 \rightarrow b_2^2$ double excitation from the second triplet configuration mentioned above and is analogous to the fourth singlet configuration. The $^3B_1$ state of cyclopropenylidene, at the $^1A_1$ equilibrium geometry, was found to be unstable by 5.6 kcal/mol with respect to dissociation to singlet acetylene and ^{3}P carbon at the single configuration level of approximation, although there was a considerable barrier to dissociation due to the triplet configuration

Table II

	R_{eq}	$R_{eq} + 1.0$	$R_{eq} + 1.5$	$R_{eq} + 2.0$	$R_{eq} + 10.0$
E(4-MC) $^3B_1$	−114.5070	−114.4125	−114.3881	−114.4357	−114.4834
configuration	mixing coefficient				
(1)	−0.0174	−0.0377	0.9975	0.9987	1.000
(2)	0.9817	0.9659	0.0380	−0.0281	$1.54E - 5$
(3)	−0.1670	−0.1841	−0.0051	0.0037	$1.79E - 6$
(4)	−0.0895	−0.1780	−0.0059	0.0413	$1.09E - 4$

(1): (1-5) a_1^2, $6a_1^2$, $7a_1$, $1b_2^2$, $2b_2^2$, $1b_1^2$, $2b_1$
(2): (1-5) a_1^2, $6a_1$, $1b_2^2$, $2b_2^2$, $3b_2^2$, $1b_1^2$, $2b_1$
(3): (1-5) a_1^2, $6a_1$, $1b_2^2$, $2b_2^2$, $3b_2^2$, $2b_1$, $1a_2^2$
(4): (1-5) a_1^2, $6a_1$, $1b_2^2$, $2b_2^2$, $4b_2^2$, $1b_1^2$, $2b_1$

curve crossing. In contrast, the 4-MC calculation, which includes the essential electron correlation effects, results in a triplet stability of 14.8 kcal/mol and a triplet–singlet crossing which lies 29 kcal/mol above the asymptotic triplet fragments.

In addition to the above-discussed MCSCF calculations, small CI calculations have been performed on both the $^1A_1$ and $^3B_1$ states. These calculations shall not be described in detail because they have been used primarily to check the precision of the MCSCF curves reported. In general, these CI calculations involved between 30 and 100 configurations and were not meant to produce quantitative measures of the total electron correlation energy but rather to measure the effectiveness of the orbital optimization and configuration selection used in the MCSCF studies.

IV. Summary and Conclusions

SCF, MCSCF, and CI calculations have been performed on the lowest $^1A_1$ and $^3B_1$ states of cyclopropenylidene using double-ζ quality basis sets. These calculations have been directed toward understanding the electron delocalization and electron correlation effects along a path of the potential energy surface that is thought to play an important role in the chemistry of these cyclic carbene intermediates. These results have been obtained using a small (4s,2p-C/2s-H) Gaussian basis set that does not include polarization functions. The addition of the important d-type functions, at least on the carbene carbon, could alter the quantitative aspects of these results but we expect that the interesting qualitative chemistry of this particular system is largely determined by the configuration mixing effects that have been included in our descriptions of the two spin states. Since the singlet–triplet curve crossing occurs so close to the configuration crossing of the triplet state, and since the singlet state is itself so correlated, single configuration SCF level calculations alone cannot properly model the relative potential surfaces of these two states. We expect that our MCSCF calculations do account for the important configuration mixing in these states and that the singlet–triplet state crossing we report is a qualitatively correct representation of the chemical feature of this geometrical distortion.

In analyzing the results of these MCSCF studies, we observe that electron configurations which violate the $4n + 2$ π-orbital occupancy are reduced in amplitude when compared to analogous configurations arising in other carbenes. Thus, it seems to be important for one to consider the effects of aromaticity in attempting to understand all of the major contributors to multiconfigurational wave functions.

We have also found that one can gain a qualitatively correct picture of the lowest singlet and triplet potential energy surfaces (including crossings and barriers) arising in the insertion into multiple bonds of reagents possessing low-energy singlet and triplet states. The proper description of these surfaces cannot be obtained within a single-configuration approach. The possible role played by the singlet–triplet curve crossings of such systems (e.g., H_2C: + RCCR, R_2CCC: + R_2CCR_2, etc.) in facilitating nonstereospecific singlet insertions and/or orbitally forbidden singlet insertion makes the results of this prototypical study quite significant.

At present, we are pursuing a more accurate description of these states of cyclopropenylidene by improving the quality of the atomic orbital basis employed. We are also carrying out MCSCF calculations on larger cyclic unsaturated carbenes in an attempt to further understand the role of $4n + 2$ aromaticity. These studies will be described in a future publication.

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