Vinylmethylene: Theoretical Investigations[1a]

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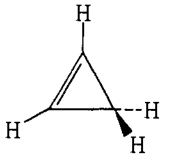
Abstract: Generalized valence bond calculations on cyclopropene and vinylmethylene (the open-shell species formed when cyclopropene undergoes ring cleavage) lead to the following conclusions: (1) the allyl-type π system is strongly distorted by the presence of the unpaired σ electron, leading to a methylene-like triplet, $^3A''$ (**4**), but a 1,3-diradical-like singlet state, $^1A''$ (**3**); (2) the lowest-lying singlet state of vinylmethylene has the form of a singlet methylene $^1A'$ (**6**) lying 12 kcal/mol above the $^3A''$ ground state, while the diradical singlet state $^1A''$ (**3**) lies at 14 kcal/mol; (3) the $^3A''$ ground state of **4** should exist in two geometrical forms (syn and anti) having nearly the same energy and separated by a large barrier (9 kcal); and (4) the diradical singlet state has only a low barrier (2 kcal/mol) between the syn and anti forms while the methylene triplet and singlet states have large barriers. These results suggest that the ring opening of cyclopropene proceeds directly to a diradical planar intermediate.

I. Introduction

In this paper we examine in some detail the electronic states involved in the ring opening of cyclopropene. Detailed ab initio calculations are performed to determine the electronic nature of these excited states.[2]

Stretching of the C–C bond in cyclopropene (**1**), without rotation of the methylene group, leads to the bisected geometry of the vinylmethylene diradical (**2**). Racemization of **1** can then result from rotation of the methylene group in **2** to give the planar geometry **3**, where the circle on the right carbon indicates a singly occupied π-orbital. As suggested by Bergman,[3] this form of the vinylmethylene diradical (**3**) would be expected to be in resonance with the vinyl carbene (**4**) so that this planar intermediate state might be represented as **5**.



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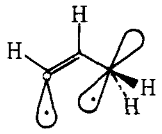

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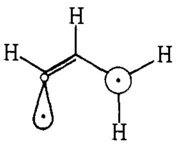

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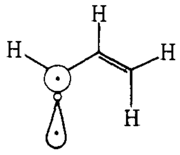

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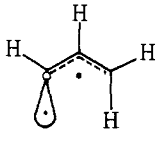

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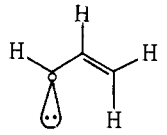
We have carried out ab initio calculations on the states of both the bisected (**2**) and planar (**3**, **4**, **5**) geometries of vinylmethylene and of cyclopropene (**1**) using Hartree-Fock (HF), generalized valence bond (GVB),[4] and configuration interaction (GVB-CI) wave functions. We find that the exchange effects in **3** and **4** are larger than the resonance effects, with the result that the triplet state favors **4** while the singlet state favors **3**. Thus the form **5** is not an appropriate description of either state.

We have also found a low-lying singlet state of the form **6** which is analogous to singlet carbene and which might play an important role in the racemization of cyclopropene **1**. The likely roles of these states in various thermal and photolytic processes is discussed.



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In order to provide simple ways of characterizing these states the wave functions of **3**, **4**, and **5** will be referred to as 3π while the wave function of **6** is referred to as 2π (indicating in each case the number of electrons in π orbitals). Using standard notation the triplet and singlet states of **3**, **4**, and **5** are denoted as $^3A''$ and $^1A''$, while the state of **6** is denoted as $^1A'$. Although redundant we will often add a (3π) or (2π) to aid in keeping track of the wave functions.

II. Calculational Details

A. Basis Sets and Geometries. Dunning's[5] (4s2p/2s) contraction of Huzinaga's (9s5p/4s) primitive Gaussian basis was used in all calculations. This double ζ basis (DZ) was augmented by a contracted set of polarization d functions (α = 0.678) on each carbon. This more extensive basis (DZd) had previously been shown to be necessary in calculating the singlet–triplet gap in methylene.[6]

Geometries appropriate for bonding structures **1–6** were utilized. The experimental geometry[7] for **1** was used, while for the others, CH bonds were taken as 1.08 Å, CC single bonds as 1.54 Å, CC double bonds as 1.34 Å, and all bond angles, except for the left HCC bond angle, were taken as 120°.

A series of calculations (DZ basis) was carried out for the planar geometry (**5**) using equal CC bond lengths of 1.38 Å (appropriate for bond order 1.5) and left HCC angles of 120, 180, and 240°. These calculations showed the triplet 3π state to have the form in **4** and the singlet 3π to have the form in **3**. We then repeated the calculations using a DZd basis and geometries appropriate for **3** and for **4** (standard bond angles and lengths as above except that in **4**, the left HCC angle was taken as 135°).

In the 2π singlet state (**6**) the left HCC angle was taken as 105° (in analogy with the σ^2 state of methylene). Two different sets of CC bond lengths were considered for **6**; initially normal CC single and double bond lengths (1.54 and 1.34 Å) were used. Final calculations on the 2π state used CC bond lengths ($R_{\text{cc-l}}$ = 1.50 and $R_{\text{cc-r}}$ = 1.32 Å), values optimized by Salem and Stroher[8] using Hartree-Fock minimum basis set wave functions.

B. The GVB Calculations. The HF wave function for the triplet state of **5** would consist of ten doubly occupied orbitals and two singly occupied orbitals:

$$\mathcal{A}[\phi_1{}^2 \ldots \phi_9{}^2\phi_{1\pi}{}^2\phi_{2\pi}\phi_\sigma\alpha\beta \ldots \alpha\beta\alpha\beta\alpha\alpha] \tag{1}$$

The most serious deficiency in this wave function is the lack of correlation between the electrons in the π orbitals, an effect that has been found to be very important in describing unsaturated systems.[9,10] This problem is eliminated by using the GVB(2) wave function in which we allow each of the three π electrons and the one unpaired σ electron to have their own orbitals. In some of our calculations we restricted the GVB(2) wave function by partitioning the four singly occupied orbitals into two sets of mutually orthogonal singlet- or triplet-coupled pairs (referred to as the perfect pairing approximation and indicated by the symbol PP). Thus the GVB(2/PP) wave function for the triplet state (eq 1) is of the form:

$$\mathcal{A}\{[\phi_1{}^2 \ldots \phi_9{}^2\alpha\beta \ldots \alpha\beta](\phi_{1\pi}\phi_{3\pi} + \phi_{3\pi}\phi_{1\pi}) \times (\alpha\beta)(\phi_{2\pi}\phi_\sigma)(\alpha\alpha)\} \tag{2}$$

This wave function was then used in all preliminary calculations to obtain the basic qualitative features of bonding.

Since we are concerned with the ordering of states within a few kilocalories, we also carried out much more extensive calculations in order to include the smaller additional correlation effects that affect excitation energies. For conjugated systems the most important correlation effects ignored in the GVB(2/PP) wave function are the *interpair* correlations involving simultaneous $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ excitations of the C–C bond pairs.[9,10] In order to include these correlations consistently, we also correlated the CC σ bonds leading to the GVB(4/PP) wave function (this results in localized CC σ bond pairs and provides σ^* orbitals for the interpair terms). These orbitals were then included in a configuration interaction calculation (GVB-CI) to include various residual electron correlation effects.

Finally, we were concerned that the perfect pairing restriction might have prejudiced the localization of the double bond, since it allows only one spin coupling. To check for this possibility we relaxed the perfect pairing restriction for the three π electrons and one σ electron using the SOGVB program.[11] Thus for example the

$$\mathcal{A}[(\phi_{1\pi}\phi_{3\pi} + \phi_{3\pi}\varphi_{1\pi})\phi_{2\pi}\phi_\sigma\alpha\beta\alpha\alpha] = \mathcal{A}[\phi_{1\pi}\phi_{3\pi}\phi_{2\pi}\phi_\sigma(\alpha\beta - \beta\alpha)\alpha\alpha]$$

part of eq 2 becomes

$$\mathcal{A}[\phi_{1\pi}\phi_{3\pi}\phi_{2\pi}\phi_\sigma\chi]$$

where

$$\chi = C_1(\alpha\beta - \beta\alpha)\alpha\alpha/\sqrt{2} + C_2(\alpha\alpha)(\alpha\beta - \beta\alpha)/\sqrt{2} + C_3[(\alpha\alpha\beta\beta + \beta\beta\alpha\alpha) - \tfrac{1}{2}(\alpha\beta + \beta\alpha)(\alpha\beta + \beta\alpha)]/\sqrt{3}$$

and both the orbitals and spin coupling coefficients (C_1, C_2, C_3) are optimized self-consistently (including self-consistent optimization of the other σ orbitals of GVB(4) wave function). Such calculations were carried out for the DZd wave function using the appropriate geometry of **4** for the triplet state and of **3** for the singlet state. No change in the extent of delocalization was observed in either case.

On the other hand the HF wave function (1) led to *delocalized* π orbitals.

III. Discussion

A. The GVB Orbitals. The GVB orbitals for the ^{3}A″, ^{1}A′, and ^{1}A″ states are shown in Figure 1. These orbitals come from the calculations [GVB(2/PP)] using the geometry of **5** and a left HCC angle of 120°. By using the equal CC bond lengths of **5**, we ensured that our wave function would not be biased toward localization. However, as can be seen in Figure 1, the π system for ^{1}A″ and ^{3}A″ is well localized.

In the ^{3}A″(3π) state the GVB π pair is localized on the right CC bond, while a singly occupied π orbital is localized on the left carbon nucleus. Therefore, the ^{3}A″ state has the form of a vinylmethylene instead of the allylic form **5**. The ^{1}A″(3π) state shows an entirely different type of localized π system in which the π pair is localized on the left CC bond while the singly occupied π is on the right nucleus. Thus the ^{1}A″ state resembles the 1,3-diradical **3**. The ^{1}A′(2π) state resembles the ^{3}A″ state in that the π pair is localized on the right; however, the extent of delocalization is somewhat larger for the ^{1}A′ state. Some delocalization is expected in ^{1}A′(2π) due to the absence of a π electron on the left carbon; however, such delocalization tends to build up a negative charge on the left center limiting this effect. The ^{3}A″ and ^{1}A′ states have the form of a vinylmethylene, while the ^{1}A″ state resembles a 2,3-diradical.

The two 3π states (^{1}A″ and ^{3}A″) had been generally assumed to be a resonance hybrid of **3** and **4**, much as in the allyl radical. However, the GVB calculation shows quite conclusively that the presence of the unpaired σ electron strongly distorts the π system. The reasons for this are analyzed next. The σ electron interacts with the π system through the exchange terms, resulting in the nondegeneracy of the two resonance contributors (**3** and **4**). We can represent the energy of each contributor as the sum or difference of a basic energy term, E_0, and an exchange term, $K_{\sigma\pi}$, which describes the interaction between the two unpaired electrons. The triplet state is stabilized by the exchange term as in eq 3, while the singlet state is destabilized by $K_{\sigma\pi}$ as in eq 4.

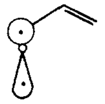
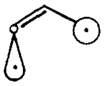
$$E_T = E_0 - K_{\sigma\pi} \tag{3}$$

$$E_S = E_0 + K_{\sigma\pi} \tag{4}$$

The magnitude of the exchange term $K_{\sigma\pi}$ is related to the proximity of the orbitals. Thus for **4** (where electrons are located on the same carbon) it is large (0.9 eV), but for **3** (where the electrons are well separated) it is small (0.05 eV).[19] Thus eq 1 shows that in the triplet state localized structure **4** will be lower than **3** by ~0.85 eV, while from eq 2, in the singlet case state **3** will be lower than **4** by the same amount. The consequences of these exchange terms are the localized orbitals depicted in Figure 1.

B. Resonance Effects. Since the ideas of resonance provide powerful arguments for qualitative discussions of organic systems, we will next analyze our wave function semiquantitatively in terms of the interaction of structures **3** and **4**. First we will consider that case with equal CC bond lengths and then the decrease in resonance effects that accompany the use of optimum CC bond lengths.

We can consider the molecular wave function for the ^{3}A″ state to be composed of two nonequivalent wave functions (eq 5), with energies E_1 and E_2 such that $E_1 < E_2$. Allowing the

$\psi_1 =$  and $\psi_2 =$  (5)

total wave function to have the form

$$\Phi = c_1\psi_1 + c_2\psi_2 \tag{6}$$

we want to determine where the two states of Φ lie in comparison with E_1 and E_2.

The final separation of the resonant and antiresonant states is calculated from our GVB(2/PP)-CI wave functions to be

$$\lambda_2 - \lambda_1 = 3.56 \text{ eV} \tag{7}$$

In Appendix A we show how to use the excitation energy (eq 7) along with the energy separation

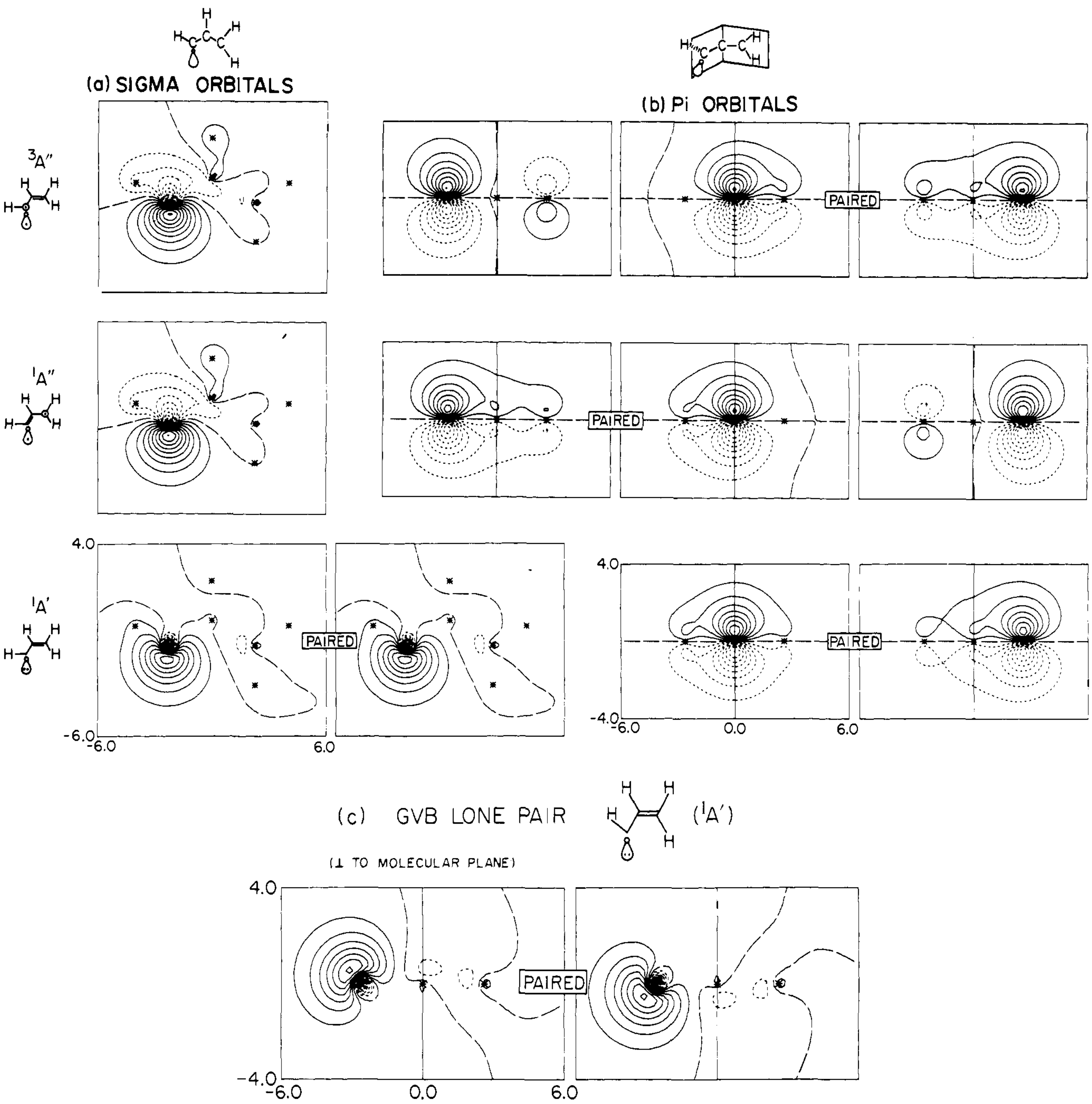


Figure 1. Selected GVB orbitals for the $^3A''(3\pi)$, $^1A''(3\pi)$, and $^1A'(2\pi)$ states of planar vinylmethylene based on the GVB(2/PP) wave function using the DZ basis set and equal bond lengths. Long dashes indicate zero amplitude; the spacing between contours is 0.05 au. The same conventions are used for all plots: (a) The σ orbitals are plotted in the molecular plane. (b) The π orbitals are plotted in two planes, both perpendicular to the molecular plane; one plane passes through the left two carbons while the other passes through the right two carbons; these are joined together at the common central carbon (the joining indicated by a vertical solid line). (c) The carbene nonbonding orbitals of part (a) are shown in the planes perpendicular to the molecular axis as in (b).

$$E_2 - E_1 = 0.85 \text{ eV} \tag{8}$$

and overlap

$$S = \langle \psi_1 | \psi_2 \rangle = 0.630 \tag{9}$$

of ψ_1 and ψ_2 (from the GVB calculations) to obtain the resonance energy for the wave function (eq 6). The result for the triplet state is

$$E^{\text{res}} = 0.29 \text{ eV} = 6.6 \text{ kcal/mol}$$

which is 60% of the resonance energy, 11.4 kcal/mol, for the allylic system.[12] These energy relationships are indicated in Figure 2.

The final wave function for the resonant state is

$$\phi_1 = 0.728\psi_1 + 0.366\psi_2 \tag{10}$$

in terms of nonorthogonal functions. Orthogonalizing (and renormalizing) ψ_2 to ψ_1, wave function 10 becomes

$$\phi_1 = 0.959\psi_1 + 0.284\bar{\psi}_2 \tag{11}$$

in terms of orthogonal functions. Here we see that the total wave function is 92% ψ_1, although the formulation (eq 10) in terms of nonorthogonal orbitals might have suggested greater delocalization.

In order to compare with a case possessing perfect allylic resonance, we set $E_1 = E_2$, obtaining

$$\phi_1 = 0.554\psi_1 + 0.554\psi_2 \tag{12}$$

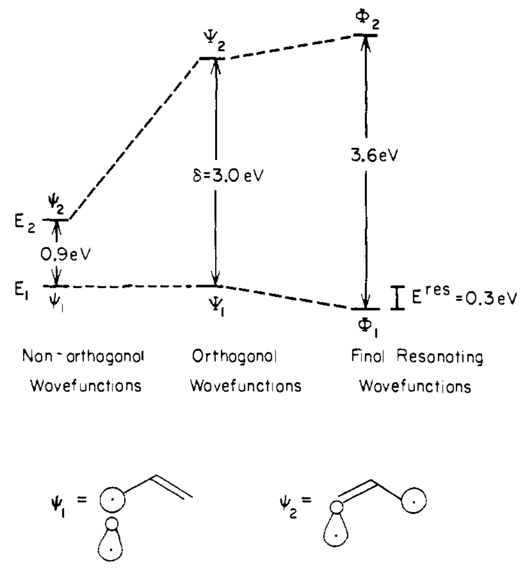


Figure 2. Resonance effects in vinylmethylene. Numbers based on the $^3A''(3\pi)$ state using equal bond lengths.

or in terms of orthogonal functions

$$\phi = 0.903\psi_1 + 0.430\bar{\psi}_2 \qquad (13)$$

From eq 13 we see that the allylic wave function is 81% ψ_1 (or ψ_2). Comparing eq 12 with eq 10 or eq 13 with eq 11, we see that vinylmethylene has about half the resonance or delocalization expected of an allylic π system.

In the above discussion all numbers were based on the case for equal bond lengths. The optimum geometry for **4** has unequal bond lengths leading to a large increase in $E_2 - E_1$ and as a result will decrease the resonance energy. For the $^3A''$ state at the optimum geometry we find the following changes from the above numbers

$$\lambda_2 - \lambda_1 = 3.79 \text{ eV} \qquad (7')$$

$$E_2 - E_1 = 1.84 \text{ eV} \qquad (8')$$

$$S = 0.598 \qquad (9')$$

leading to a resonance energy of

$$E^{\text{res}} = 2.3 \text{ kcal}$$

and wave functions

$$\phi_1 = 0.836\psi_1 + 0.243\psi_1 \qquad (10')$$

$$= 0.981\psi_1 + 0.195\bar{\psi}_2 \qquad (11')$$

C. Inversion Barriers. To study the interconversion of the syn and anti isomers of **5**, we carried out calculations at HCC angles of 120 (anti), 180 (linear), and 240° (syn) using the equal bond lengths restrictions of **5**. Because of this restriction, the separations between electronic states are not as accurate, but the shapes of the potential surfaces should be reliable. In the $^3A''$ state the calculations predict relative energies of 0.48, 8.76, and 0.0 kcal for these angles, indicating that the syn and anti forms are nearly degenerate (with syn more stable), but are separated by a relatively large inversion barrier. This barrier compares well with the inversion barrier of triplet methylene (9 kcal/mol),[6] in agreement with our qualitative picture of the $^3A''$ state as a substituted methylene. In the $^1A''$ state the relative energies were 0.0, 1.56, and 0.84 kcal/mol; here there is a small inversion barrier, as one would have expected for a vinyl radical (~2 kcal/mol).[13] Finally, the $^1A'$ state gave energies of 0.0, 18.12, and 1.44 kcal/mol, corresponding to the large barrier observed in the inversion of singlet methylene ($^1A_1$).[6] In all three cases, the inversion barriers compare well with the qualitative picture of a localized π system.

D. Excitation Energies. The localization of the π system in the $^3A''$ and $^1A''$ states suggested that the carbon-carbon bond lengths should not be equal as assumed in the previous calculations. Appropriate geometries (see section II.A) were therefore used for the $^3A''$, $^1A''$, and $^1A'$ states. These modified geometries resulted in an energy lowering of 6-8 kcal/mol for each of the three states (see Table I).

In studies on methylene, Hay, Hunt, and Goddard[6] found that the inclusion of 3d polarization functions lowered the $^3B_1 - {}^1A_1$ energy separation from 22.4 to 11.0 kcal/mol. In vinyl carbene, inclusion of d functions lowered the $^3A'' - {}^1A'$ excitation energy by 18 kcal/mol.

The $^3A''(3\pi) - {}^1A'(2\pi)$ separation was found to be sensitive not only to inclusion of d functions, but also to inclusion of CC σ bond correlation. Previous calculations[9,10] on systems containing multiple bonds had showed that ($\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$) excitations are important in obtaining accurate excitation energies. In vinylmethylene these correlations involving CC σ bonds were included, leading to an increase in the $^3A'' - {}^1A'$ excitation energy of 4 kcal/mol.

The excitation energies for the planar states are shown in Figure 3. We predict a $^3A''(3\pi) - {}^1A'(2\pi)$ separation of 11.8 kcal/mol, which should be compared with the separation between the analogous triplet $^3B_1(\sigma\pi)$ and singlet $^1A_1(\sigma^2)$ states of methylene. Harding and Goddard[14] calculate the methylene $^3B_1(\sigma\pi) - {}^1A_1(\sigma^2)$ separation as 16 kcal[20] (recent experimental results[21] lead to 19 kcal). This decrease in excitation energy from 16 to 12 kcal upon replacement of one H of CH_2 by a vinyl group is expected because of the extra stabilization of the 2π state by some delocalization of the vinyl π bond into the nearly empty π orbital on the methylene center.

The $^3A''(3\pi) - {}^1A''(3\pi)$ separation is 14.0 kcal/mol, which is considerably less than the separation of the open-shell triplet and singlet states of CH_2 where

$$E[{}^1B_1(\sigma\pi)] - E[{}^3B_1(\sigma\pi)] = 1.9 \text{ eV} = 44 \text{ kcal} \approx 2K_{\sigma\pi}$$

As discussed above, the reason for such a large decrease upon vinyl substitution is that the vinyl substituent singlet state changes form completely (from **4** to **3**), leading to a large extra stabilization and a much smaller triplet-singlet separation.

In CH_2 the separation of the closed-shell singlet state $^1A_1(\sigma^2)$ and the open-shell state $^1B_1(\sigma\pi)$ is 28 kcal (with $^1A_1$ lower). As discussed above, vinyl substitution on $^1B_1(\sigma\pi)$ leads to a very large stabilization of the resulting $^1A''(3\pi)$ state, whereas vinyl substitution on $^1A_1(\sigma^2)$ leads to a small stabilization of the resulting $^1A'(2\pi)$ state. The result of these effects is that the $^1A''(3\pi)$ and $^1A'(2\pi)$ states are nearly degenerate, with a calculated separation of 2.3 kcal ($^1A'$ lower). (Our estimate of the residual correlation and basis corrections to our calculations is that the $^3A''$ and $^1A''$ states could move down with respect to the $^1A'$ state by as much as 2.5 kcal, leading to even more nearly degenerate singlet states.)

Also shown in Figure 3 are the excitation energies for the bisected, twisted geometry **2** of vinylmethylene and for cyclopropene. The triplet-singlet splitting for **2** is found to be only 0.4 kcal/mol, as expected for a $\sigma\pi$ 1,3-diradical. The triplet-singlet splitting for cyclopropene is found to be 119.9 kcal/mol (compare with 106.1 kcal/mol from similar calculations on ethylene[14]).

E. The Ring Opening of Cyclopropene. As shown in Figure 3, the two states which correlate directly with ground state cyclopropene are the twisted $^1A'(2\pi)$ state and the planar $^1A''(3\pi)$ state. The GVB orbitals for cyclopropene and these two states are shown in Figure 4.

In cyclopropene there are two basic types of bond pairs for the σ system. The first type (Figure 4A) is the CC σ bond be-

Table I. Total Energies for Vinylmethylene for Various Wave Functions[a]

Wave function	Basis	Geometries ${}^3A''$	Geometries ${}^1A''$	Geometries ${}^1A'$	Energies ${}^3A''$	Energies ${}^1A''$	Energies ${}^1A'$
HF	DZ	5	5	5	−115.77162	−115.74380	−115.73399
GVB(2)	DZ	5	5	5	−115.78984	−115.76500	−115.76939
GVB(2)-CI	DZ	5	5	5	−115.81669	−115.77557	−115.77317
GVB(2)	DZ		3	6		−115.78055	−115.77826
GVB(2)-CI	DZ		3	6		−115.78780	−115.78228
HF	DZd	4	3	6	−115.81458	−115.79666	−115.78991
GVB(2)	DZd	4	3	6	−115.83625	−115.81935	−115.83144
GVB(2)-CI	DZd	4	3	6	−115.85135	−115.82981	−115.83804
GVB(4)	DZd	4	3	6	−115.85975	−115.84327	−115.85538
SOGVB(4)	DZd	4	3		−115.86579	−115.84332	
GVB(4)-CI	DZd	4	3	6	−115.90144	−115.87908	−115.88271

[a] Energies in atomic units, 1 h = 27.2116 eV = 627.510 kcal/mol.

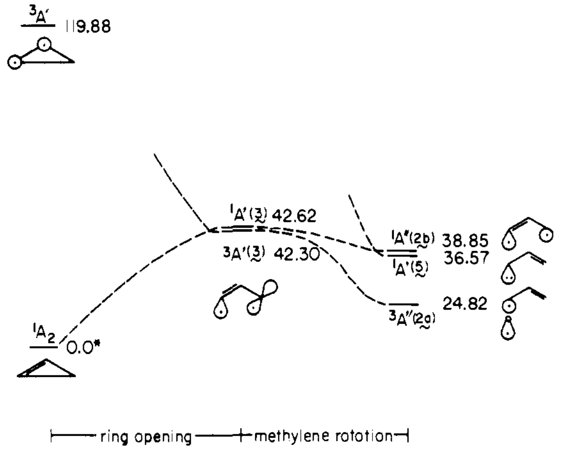


Figure 3. Electronic states of vinylmethylene (energies in kcal/mol) from GVB(4)-CI using DZd basis. CH bonds are omitted in the diagrams. The lowest energy pathway (not shown) involves simultaneous ring opening and methylene rotation.

tween centers 1 and 2 (the atoms connected by a double bond) and consists of one orbital centered on carbon 1 and hybridized $(sp^{1.6})$[15] toward carbon 2 and one orbital on carbon 2 hybridized $(sp^{1.6})$ toward carbon 1. As expected from the symmetry of the molecule, these two orbitals are mirror images of each other. The second type of bonding pair includes the two identical CC bonds between centers 3 and 1 and centers 3 and 2. In each pair one orbital is centered on carbon 3 with $sp^{3.8}$ hybridization, while its bonding partner, a carbon on 1 or 2, is $sp^{2.6}$ hybridized. Thus these pairs (sets B and C) consist of orbitals that contain a greater amount of p character than those of set A; they are less spherical and more directional. Furthermore, each orbital in the pair is not pointed directly at the opposing carbon, but instead is hybridized so as to point toward the outside of the ring. The resulting picture is that of a bowed or strained three-membered ring.

Stretching the CC bond of cyclopropene (carbons 1 and 3) to give the ring opened form—the twisted ${}^1A'$ state—we can see the effect strain had on the cyclopropene bonds. In sets A and B, the bonding pairs of the two CC σ bonds now consist of orbitals each pointing directly at the center of its bonding partner. The bowing of the σ bonds is no longer present. The left CC bond (the double-bonded atoms) is composed of two orbitals which are $sp^{1.4}$ and $sp^{1.7}$ hybrids on carbons 1 and 2, while the right CC bond is composed of $sp^{2.4}$ and $sp^{2.0}$ hybrids on carbons 3 and 2.

The σ-bond pair corresponding to the broken CC bond (set C) shows extensive rehybridization upon ring opening. The orbital on the left carbon is now an $sp^{5.4}$ hybrid (this is determined by the 135° bond angle), while the orbital on the right is a pure p orbital.

As the right methylene group is rotated to give the ${}^1A''$ state (geometry **3**), we see that the two CC σ bond pairs change very little. In addition, the unpaired σ orbital on carbon 1 does not change. The only substantial change in the system is that the p orbital previously in the plane is now perpendicular to the plane. We see further that this singly occupied π orbital is largely localized on the right carbon.

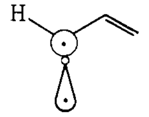
The π-bonding pairs for the three states are shown in set D. We see that ring opening has little effect on the π system. Rotation of the methylene group leads to only small amounts of delocalization.

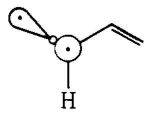
In the above discussion we have artificially separated the ring opening of cyclopropene into two modes—bond stretching and methylene rotation. In reality the reaction path near the saddle point no doubt involves simultaneous rotation and bond stretching. Thus the activation energy for ring opening—42.6 kcal/mol—shown in Figure 3 is probably a bit high; we expect the activation energy to lie between 38 and 42 kcal/mol. For an unstrained system, the CC bond energy would have been ~96 kcal/mol,[22a] and thus our calculations indicate a strain energy of ~53 kcal/mol for cyclopropene (empirical estimates are ~54 kcal/mol).[22b,23]

Our calculations show that the 1,3-diradical singlet state, ${}^1A''(3\pi)$, correlates well with ground state cyclopropene, and therefore suggest that ${}^1A''$ is the state most important to the isomerization. The "1,3-diradical" state ${}^1A''$ could possibly decay to the "carbene" states ${}^1A'(2\pi)$ and ${}^3A''(3\pi)$, leading to products characteristic of singlet and triplet methylene; however, in this case ring closure must then be preceded by reconversion to ${}^1A''$.

On the other hand, formation of vinylmethylenes by extrusion of nitrogen from a vinyl diazo compound should lead directly to ${}^1A'$, which may react as a carbene, or decay to ${}^3A''$, which would react as a triplet methylene. We would not expect significant formation of ${}^1A''$.

F. Comparison with ESR Spectra. Recent ESR experiments by Wasserman[16] and Chapman[17] have led to the observation of two triplet vinylmethylenes having the following zero-field





splitting parameters: $D = 0.4578$ (0.4130), $E = 0.0193$ (0.0176), and $D = 0.4093$ (0.4090), $E = 0.0224$ (0.0233).

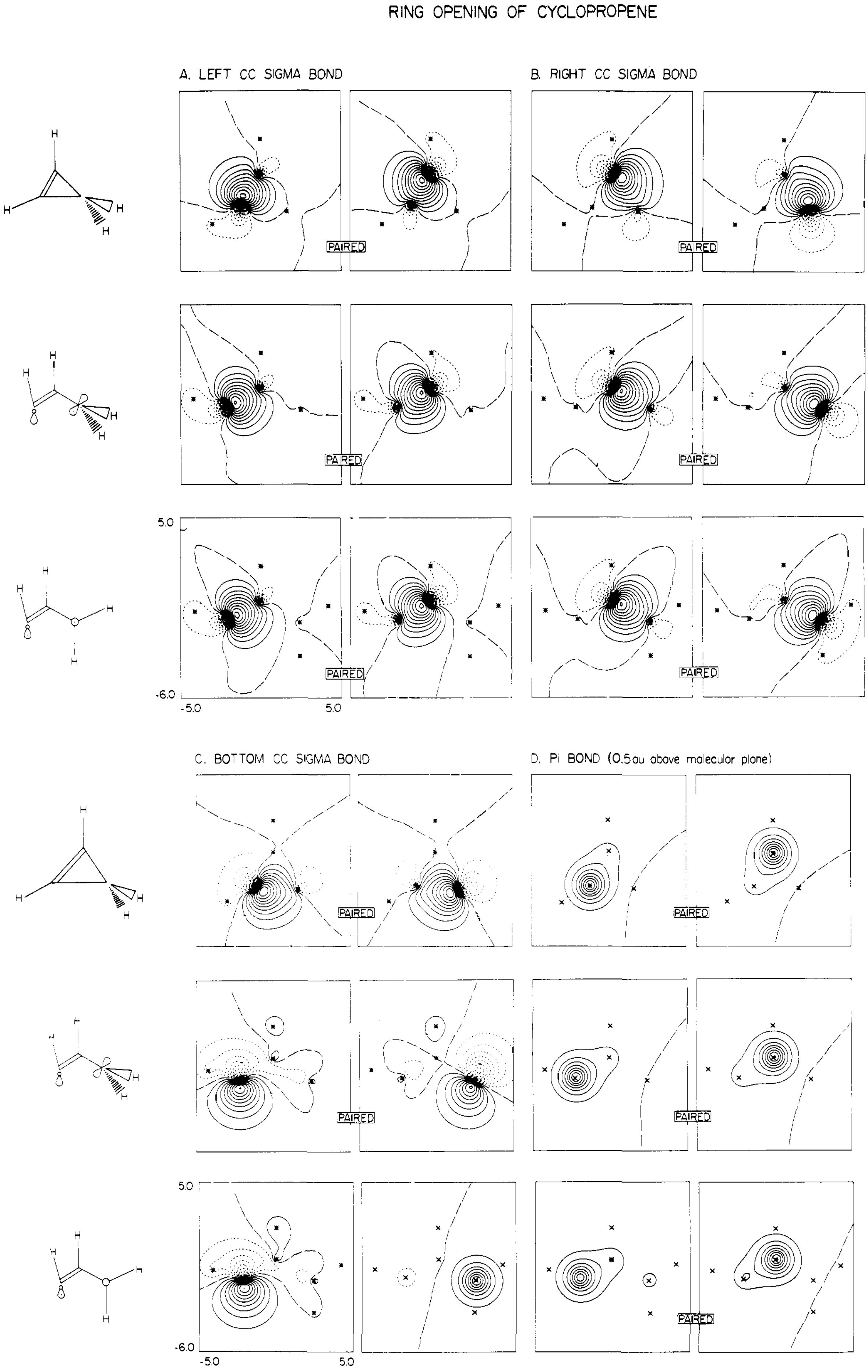


Figure 4. GVB orbitals for ring opening of cyclopropene. All carbon-carbon bond orbitals are shown for the geometries **1**, **2**, and **3**. Based on the GVB(4) wave functions using the DZd basis for **1** and **2** and the SOGVB(4) using the DZd basis wave function for **3**.

(Numbers in parentheses refer to Chapman's work.) The two triplets observed were interpreted[16] as the syn and anti $^3A''$ vinylmethylenes. The low values for the D parameters were interpreted as being indicative of a fully delocalized allyl π system.

The observation of two triplets in the ESR is in agreement with our calculations, which predict the two isomeric forms of the $^3A''$ to be nearly degenerate (separated by ~0.5 kcal) and separated by a substantial barrier (9 kcal/mol). Thus both isomers should be observable in the ESR.

Our calculations, however, do *not* support the interpretation of a fully delocalized allylic π system for vinylmethylene. In fact, our calculations suggest a considerable amount of localization. (We should emphasize here that without the electron correlation effects, that is, with the use of Hartree-Fock wave functions, we find delocalized MO's as expected for an allylic system; however, with inclusion of the electron correlation effects, this delocalization is drastically reduced.) In order to help resolve this apparent discrepancy, we sketch below a simplified calculation of the ESR D value for our wave function.

The D value for our total wave function Φ [see eq 1] can be written as

$$\begin{aligned} D &= \langle \Phi | \mathcal{H}_D | \Phi \rangle \\ &= c_1{}^2 \langle \psi_1 | \mathcal{H}_D | \psi_1 \rangle + c_2{}^2 \langle \psi_2 | \mathcal{H}_D | \psi_2 \rangle \\ &\qquad + 2 c_1 c_2 \langle \psi_1 | \mathcal{H}_D | \psi_2 \rangle \end{aligned} \tag{14}$$

in terms of our nonorthogonal wave functions where $\mathcal{H}_D$ is the spin-spin interaction Hamiltonian. Using the Mulliken approximation

$$\psi_1 \psi_2 = \tfrac{1}{2} S (\psi_1 \psi_1 + \psi_2 \psi_2) \tag{15}$$

for the cross terms we find

$$\begin{aligned} D = (c_1{}^2 + c_1 c_2 S) \langle \psi_1 | \mathcal{H}_D | \psi_1 \rangle \\ + (c_2{}^2 + c_1 c_2 S) \langle \psi_2 | \mathcal{H}_D | \psi_2 \rangle \end{aligned} \tag{16}$$

The second term of eq 16 represents the spin interaction between an electron in the σ orbital on carbon 1 with an electron in the π orbital on carbon 3. Consequently, the term should be negligible compared with $\langle \psi_1 | \mathcal{H}_D | \psi_1 \rangle$. Thus,

$$D = (c_1{}^2 + c_1 c_2 S) \langle \psi_1 | \mathcal{H}_D | \psi_1 \rangle \tag{17}$$

Assuming that the one-center integral here is the same (0.627 cm^{-1}) as for methylene[18] (neglecting then possible changes in the "methylene" HCC angles) leads to the following D values:

$D = 0.627$ cm^{-1} for methylene

$D = 0.438$ cm^{-1} for wave function 10

$D = 0.514$ cm^{-1} for wave function 10′

$D = 0.318$ cm^{-1} for wave function 12

where wave functions 10 and 10′ are vinylmethylene with equal and unequal bond lengths, respectively, and wave function 12 is vinylmethylene assuming perfect resonance (equal bond lengths). Our predicted[22] D of 0.44-0.51 is in reasonable agreement with the experimental value[16] of 0.43 (average of syn and anti isomers), especially considering the possible changes in the methylene HCC bond angle. Thus, because of the cross term $c_1 c_2 S \langle \psi_1 | \mathcal{H}_D | \psi_1 \rangle$, even a fairly localized π system can have substantially smaller zero-field parameters than the perfectly localized system.

On the basis of the line broadening of the ESR lines with temperature, Chapman[17] has suggested that the singlet state of vinylmethylene, **3**, is 0.2 kcal/mol above the triplet state. We find that the (vertical) singlet-triplet gap is 12 kcal/mol. Although distortions of the molecule may serve to decrease this splitting, we cannot accept the Chapman interpretation of the line broadening. Other possible interpretations of the experiments could be: changes in the D and E values due to varying population of vibrational levels as a function of temperature[24a] or rotation and oscillation in the matrix.[24b]

IV. Summary

Summarizing, our calculations predict that: (1) the allyl-type π system is strongly distorted by the presence of the unpaired σ electron leading to a methylene-like triplet, $^3A''$ (**4**), but a 1,3-diradical-like singlet state, $^1A''$ (**3**); (2) the lowest-lying singlet state of vinylmethylene has the form of a singlet methylene $^1A'$ (**6**) lying 12 kcal/mol above the $^3A''$ ground state, while the diradical singlet state $^1A''$ (**3**) lies at 14 kcal/mol; (3) the $^3A''$ ground state of **4** should exist in two geometrical forms (syn and anti) having nearly the same energy and separated by a large barrier (9 kcal); and (4) the 1,3-diradical singlet state has only a low barrier (2 kcal/mol) between the syn and anti forms, while the methylene triplet and singlet states have large barriers. These results suggest that the ring opening of cyclopropene proceeds directly to a diradical planar intermediate.

Appendix

A. Calculation of Resonance Energy. Since ψ_1 and ψ_2 are nonorthogonal, we will construct a new wave function $\overline{\psi}_2$ that is orthogonal to ψ_1. Thus,

$$\overline{\psi}_2 = (\psi_2 - S\psi_1)/\sqrt{1 - S^2} \tag{A1}$$

where

$$S = \langle \psi_1 | \psi_2 \rangle \tag{A2}$$

The molecular wave function A1 is now rewritten in terms of the orthogonal ψ_1 and $\overline{\psi}_2$ to give

$$\phi = \bar{c}_1 \psi_1 + \bar{c}_2 \overline{\psi}_2 \tag{A3}$$

and the solutions are given by

$$\begin{pmatrix} \overline{H}_{11} & \overline{H}_{12} \\ \overline{H}_{21} & \overline{H}_{22} \end{pmatrix} \begin{pmatrix} \bar{c}_1 \\ \bar{c}_2 \end{pmatrix} = \lambda \begin{pmatrix} \bar{c}_1 \\ \bar{c}_2 \end{pmatrix} \tag{A4}$$

where

$$\begin{aligned} \overline{H}_{11} &= \langle \psi_1 | \mathcal{H} | \psi_1 \rangle = E_1 \\ \overline{H}_{12} &= \langle \psi_1 | \mathcal{H} | \overline{\psi}_2 \rangle = (H_{12} - SE_1)/\sqrt{1 - S^2} \\ \overline{H}_{22} &= \langle \overline{\psi}_2 | \mathcal{H} | \overline{\psi}_2 \rangle = (E_2 - 2SH_{12} + S^2 E_1)/(1 - S^2) \\ &= E_2 + [S(E_1 + E_2) - 2H_{12}]S/(1 - S^2) \end{aligned}$$

Taking E_1 as our energy zero leads to the following expressions,

$$\begin{aligned} \overline{H}_{11} &= 0 \\ \overline{H}_{12} &= H_{12}/\sqrt{1 - S^2} \\ \overline{H}_{22} &= E_2 + [SE_2 - 2H_{12}]S/(1 - S^2) = E_2 + d = \delta \end{aligned}$$

where

$$d = [SE_2 - 2H_{12}]S/(1 - S^2)$$

The energy E_2 now represents the difference in energy between ψ_1 and ψ_2 before orthogonalization, while the energy δ is the difference in energy between ψ_1 and $\overline{\psi}_2$ (i.e., after orthogonalization). The solutions of eq A4 have energies

$$\lambda = E_1 + \tfrac{1}{2}\delta \pm \sqrt{\tfrac{1}{4}\delta^2 + H_{12}{}^2/(1 - S^2)} \tag{A5}$$

The lower energy solution uses the minus sign in eq A5, leading to an energy we can represent as

$$\lambda_1 = E_1 - E^{\text{res}}$$

where

$$E^{\mathrm{res}} = -RH_{12}/(1+S)$$

$$R = \left\{\sqrt{\left(S + \frac{E_2}{2H_{12}}\right)^2 + (1 - S^2)} - \left(S + \frac{E_2}{2H_{12}}\right)\right\} \Big/ (1 - S)$$

The quantity E^{res} is the stabilization or *resonance energy* of the state ψ_1 due to mixing in of state $\bar{\psi}_2$; $R = 1$ for $E_1 = E_2$ and decreases toward zero as $E_2 - E_1$ increases. The full resonance, $R = 1$, is obtained when $E_1 = E_2$ as, for example, in the allyl radical.

The upper state of **5** has energy

$$\lambda_2 = E_1 + \delta + E^{\mathrm{res}}$$

Thus in terms of the nonorthogonal functions the antiresonance energy is

$$E^{\mathrm{res}} + \delta - (E_2 - E_1)$$

B. Calculation of Zero-Field Parameter *D*. Expanding the molecular wave function Φ in terms of ψ_1 and ψ_2 leads to

$$\begin{aligned} D = \langle \Phi | \mathcal{H}_D | \Phi \rangle &= \langle c_1\psi_1 + c_2\psi_2 | \mathcal{H}_D | c_1\psi_1 + c_2\psi_2 \rangle \\ &= c_1^2 \langle \psi_1 | \mathcal{H}_D | \psi_1 \rangle + c_2 \langle \psi_2 | \mathcal{H}_D | \psi_2 \rangle + 2c_1c_2 \langle \psi_1 | \mathcal{H}_D | \psi_2 \rangle \end{aligned}$$

Using the Mulliken approximation that

$$\langle \psi_1 | \hat{p} | \psi_2 \rangle = \tfrac{1}{2} \langle \psi_1 | \psi_2 \rangle [\langle \psi_1 | \hat{p} | \psi_1 \rangle + \langle \psi_2 | \hat{p} | \psi_2 \rangle]$$

for a one-electron operator $\hat{p}$,

$$\begin{aligned} D = (c_1^2 + c_1c_2S) \langle \psi_1 | \mathcal{H}_D | \psi_1 \rangle \\ + (c_2^2 + c_1c_2S) \langle \psi_2 | \mathcal{H}_D | \psi_2 \rangle \end{aligned}$$

where

$$S = \langle \psi_1 | \psi_2 \rangle$$

For a totally localized wave function $c_1 = 1$ and $c_2 = 0$, and hence

$$D = \langle \psi_1 | \mathcal{H}_D | \psi_1 \rangle$$

The ψ_1 and ψ_2 in the above represent the many-electron wave function which we found to be $S = 0.630$ for the triplet state of vinylmethylene (DZ basis, equal bond lengths). Since the overlap of the singly occupied π orbital of ψ_1 with the singly occupied π orbital of ψ_2 is 0.631, we can consider ψ_1 as the product of $\sigma\pi_l$ and ψ_2 as $\sigma\pi_r$, and hence the use of the Mulliken approximation seems justified.

References and Notes

(1) (a) This work was partially supported by grants (CHE73-05132 and DMR74-04965) from the National Science Foundation; (b) John and Beverly Stauffer Foundation Fellow, 1975–1976.

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(19) These energies were evaluated by using the $^3A''(3\pi)$ orbitals in the singlet wave function leading to an energy increase of 1.8 eV, which we identify as $2K_{\sigma\pi}$ for **4**, and by using the $^1A''(3\pi)$ orbitals in the triplet wave function leading to an energy decrease of 0.1 eV, which we identify as $2K_{\sigma\pi}$ for **3**.

(20) The calculations in ref 14 included angular and in–out correlation of the bond pairs and p basis functions on the hydrogens, leading to a $^3B_1(\sigma\pi) - {}^1A_1(\sigma^2)$ splitting of 16 kcal; including only the dominant left–right correlations and no p functions on the H leads to 11.0 kcal (ref 6). Because of the replacement of one H by the vinyl group, such effects beyond the GVB-CI should be much smaller for vinylmethylene.

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(22) (a) For example: $D_0(C_2H_3 - C_2H_5) = \Delta H_f(C_2H_3) + \Delta H_f(C_2H_5) - \Delta H_f(\text{1-butene}) = 70 + 26 - 0 = 96$ kcal/mol; (b) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968.

(23) The good agreement between the calculated and experimental bond energies is partially due to a cancellation of errors. Even for highly correlated wave functions such as ours, the calculated bond energy may be 3–10 kcal low. However, to compare theoretical values with experiment, we should decrease the calculated value by a correction for changes in the zero-point energies. These corrections are in opposite directions and of approximately the same size.

(24) (a) S. I. Chan, private communication; (b) E. Wasserman, private communication.