

**Table VII.** Calculated and Experimental Electronic spectra (eV) of 1,4-Dithiin and Dibenz-1,4-dithiin

X $\alpha$ -SW		experimental
1,4-dithiin		
$\pi(6a_1) \rightarrow \pi^*(5b_1)$	4.55	
$\pi(6a_1) \rightarrow \pi^*(7a_1)$	4.66	4.59 <sup>a</sup>
$\pi(6a_1) \rightarrow \pi^*(5b_2)$	5.33	
$\pi(6a_1) \rightarrow \pi^*(8a_1)$	5.37	5.75
dibenzo-1,4-dithiin		
$\pi(11a_1) \rightarrow \pi^*(7a_2)$	3.92	
$\pi(8b_2) \rightarrow \pi^*(7a_2)$	4.25	4.13 <sup>b</sup>
$\pi(11a_1) \rightarrow \pi^*(9b_2)$	4.39	
$\pi(11a_1) \rightarrow \pi^*(10b_1)$	4.40	4.81
$\pi(11a_1) \rightarrow \sigma^*(12a_1)$	4.88	
$\pi(11a_1) \rightarrow \sigma^*(11b_1)$	5.14	
$\pi(11a_1) \rightarrow \sigma^*(13a_1)$	5.19	
$\pi(11a_1) \rightarrow \pi^*(8a_2)$	5.32	5.10
$\pi(11a_1) \rightarrow \pi^*(14a_1)$	5.62	
$\pi(11a_1) \rightarrow \pi^*(10b_2)$	5.80	5.93

<sup>a</sup> From ref 57. <sup>b</sup> From ref 50.

However, the VEH method would be more appropriate for this type of routine application, because it is very easy to use and it gives ab initio quality results with negligible computer time.

The negatives of the highest occupied molecular orbital (HOMO) energies for various compounds are presented in Table VI, together with the available experimental data on ionization potentials. Theoretical values differ from one method to another. However, the order of experimental values across compounds within a particular method are essentially preserved. The only exception occurs at dibenzo-1,4-dithiin. Our theoretical calculations predict that there is about a 0.5 eV increase in IP from 1,4-dithiin to dibenzo-1,4-dithiin, while the experimental data indicates a decrease of 0.35 eV. It is interesting to note that previous semiempirical SCF-MO-CI calculations<sup>50</sup> also predicted a net IP increase of 0.6 eV in going from 1,4-dithiin to dibenzo-1,4-dithiin.

For the calculation of spectroscopic quantities within the X $\alpha$  methodology, Slater has proposed the transition-state concept.<sup>9</sup>

Within this method, the ionization potentials are approximated as the energy of the orbital from which one-half unit of electronic charge has been removed. A SCF calculation is then performed for the transition state, which allows the orbital to relax and thus to overcome the basic deficiency in the KT treatment of ionization potentials. Calculated results using the transition state concept are also listed in Table V for 1,4-dithiin. The transition-state approach, indeed, gives the best overall results of all the methods.

The transition-state concept is also used to predict energies of optical transitions for both 1,4-dithiin and dibenzo-1,4-dithiin. As can be seen from Table VII the calculated results are in good agreement with experimental spectra. Importantly, the theoretical calculations provide the nature of virtual orbitals and the characteristics of electronic transitions.

### Conclusions

We have described the potential of the complementary use of theoretical tools to study geometrical structures, energies, conformations, and electronic structures of large molecules. A force field has been developed, on the basis of experimental and ab initio data, permitting molecular mechanics calculations to be performed on large molecules which is necessary for deriving structures within a negligible CPU time. Undoubtedly, the best set of parameters can only be reliably evaluated when new experimental values are available and the older ones redetermined. Nevertheless, we do expect that this is a reasonable force field and its predictions are at least qualitatively correct. A physical linkage has been made between the molecular mechanics method and the VEH method so that one can easily use molecular mechanics geometries along with the VEH approach in obtaining molecular orbitals and energies of ab initio quality with inexpensive CPU time. The X $\alpha$ -SCF method has been shown to produce very good optical transitions, and its development and applications for large organic molecules should be encouraged. It is our hope that this work will stimulate further theoretical and experimental research in this area.

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## Ab Initio Studies of the C<sub>3</sub>H<sub>4</sub> Surface. 1. SCF and CI Study of Structures and Stabilities of Isomers

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**Abstract:** SCF and CI calculations have been performed to study structures and stabilities of possible C<sub>3</sub>H<sub>4</sub> isomers. The stable singlet isomers considered are methylacetylene (0), allene (0.7), cyclopropene (22.5), propenylidene (43.6), and cyclopropylidene (63.3), where calculated relative energies in kcal/mol are given in parentheses. For reactive intermediates, vinylmethylenes, low-lying states for six possible conformations (trans or cis planar carbene; trans or cis planar and bisected diradicals) are studied. Our best results show that the <sup>3</sup>A'' states of trans and cis planar carbene structures are the most stable and isoenergetic lying 50.5 kcal/mol above the singlet methylacetylene. The lowest singlet vinylmethylene is the <sup>1</sup>A' state of planar carbene which lies 10 kcal/mol above the <sup>3</sup>A'' states of vinylmethylene. A study of the rotation of the CH<sub>2</sub> group revealed that both singlet and triplet bisected diradicals and also the triplet planar diradicals are not stable. A study of cis-trans isomerization for vinylmethylene conformers indicates 7-8 kcal/mol potential energy barriers for the singlet carbenes and diradicals and 5 kcal/mol for the triplet carbenes. From the analysis of the relative stabilities of the singlet C<sub>3</sub>H<sub>4</sub> isomers, a new possible mechanism that involves propenylidene emerged for the thermal cyclopropene to methylacetylene isomerization.

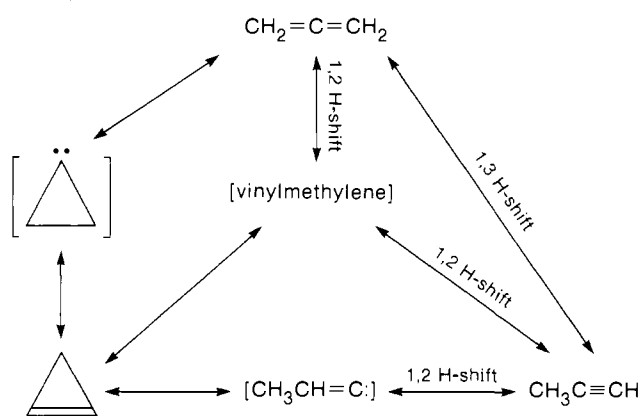
### I. Introduction

Many of the mechanisms for the thermal interconversion of isomers on the C<sub>3</sub>H<sub>4</sub> surface play a central role in organic chemistry. Thus, they not only serve as models for much larger

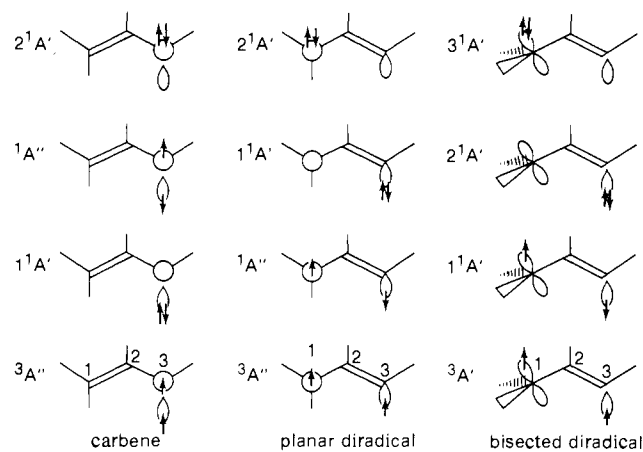
systems, but also provide a fundamental basis for reactions of hydrocarbons.

In Scheme I (see also Figure 1) a number of possible thermal reactions are shown that provide the basis for our ab initio study.

## Scheme I



## Scheme II



These mechanisms for thermal interconversions of cyclopropene, allene, and methacetylene involve ring opening and closing reactions, 1,2- and 1,3-hydrogen shifts, formation of double and triple bonds, and reactive intermediates like the carbene and diradical forms of vinylmethylene.

Although many experiments<sup>1-3</sup> have been conducted to elucidate kinetics and mechanisms for the possible reactions shown in Scheme I, their details have not been established.<sup>4</sup> For example, gas-phase pyrolysis experiments indicate that the conversion of allene to methacetylene goes through cyclopropene, and that cyclopropene undergoes bond fission to form an intermediate that produces allene and methacetylene.<sup>2d,e</sup> A convenient structure for this intermediate, proposed by Bailey et al.,<sup>2e</sup> is the 1,3-diradical form of vinylmethylene. Photochemical interconversion of the C<sub>3</sub>H<sub>4</sub> isomers is low-temperature matrices indicated that the stable isomers also interconvert through a common intermediate, for which the bisected diradical form of vinylmethylene has been proposed.<sup>3a</sup> Consequently, since a number of experimental studies propose a "vinylmethylene" intermediate, then a key to understanding the chemistry on the C<sub>3</sub>H<sub>4</sub> surface may be to characterize the structure of vinylmethylene. With this goal in mind, consider

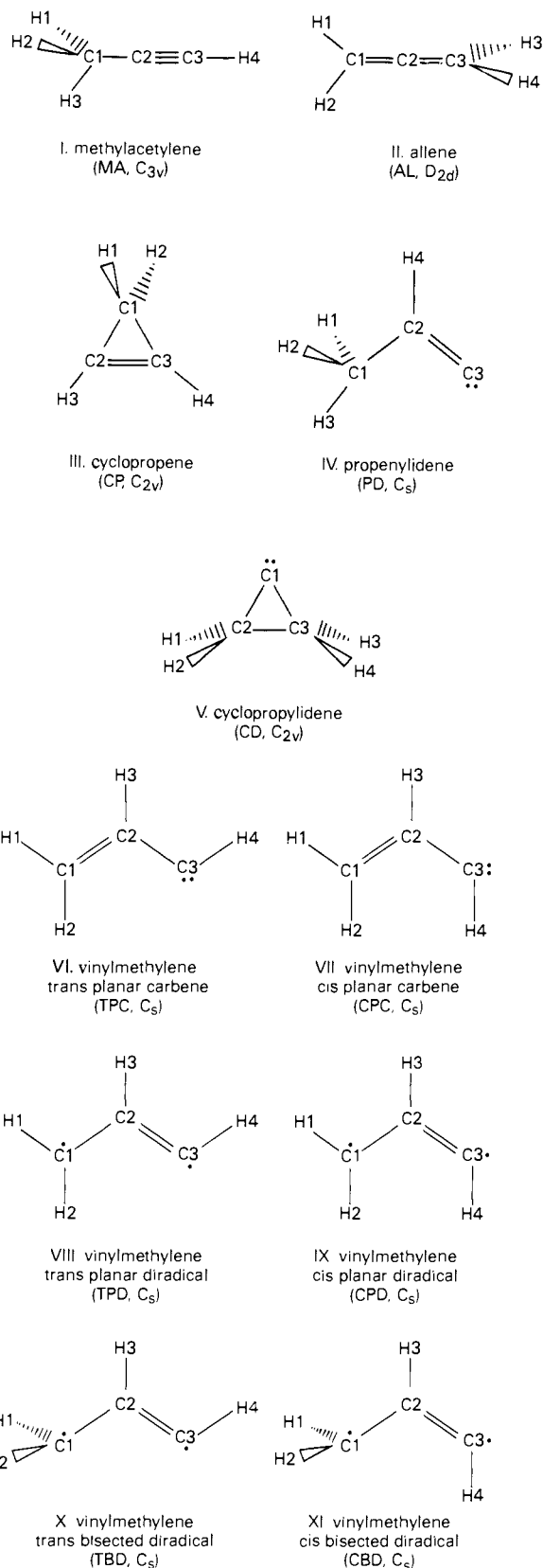


Figure 1. Structures of the possible C<sub>3</sub>H<sub>4</sub> isomers. Abbreviation and symmetry of each isomer are given in parentheses.

the possible structures which may be drawn for what is generally called vinylmethylene shown in Figure 1. The structure for vinylmethylene may be drawn as a carbene, a 1,3-planar diradical, or a bisected 1,3 diradical. The major difference between the carbene and the diradical structures is the location of the double bond that either forces vinylmethylene to have a divalent carbon or an electron localized on each of the carbon atoms C1 and C3.

(1) (a) Hutton, R. S.; Manion, M. L.; Roth, H. D.; Wessermann, E. *J. Am. Chem. Soc.* **1974**, *96*, 4680. (b) Palmer, G. E.; Bolton, J. R.; Arnold, D. R. *Ibid.* **1974**, *96*, 3708. (c) Chapman, O. L.; Chedekel, M.; Pacansky, J.; Rosenquist, N.; Roth, R.; Sheridan, R. S., unpublished.

(2) (a) York, E. J.; Dittmar, W.; Stevenson, R. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 5680. (b) Bradley, J. H.; West, K. O. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 967. (c) Lifshitz, A.; Frenklack, M.; Burcat, A. *J. Phys. Chem.* **1975**, *79*, 1148. (d) Walsh, R. J. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2137. (e) Bailey, I. M.; Walsh, R. *Ibid.* **1978**, *74*, 1146. (f) Hopf, H.; Priebe, H.; Walsh, R. *J. Am. Chem. Soc.* **1980**, *102*, 1210.

(3) (a) Chapman, O. L. *Pure Appl. Chem.* **1975**, 511. (b) Arnold, D. R.; Humphreys, R. W.; Leigh, W. J.; Palmer, G. E. *J. Am. Chem. Soc.* **1976**, *98*, 6225.

(4) Steinmetz, M. G.; Srinivasan, R.; Leigh, W. J. *Rev. Chem. Intermed.* **1983**, *5*, 57.

As shown in Figure 1, when the double bond is located between C1 and C2, a carbene structure is formed, and when between C2 and C3, planar or bisected diradical structures are possible. For each structure described above, there exist trans and cis isomers; cis isomers may be generated from trans isomers by rotating the C3H4 bond 180° about the C2C3 bond.

The possible electronic states for vinylmethylene shown in Scheme II are drawn to illustrate only that the two electrons on the divalent carbon C3 may be put into a  $\sigma$  or a  $\pi$  orbital, to form one triplet and three singlet electronic states. The four electronic states for the planar or bisected diradical are generated by distributing the two electrons between the available  $\sigma$  or  $\pi$  orbital on C1 or the  $\sigma$  orbital on C3.

A number of theoretical calculations<sup>5-9</sup> have been reported, but most of them deal with only a particular part of the C<sub>3</sub>H<sub>4</sub> surface. Since these interconversions are related, a systematic and uniform study of the C<sub>3</sub>H<sub>4</sub> surface is needed for a full understanding of mechanistic details. For such studies the first step is to locate possible local minima (stable isomers) so that the connecting paths and transition states between them may be determined. In this paper we report in detail a self-consistent-field (SCF) and configuration-interaction (CI) study for the structures and relative stabilities of the reasonable isomers on the C<sub>3</sub>H<sub>4</sub> surface;<sup>10</sup> the structures for those considered are sketched in Figure 1. Studies of the reaction paths will be reported separately in subsequent papers.

The thermal interconversions most likely occur on the singlet surface, and our main objective was the lowest singlet states. In addition we also calculated triplet states for those isomers which contain a divalent carbon in order to settle a question of the multiplicity of their ground states. For vinylmethylene, we have calculated a few low-lying states for each structure and transition states for cis-trans isomerizations in order to obtain some insight on the vinylmethylene potential energy surface. Finally, a new mechanism for the cyclopropene to methylacetylene rearrangement is proposed and discussed.

## II. Computational Details

Two contracted Gaussian basis sets were used throughout this study. The first is the 4-31G basis (431G)<sup>11</sup> which was used primarily in exploratory calculations. The second is a double-zeta ( $\zeta$ ) plus polarization function basis (DZP) that was employed in the calculations for the isoelectronic C<sub>2</sub>H<sub>2</sub>O system and gave reasonably accurate results.<sup>12</sup> The types and exponents are given in ref 12.

Structure optimizations were first carried out using SCF(431G) wave functions in appropriate symmetry with the gradient method.<sup>13</sup> The structures were then reoptimized with SCF(DZP) wave functions again using the gradient method. We did not carry out a CI structure optimization. As will be shown below, the SCF(DZP) structures and our best estimates of relative stabilities evaluated at these structures are in

**Table I.** Symmetry, State, Number of CSF's Used in SDCI(DZP) Calculations, and SCF Valence Electronic Configuration for Various Isomers

isomer <sup>a</sup>	sym	state	CSF's	valence configuration
1. MA	C <sub>3v</sub>	<sup>1</sup> A <sub>1</sub>	48 729 <sup>b</sup>	(4,5,6,7a <sub>1</sub> <sup>2</sup> ), (1,2e <sup>4</sup> )
2. AL	D <sub>2d</sub>	<sup>1</sup> A <sub>1</sub>	25 293 <sup>b</sup>	(3,4a <sub>1</sub> <sup>2</sup> ), (2,3b <sub>1</sub> <sup>2</sup> ), (1,2e <sup>4</sup> )
3. CP	C <sub>2v</sub>	<sup>1</sup> A <sub>1</sub>	24 609	(3,4,5,6a <sub>1</sub> <sup>2</sup> ), (2,3b <sub>1</sub> <sup>2</sup> ), (1,2b <sub>2</sub> <sup>2</sup> )
4. PD	C <sub>s</sub>	<sup>1</sup> A'	48 729	(4,.....9a <sup>2</sup> ), (1,2a'' <sup>2</sup> )
5. PD	C <sub>s</sub>	<sup>3</sup> A'	72 092	(4,.....8a <sup>2</sup> ,9a',10a'), (1,2a'' <sup>2</sup> )
6. CD	C <sub>2v</sub>	<sup>1</sup> A <sub>1</sub>	24 069	(3,4,5,6a <sub>1</sub> <sup>2</sup> ), (2,3b <sub>1</sub> <sup>2</sup> ), (1b <sub>1</sub> <sup>2</sup> ), (1a <sub>2</sub> <sup>2</sup> )
7. CD	C <sub>2v</sub>	<sup>3</sup> B <sub>1</sub>	34 986	(3,4,5a <sub>1</sub> <sup>2</sup> ,6a <sub>1</sub> ), (2,3b <sub>2</sub> <sup>2</sup> ), (1b <sub>1</sub> <sup>2</sup> ,2b <sub>1</sub> ), (1a <sub>2</sub> <sup>2</sup> )
8. TPC, CPC	C <sub>s</sub>	<sup>1</sup> A'	52 345	(4,.....10a <sup>2</sup> ), (1a'' <sup>2</sup> )
9. TPC, CPC	C <sub>s</sub>	<sup>3</sup> A''	73 124	(4,.....9a <sup>2</sup> ,10a'), (1a'' <sup>2</sup> ,2a'')
10. TPD, CPD	C <sub>s</sub>	<sup>1</sup> A''	62 117	(4,.....9a <sup>2</sup> ,10a'), (1a'' <sup>2</sup> ,2a'')
11. TBD, CBD	C <sub>s</sub>	<sup>1</sup> A'	60 700	(4,.....8a <sup>2</sup> ,9a',10a'), (1,2a'' <sup>2</sup> )
12. TBD, CBD	C <sub>s</sub>	<sup>3</sup> A'	72 092	(4,.....8a <sup>2</sup> ,9a',10a'), (1,2a'' <sup>2</sup> )
13. TS <sup>c</sup>	C <sub>1</sub>	<sup>1</sup> A	93 961	(4,.....11a <sup>2</sup> )
14. TS <sup>c</sup>	C <sub>1</sub>	<sup>3</sup> A	138 419	(4,.....10a <sup>2</sup> ,11a,12a)

<sup>a</sup>See Figure 1 for abbreviations of isomer names. <sup>b</sup>C<sub>s</sub> symmetry was used in CI because of the program limitation. <sup>c</sup>Used for transition-state calculations.

good agreement with the experimental structures and stabilities for methylacetylene, allene, and cyclopropene.

Correlation energy corrections on the total energy were estimated by CI calculations with the DZP basis only. The CI wave function includes all singly and doubly excited configurations with respect to a SCF configuration (SDCI(DZP)). For the open-shell SCF calculations, a partial interacting space was used for those configurations generated by double excitation from the closed shells into the virtual orbital space. All configurations are kept for excitations from the open shell and for the semi-internal excitations. The inner atomic shells, the 1s orbitals of three carbons, were frozen and the corresponding core complement virtual orbitals are excluded from the virtual orbital space. The numbers of configuration-state function (CSF) generated and SCF valence electronic configurations for each state of the isomers studied are listed in Table I. Quadruple excitation corrections were estimated by Davidson's formula<sup>14</sup> and the results will be designated as SDQCI.

Computer programs HONDO<sup>13</sup> and GAMESS<sup>15</sup> were used for the structure optimization, and the GENERALIZED DIRECT CI<sup>16</sup> and ALCHEMY II<sup>17</sup> programs were used for CI calculations.

## III. Results and Discussion

Geometrical parameters determined by the SCF(DZP) wave function for all of the states of the isomers studied are collected together in Table II, and total energies calculated in various approximations at these geometries are given in Table III. The SCF(431G) energies evaluated at the SCF(431G) geometries are also included in Table III for comparison.

**A. Methylacetylene, Allene, Cyclopropene.** Methylacetylene, allene, and cyclopropene are known to be stable isomers and all have a singlet closed-shell ground state. The SCF(DZP) results for the geometrical structures of these isomers (see Table II) are in good agreement with the experimental values,<sup>18</sup> differences being <0.02 Å and <1° for bond lengths and bond angles, respectively. From this comparison we infer that calculated geometrical parameters for other isomers should also have a similar accuracy.

Relative stabilities of these three isomers calculated in various approximations are given in Table IV and compared with the experimental values. The SDQCI results are in good agreement with the experimental values.<sup>6a</sup> The errors are less than 1.5 kcal/mol, which most likely represents the limitation of the wave functions employed in this study. We have repeated SCF(DZP) and SDCI(DZP) calculations at the experimental geometries to

(5) (a) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485. (b) Davis, J. H.; Goddard, W. A., III; Bergman, R. G. *Ibid.* **1976**, *98*, 4015; **1977**, *99*, 2424. (c) Sevin, A.; Arrand-Danon, L. *J. Org. Chem.* **1981**, *46*, 2346. (d) Feller, D.; Borden, W. T.; Davidson, E. R. *J. Phys. Chem.* **1983**, *87*, 483.

(6) (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Chem. Phys. Lett.* **1975**, *36*, 1. (b) Nomura, O.; Iwata, S. *J. Chem. Phys.* **1981**, *74*, 6830.

(7) (a) Shaad, L. J.; Burnelle, L. A.; Dressler, K. P. *Theor. Chim. Acta* **1969**, *15*, 91. (b) Dykstra, C. E. *J. Am. Chem. Soc.* **1977**, *99*, 2060. (c) Staemmler, V. *Theor. Chim. Acta* **1977**, *45*, 89. (d) Rauk, A.; Drake, A. F.; Mason, S. F. *J. Am. Chem. Soc.* **1979**, *101*, 2284. (e) Lam, B.; Johnson, R. P. *Ibid.* **1983**, *105*, 7479.

(8) (a) Peyerimhoff, S. D.; Buenker, R. *Theor. Chim. Acta* **1969**, *14*, 305. (b) Kao, J.; Radom, L. *J. Am. Chem. Soc.* **1978**, *100*, 379. (c) Wiber, K. B.; Wendoloski, J. J. *Ibid.* **1978**, *100*, 723. (d) Gordon, M. S. *Ibid.* **1980**, *102*, 7419.

(9) (a) Dillon, P. W.; Underwood, G. R. *J. Am. Chem. Soc.* **1974**, *96*, 779; **1977**, *99*, 2435. (b) Baird, N. C.; Taylor, K. F. *Ibid.* **1978**, *100*, 1333. (c) Pasto, D. J.; Haley, M.; Chipman, D. M. *Ibid.* **1978**, *100*, 5272. (d) Minato, T.; Osamura, Y.; Yamabe, S.; Fukui, K. *Ibid.* **1980**, *102*, 581.

(10) For the preliminary communication see: Honjou, N.; Pacansky, J. *Yoshimine, M. J. Am. Chem. Soc.* **1984**, *106*, 5361.

(11) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

(12) Tanaka, K.; Yoshimine, M. *J. Am. Chem. Soc.* **1980**, *102*, 7655.

(13) Dupuis, M.; Rys, J.; King, H. F. *J. Chem. Phys.* **1976**, *65*, 111. Dupuis, M.; King, H. F. *Ibid.* **1978**, *68*, 3998.

(14) Langhoff, S. R.; Davidson, E. R. *J. Int. Quantum Chem.* **1974**, *8*, 61.

(15) Dupuis, M.; Wendoloski, J. J.; Spangler, D. *Natl. Res. Comput. Chem. Software Cat.* **1980**, *1*, QG01.

(16) Siegbahn, P. E. M. *J. Chem. Phys.* **1979**, *70*, 5391; **1980**, *72*, 1647.

(17) Lengsfeld, B. H., III. *J. Chem. Phys.* **1980**, *73*, 382. Lengsfeld, B. H.; Liu, B. *Ibid.* **1981**, *75*, 478. Liu, B.; Yoshimine, M. *Ibid.* **1981**, *74*, 612.

(18) (a) Costain, C. C. *J. Chem. Phys.* **1958**, *29*, 864. (b) Maki, A. G.; Toth, R. A. *J. Mol. Spectrosc.* **1965**, *17*, 136. (c) Stigliani, W. M.; Laure, V. W.; Li, J. C. *J. Chem. Phys.* **1975**, *62*, 1980.

Table II. Geometrical Parameters Determined by SCF(DZP) Wave Functions for the Low-Lying States of the Various C<sub>3</sub>H<sub>4</sub> Isomers.<sup>a</sup>

	methylacetylene (C <sub>3v</sub> )		allene (D <sub>2d</sub> )			methylacetylene (C <sub>3v</sub> )		allene (D <sub>2d</sub> )	
	<sup>1</sup> A <sub>1</sub>		<sup>1</sup> A <sub>1</sub>			<sup>1</sup> A <sub>1</sub>		<sup>1</sup> A <sub>1</sub>	
C1C2	1.472	(1.459)	1.302	(1.308)	C3H4	1.060	(1.056)		
C2C3	1.191	(1.206)			H1C1C2	110.2	(110.3)	121.0	(120.9)
C1H1	1.084	(1.105)	1.077	(1.087)					
cyclopropene (C <sub>2v</sub> )					cyclopropene (C <sub>2v</sub> )				
	<sup>1</sup> A <sub>1</sub>		<sup>1</sup> A <sub>1</sub>			<sup>1</sup> A <sub>1</sub>		<sup>1</sup> A <sub>1</sub>	
C1C2	1.500	(1.509)			C1C2C3	64.7	(64.6)		
C2C3	1.281	(1.296)			H1C1C2	119.7	(119.1)		
C1H1	1.084	(1.088)			H3C2C3	150.1	(149.9)		
C2H3	1.070	(1.072)			H1C1H2	113.6	(114.6)		
cyclopropylidene (C <sub>2v</sub> )					cyclopropylidene (C <sub>2v</sub> )				
	<sup>1</sup> A <sub>1</sub>		<sup>3</sup> B <sub>1</sub>			<sup>1</sup> A <sub>1</sub>		<sup>3</sup> B <sub>1</sub>	
C1C2	1.497	1.451	1.510	1.510	C1C2C3	59.4	65.7	127.2	125.3
C1C3	1.483	1.574			H1C1C2	115.9	119.9	110.1	110.2
C2C3			1.298	1.310	H3C1C2			111.1	111.4
C1H1	1.079	1.079	1.084	1.087	H4C2C3			112.1	118.0
C1H3			1.083	1.083	H1C1C2C3	111.0	104.6	120.2	120.9
C2H4			1.085	1.083					
vinylmethylene planar carbene (C <sub>s</sub> )					vinylmethylene planar carbene (C <sub>s</sub> )				
	trans <sup>1</sup> A'		cis <sup>1</sup> A'			trans <sup>1</sup> A'		cis <sup>1</sup> A'	
C1C2	1.341	1.340	1.332	1.334	C1C2C3	117.1	123.6	124.4	124.7
C2C3	1.453	1.461	1.440	1.440	H1C1C2	119.9	121.6	121.6	121.9
C1H1	1.076	1.078	1.076	1.078	H2C1C2	122.4	121.7	121.2	121.0
C1H2	1.079	1.079	1.076	1.076	H3C2C3	124.3	117.8	116.2	116.1
C2H3	1.081	1.079	1.080	1.079	H4C3C2	109.2	106.9	129.6	129.6
C3H4	1.097	1.097	1.075	1.075					
vinylmethylene planar diradical (C <sub>s</sub> )					vinylmethylene planar diradical (C <sub>s</sub> )				
	trans <sup>1</sup> A''		cis <sup>1</sup> A''			trans <sup>1</sup> A''		cis <sup>1</sup> A''	
C1C2		1.462		1.467	C1C2C3		125.2		125.4
C2C3		1.317		1.317	H1C1C2		120.5		120.7
C1H1		1.073		1.074	H2C1C2		120.3		120.3
C1H2		1.073		1.073	H3C2C3		118.0		117.9
C2H3		1.083		1.080	H4C3C2		134.5		136.0
C3H4		1.073		1.075					
vinylmethylene bisected diradical (C <sub>s</sub> )					vinylmethylene bisected diradical (C <sub>s</sub> )				
	trans <sup>1</sup> A'		cis <sup>3</sup> A'			trans <sup>1</sup> A'		cis <sup>3</sup> A'	
C1C2	1.487	1.491	1.483	1.490	C1C2C3	125.4	125.6	125.0	125.8
C2C3	1.312	1.311	1.310	1.308	H1C1C2	119.7	118.9	120.1	119.3
C1H1	1.076	1.077	1.076	1.077	H3C2C3	117.1	117.4	117.3	117.5
C2H3	1.084	1.083	1.086	1.084	H4C3C2	133.4	134.5	134.2	135.2
C3H4	1.075	1.075	1.074	1.075	H1C1C2C3	99.2	103.0	99.2	101.9

<sup>a</sup> See Figure 1 for a schematic of the structures. Bond lengths are in angstroms and bond angles are in degrees. Values in parentheses are experimental values taken from ref 18a, 18b, and 18c for methylacetylene, allene, and cyclopropene, respectively.

measure the geometrical effect on the stability, which turned out to be negligible. This gives a justification for the use of SCF(DZP) optimized geometries. From these observations we may conclude that our SDQCI(DZP) results for the relative stabilities of the other stable isomers should be accurate to within 2 kcal/mol.

It is of interest to note that the geometrical effects on the SCF results (about 0.8 kcal/mol) are slightly larger than those on the CI results (about 0.2 kcal/mol). This may explain the differences between our SCF(431G) results (1.2 and 36.5 kcal/mol for allene and cyclopropene, respectively) and the previous SCF(431G) results of Binkley et al. (0.8 and 36.4 kcal/mol)<sup>6a</sup> since they used the SCF(STO3G) optimized geometries. We also note that the polarization and correlation effects on the relative energy of cyclopropene are substantial, being 9.4 and 4.5 kcal/mol, respectively. This may be due to the fact that cyclopropene is a highly strained system.

**B. Ground States of Cyclopropylidene and Propenylidene.** The two known carbenes on the C<sub>3</sub>H<sub>4</sub> surface are cyclopropylidene

and propenylidene (see Figure 1). There have been no experimental data available on the multiplicity of the ground state for either of these carbenes. Several theoretical calculations have been reported for cyclopropylidene, but there is a disparity in their findings over the ground-state electronic structure. In 1978, Pasto et al.<sup>9c</sup> reported that a triplet state is 8.4 kcal/mol lower in energy than a singlet state. In their study a RHF(431G) wave function was used for the singlet state, but a UHF(431G) wave function was used for the triplet state. On the other hand, Baird et al.<sup>9b</sup> found that the triplet state is 6.4 kcal/mol higher than the singlet state. They employed the STO3G basis but used RHF wave functions for both singlet and triplet states. In addition, 3d functions were added on the divalent carbon and a two CSF CI calculation for a singlet state was performed for determination of the singlet-triplet energy separation. In 1980, Minato et al.<sup>9d</sup> reported a first-order CI calculation with the STO3G basis on cyclopropylidene, which predicted the triplet state is lower. In general, the wave functions employed in all previous calculations

**Table III.** Total Energies in Hartrees of the Low-Lying States of the C<sub>3</sub>H<sub>4</sub> Isomers Calculated in Various Approximations and Dominant CI Coefficients (C<sub>0</sub>).<sup>a</sup>

isomer	state	SCF (431G)	SCF (DZP)	SDCI (DZP)	SDQCI (DZP)	C <sub>0</sub>
1. MA	<sup>1</sup> A <sub>1</sub>	0.700 65	0.892 61	0.269 47	0.313 83	0.939 31
2. AL	<sup>1</sup> A <sub>1</sub>	0.698 77	0.888 87	0.267 04	0.312 66	0.937 74
3. CP	<sup>1</sup> A <sub>1</sub>	0.642 57	0.849 46	0.232 86	0.277 91	0.939 41
4. PD	<sup>1</sup> A'	0.632 71	0.830 86	0.200 00	0.244 39	0.937 95
	<sup>3</sup> A'	0.588 76	0.779 53	0.134 53	0.176 47	0.939 08
5. PD	<sup>3</sup> A'	0.589 34	0.780 84	0.136 24	0.178 46	0.938 73
	<sup>1</sup> A'	0.132 29	0.830 19	0.199 75	0.244 38	0.937 68
6. CD	<sup>1</sup> A <sub>1</sub>	0.584 05	0.795 91	0.168 67	0.212 58	0.939 25
	<sup>3</sup> B <sub>1</sub>		0.784 69	0.143 72	0.184 16	0.942 00
7. CD	<sup>3</sup> B <sub>1</sub>	0.590 51	0.792 48	0.152 33	0.192 90	0.941 94
	<sup>1</sup> A <sub>1</sub>		0.786 71	0.159 30	0.203 29	0.939 12
8. TPC	<sup>1</sup> A'	0.605 31	0.807 66	0.174 13	0.217 87	0.938 42
	<sup>3</sup> A''		0.820 89	0.176 35	0.217 99	0.939 61
	<sup>1</sup> A''		0.771 10	0.133 39	0.176 42	0.938 73
9. CPC	<sup>1</sup> A'	0.601 62	0.804 27	0.171 02	0.214 98	0.938 15
	<sup>3</sup> A''		0.823 73	0.179 02	0.220 65	0.939 59
	<sup>1</sup> A''		0.769 44	0.132 08	0.175 41	0.938 36
10. TPD	<sup>1</sup> A''	0.623 60	0.816 79	0.172 43	0.212 88	0.941 42
	<sup>3</sup> A''		0.826 36	0.187 01	0.230 24	0.938 16
	<sup>1</sup> A'		0.762 29	0.130 13	0.174 60	0.937 60
11. CPD	<sup>1</sup> A''	0.621 93	0.814 60	0.169 79	0.210 15	0.941 47
	<sup>3</sup> A''		0.826 03	0.186 76	0.230 04	0.938 09
	<sup>1</sup> A'		0.760 06	0.128 58	0.173 35	0.937 29
12. TBD	<sup>1</sup> A'	0.61733	0.809 92	0.165 23	0.206 17	0.940 62
	<sup>3</sup> A'		0.812 87	0.169 01	0.210 31	0.940 23
13. CBD	<sup>1</sup> A'	0.616 08	0.808 67	0.165 36	0.207 70	0.938 78
	<sup>3</sup> A'		0.812 26	0.168 20	0.209 49	0.940 21
14. TPC	<sup>3</sup> A''	0.64552	0.836 36	0.191 93	0.233 40	0.939 88
	<sup>1</sup> A'		0.791 19	0.155 96	0.199 22	0.938 83
	<sup>1</sup> A''		0.791 06	0.152 51	0.195 12	0.939 21
15. CPC	<sup>3</sup> A''	0.64556	0.836 48	0.191 90	0.233 33	0.939 91
	<sup>1</sup> A'		0.790 51	0.155 42	0.198 75	0.938 75
	<sup>1</sup> A''		0.788 52	0.149 61	0.192 20	0.939 18
16. TBD	<sup>3</sup> A'	0.62075	0.812 90	0.168 98	0.210 22	0.940 31
	<sup>1</sup> A'		0.809 91	0.165 15	0.206 03	0.940 71
17. CBD	<sup>3</sup> A'	0.62027	0.812 26	0.168 25	0.209 53	0.940 24
	<sup>1</sup> A'		0.808 62	0.165 37	0.207 71	0.938 78

<sup>a</sup>All energies are calculated at the SCF(DZP) geometries given in Table II except the SCF(431G) energies which are calculated at the SCF(431G) geometries; only fractional parts are given and integer parts for SCF and CI are -115 and -116, respectively. Each geometry is specified by the isomer and state listed first; see Figure 1 for the abbreviations for the names of the isomers.

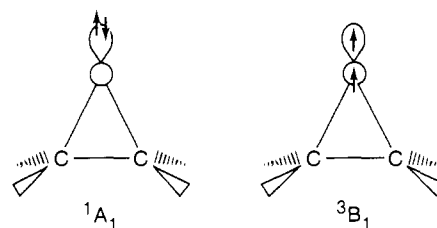
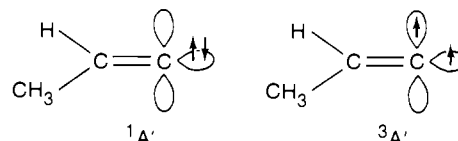
**Table IV.** Energies (kcal/mol) of Allene and Cyclopropene Relative to Methylacetylene Calculated at SCF(DZP) and Experimental (exptl) Geometries<sup>a</sup> in Various Approximations

	allene		cyclopropene	
	SCF(DZP)	exptl	SCF(DZP)	exptl
SCF(431G)	1.2		36.5	
SCF(DZP)	2.3	1.6	27.1	26.4
SDCI(DZP)	1.5	1.4	23.0	22.7
SDQCI(DZP)	0.7	0.8	22.5	22.4
experimental		2.1 <sup>b</sup>		22.3 <sup>b</sup>

<sup>a</sup>Reference 18. <sup>b</sup>Reference 6a.

may be too limited for any quantitative determination of the triplet-singlet separation.

To investigate this problem further, we have carried out a structure optimization for the lowest singlet (<sup>1</sup>A<sub>1</sub>) and triplet (<sup>3</sup>B<sub>1</sub>) formed by distributing the electrons between the σ or π orbitals on the divalent carbon as shown in Scheme III and described in Table I. Results shown in Table V clearly predict that cyclopropylidene has a singlet ground state with the triplet state lying 12 kcal/mol above. It is of interest to note that there are noticeable differences in structure between these two states (see Table II). Compared with the <sup>3</sup>B<sub>1</sub> structure, the <sup>1</sup>A<sub>1</sub> structure has a 0.05 Å longer C1-C2 bond length, a 0.09-Å shorter C2-C3 bond length, and a 6° smaller C1C2C3 bond angle. This suggests that the <sup>1</sup>A<sub>1</sub> state may have a larger ring strain than the <sup>3</sup>B<sub>1</sub> state and

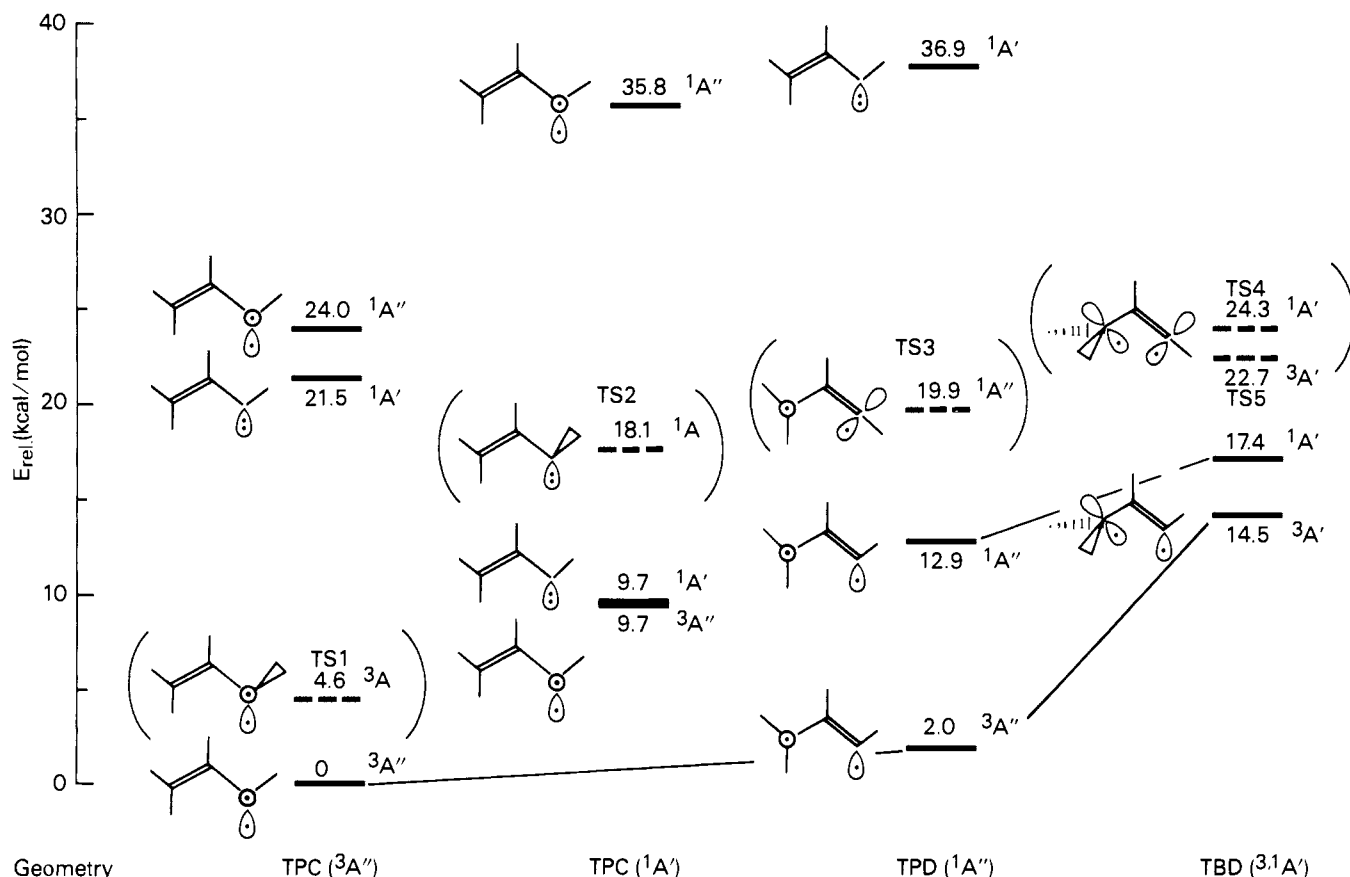
**Scheme III****Scheme IV****Table V.** Relative Energies (kcal/mol) of the Lowest Singlet and Triplet States for Cyclopropylidene and Propenylidene Calculated at SCF(DZP) Singlet and Triplet Geometries in Various Approximations

geometry	state	SCF- (431G)	SCF- (DZP)	SDCI- (DZP)	SDQCI- (DZP)
cyclopropylidene					
<sup>1</sup> A <sub>1</sub>	<sup>1</sup> A <sub>1</sub>	0.0	0.0	0.0	0.0
<sup>1</sup> A <sub>1</sub>	<sup>3</sup> B <sub>1</sub>		7.0	15.7	17.8
<sup>3</sup> B <sub>1</sub>	<sup>1</sup> A <sub>1</sub>		5.8	5.9	5.8
<sup>3</sup> B <sub>1</sub>	<sup>3</sup> B <sub>1</sub>	-4.1	2.2	10.3	12.4
propenylidene					
<sup>1</sup> A'	<sup>1</sup> A'	0.0	0.0	0.0	0.0
<sup>1</sup> A'	<sup>3</sup> A'	27.6	32.2	41.1	42.6
<sup>3</sup> A'	<sup>1</sup> A'	0.3	0.4	0.2	0.0
<sup>3</sup> A'	<sup>3</sup> A'	27.2	31.4	40.0	41.4

the polarization function effect could be more significant for the <sup>1</sup>A<sub>1</sub> state. Indeed, the polarization effect is substantial, 6.3 kcal/mol for the singlet-triplet separation (see Table V). In fact, at the SCF(431G) level the triplet state appears to be lower in energy. As expected, the correlation energy effect is also significant, 10 kcal/mol. The importance of these effects on the singlet-triplet separation calculation is also clearly reflected in the fact that the calculation of Baird et al.<sup>9b</sup> which includes some of both effects yielded a separation of 6.4 kcal/mol although the basis set used was minimal.

For propenylidene we have also performed a structure optimization for both the lowest singlet and triplet states, illustrated in Scheme IV. Structures and total energies calculated are shown in Tables II and III, respectively, and the relative energies calculated in various approximations are listed in Table V. Our results clearly show that the closed-shell <sup>1</sup>A' state is the most stable and the <sup>3</sup>A' state lies 41 kcal/mol above it. Because the C2-C3 π bond is occupied, the lowest triplet state has a <sup>3</sup>A' symmetry (a'a' configuration). This may explain the relatively large singlet-triplet separation compared with that in cyclopropylidene where the triplet state has an a'a'' configuration. We note that the structures are essentially the same for both states, and the polarization and correlation effects on the separation are significant, being 4 and 10 kcal/mol, respectively.

**C. Vinylmethylene: Energies of Isomers.** It has been suggested that vinylmethylene may play a central role in the interconversions on the C<sub>3</sub>H<sub>4</sub> surface. Thus, we have carried out a rather extensive calculation for the low-lying states of the possible stable isomers (see Scheme II). The six possible structures for vinylmethylene are drawn and labeled in Figure 1 to facilitate further discussion. They are trans and cis planar carbene (TPC and CPC, <sup>1</sup>A', <sup>3</sup>1A''), trans and cis planar diradicals (TPD and CPD, <sup>3</sup>1A''), and trans and cis bisected diradicals (TBD and CBD, <sup>3</sup>1A'), where abbreviations and possible states are given in parentheses. Structures and total energies are listed in Table II and III, respectively, and SDQCI energy results for various conformations of vinylmethylene



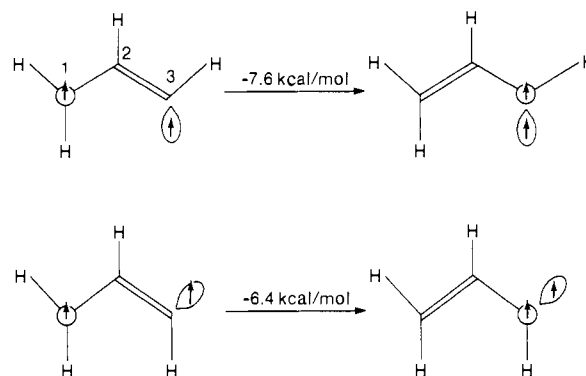
**Figure 2.** SDQCI vertical excitation energies calculated at the five SCF(DZP) geometries of trans vinylmethylene (see Table II for geometrical parameters). All energies are relative to the  $^3A''$  state of trans planar carbene. The states in parentheses are the transition states for the cis-trans isomerization and their geometries are different (see Table VII). For the bisected diradical, the singlet and triplet states are given in a column since their geometries are essentially the same.

are summarized in Figure 2 for the trans isomers and in Figure 3 for the cis isomers. Within each figure the geometry was optimized for the structure and state labeled at the bottom of the drawing. Other states shown in the same column were calculated at the labeled geometry.

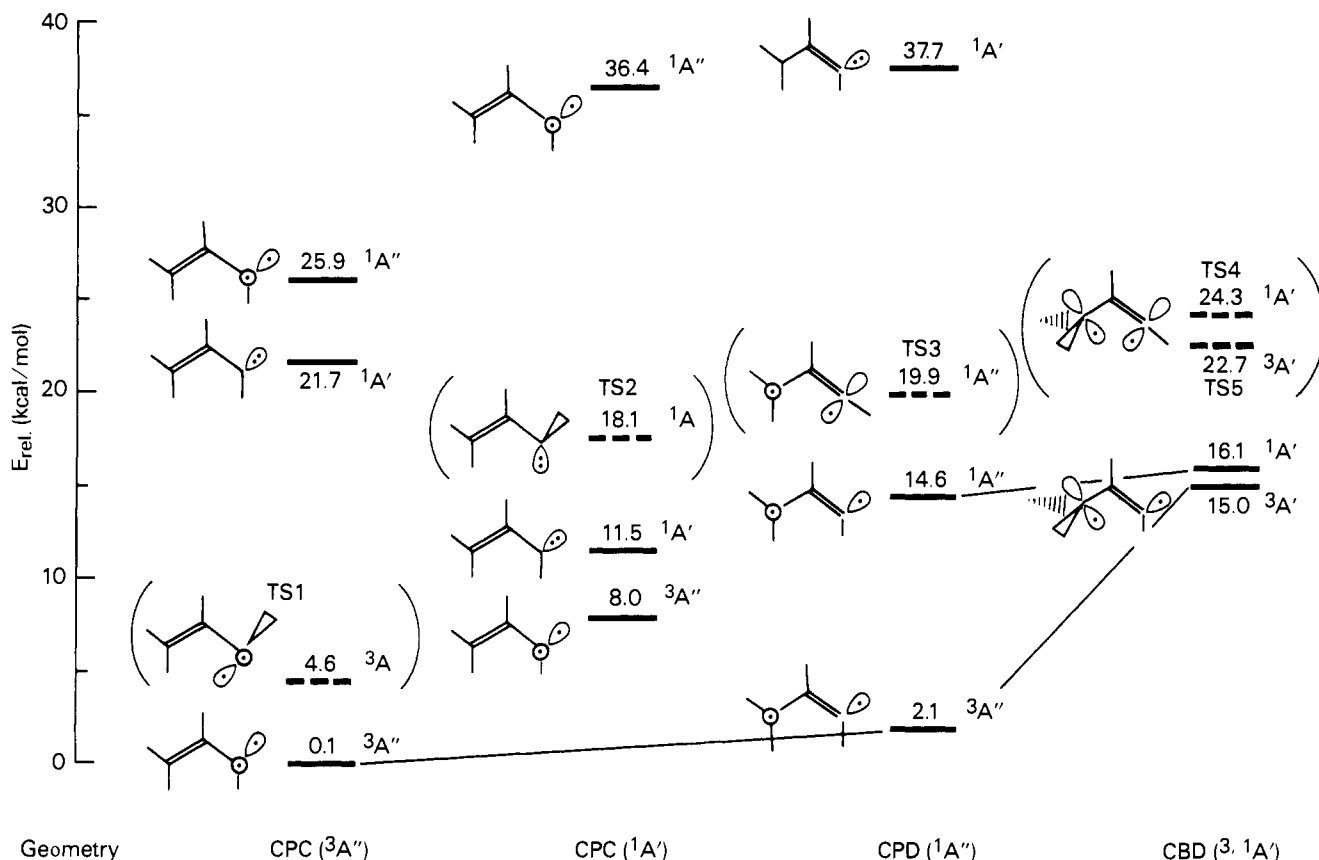
Structure optimizations with the symmetry-constrained SCF method yielded four and six possible local minima for triplet and singlet states, respectively. The most stable are the  $^3A''$  states of trans and cis planar carbene structures, which are isoenergetic and lie 50.5 kcal/mol above the  $^1A_1$  state of methylacetylene. For the singlet states, the closed-shell  $^1A'$  state of trans planar carbene is the lowest followed by the  $^1A'$  state of cis planar carbene. The SDQCI results place these two states 9.7 and 11.5 kcal/mol above the  $^3A''$  states. A few kcal/mol above the  $^1A'$  states of the planar carbene lie the  $^1A''$  states of trans and cis planar diradicals; their relative energies with respect to the  $^3A''$  state of the planar carbene are 12.9 and 14.6 kcal/mol, respectively. The structures mentioned above are local minima, at least in the SDQCI approximation.

**Stabilities of the Bisected Diradical toward Rotation of CH<sub>2</sub> about the C1-C2 Bond.** Since the singlet and triplet bisected diradicals have relative energies ranging from 15 to 17 kcal/mol above the  $^3A''$  state of the planar carbene, as shown in Figures 2 and 3, the total energy as a function of rotation of the methylene group was calculated to determine whether the bisected structures represented stable minima. In Figures 2 and 3 this path is highlighted by a solid line, and in Figures 4, 5, and 6 the calculated reaction paths are shown for the triplet trans, triplet cis, and singlet isomers, respectively. The approximate reaction paths were determined using the SCF(431G) wave functions by rotating the CH<sub>2</sub> group in increments of 5° from the bisected position and performing a structure optimization; thus, these are maximum gradient paths. Both singlet and triplet bisected diradicals are unstable with respect to a rotation of the methylene group about the C1-C2 bond. For the triplet systems, the rotation paths proceed from the bisected diradicals, through a planar diradical,

**Scheme V**



to a planar carbene. The points located in the vicinity of the middle of Figures 4 and 5 are interesting because, relative to the point at the right side of the figures, they represent the energy required to shift the double bond from the planar diradical structure to the planar carbene structure in the triplet state, i.e., as shown in Scheme V. The direct consequence of the 6-8 kcal/mol exothermic change in energy is that within the SCF(431G) approximation the planar triplet diradicals are also unstable with respect to the triplet carbene. The rotation of the CH<sub>2</sub> group for the cis system appears to be slightly hindered, taking 23 steps to reach the planar diradical and then taking only a few steps to reach the planar carbene structure. For the trans system, the reaction path is smoother, reaching a planar diradical geometry in 15 steps, but the transition to a planar carbene needs more steps. In both cases there are no barriers for the pathways between planar diradicals and carbene structures. We note that these reaction paths should be reliable since the polarization and correlation energy effects on the relative energies of the triplet



**Figure 3.** SDQCI vertical excitation energies calculated at the five SCF(DZP) geometries of cis vinylmethylene (see Table II for geometrical parameters). All energies are relative to the  $^3A''$  state of trans planar carbene. The states in parentheses are the transition states for the cis-trans isomerization and their geometries are different (see Table VII). For the bisected diradical, the singlet and triplet states are given in a column since their geometries are essentially the same.

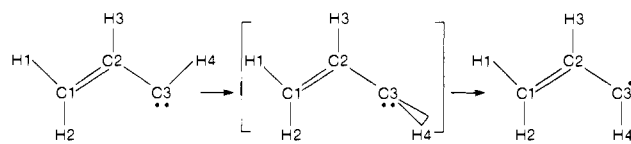
**Table VI.** Relative Energies (kcal/mol) with Respect to the Lowest  $^3A''$  State for Low-Lying States of Various Conformations of Vinylmethylene

conformation	state	SCF-(431G)	SCF-(DZP)	SDCI-(DZP)	SDQCI-(DZP)
TPC $^3A''$	$^3A''$	0.0	0.0	0.0	0.0
	$^1A'$		28.3	22.6	21.5
	$^1A''$		28.4	24.7	24.0
TBD $^3A'$	$^3A'$	15.5	14.7	14.4	14.6
	$^1A'$		16.6	16.8	17.2
TPC $^1A'$	$^3A''$		9.7	9.8	9.7
	$^1A'$	25.2	18.0	11.2	9.7
TPD $^1A''$	$^1A''$		41.0	36.7	35.8
	$^3A''$		6.3	3.1	2.0
TBD $^1A'$	$^1A''$		46.5	38.8	36.9
	$^1A''$	13.8	12.3	12.2	12.9
CPC $^3A''$	$^3A'$		14.7	14.4	14.5
	$^1A'$	17.7	16.6	16.8	17.4
CBD $^3A'$	$^3A''$	0.0	-0.1	0.0	0.1
	$^1A''$		30.0	26.6	25.9
CPC $^1A'$	$^3A''$	15.9	15.1	14.9	15.0
	$^1A'$		17.4	16.7	16.1
CPD $^1A''$	$^3A''$		7.9	8.1	8.0
	$^1A'$	27.6	20.1	13.1	11.5
CBD $^1A'$	$^1A''$		42.0	37.6	36.4
	$^3A''$		6.5	3.2	2.1
CPD $^1A'$	$^1A'$		47.9	39.8	37.7
	$^1A''$	14.8	13.6	13.9	14.6
CBD $^1A'$	$^3A'$		15.1	14.9	15.0
	$^1A'$	18.5	17.4	16.7	16.1

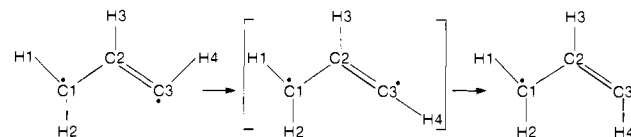
system are small. For example, relative energies of triplet trans bisected diradicals are 15.5 and 14.6 kcal/mol in the SCF(431G) and SDQCI approximations, respectively.

Similar calculations on the paths between singlet bisected and planar diradicals (see Figures 2, 3, and 6 for the rotation paths)

**Scheme VI**

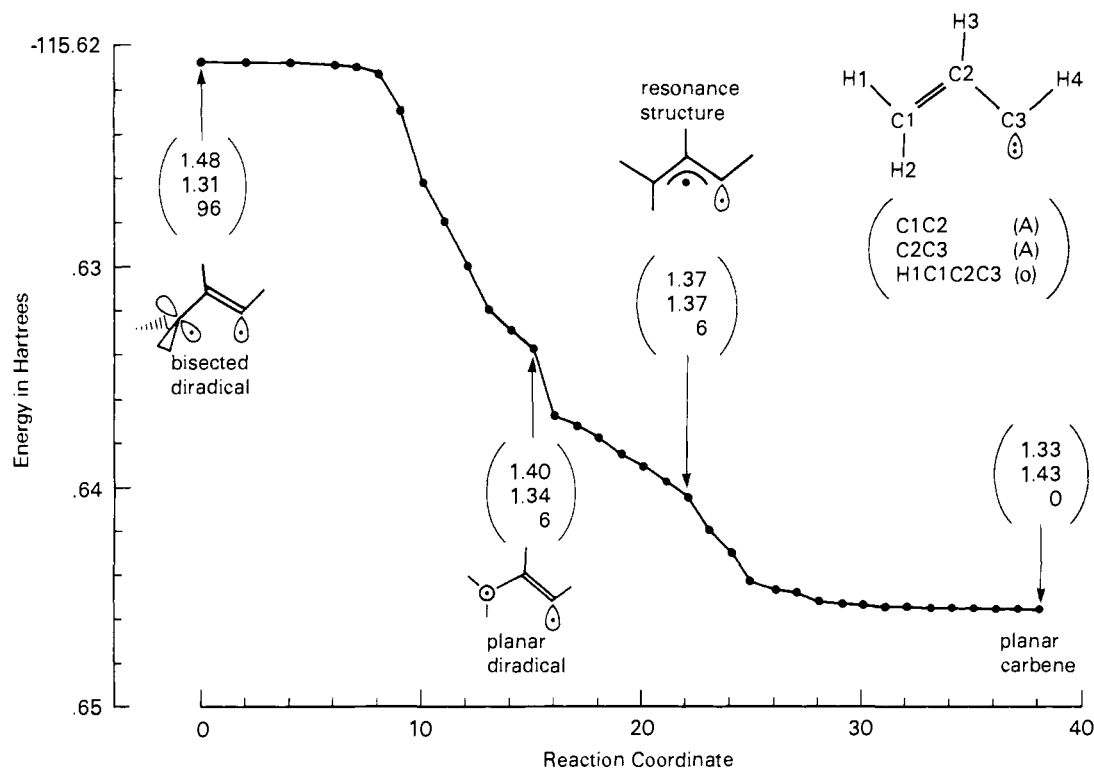


**Scheme VII**

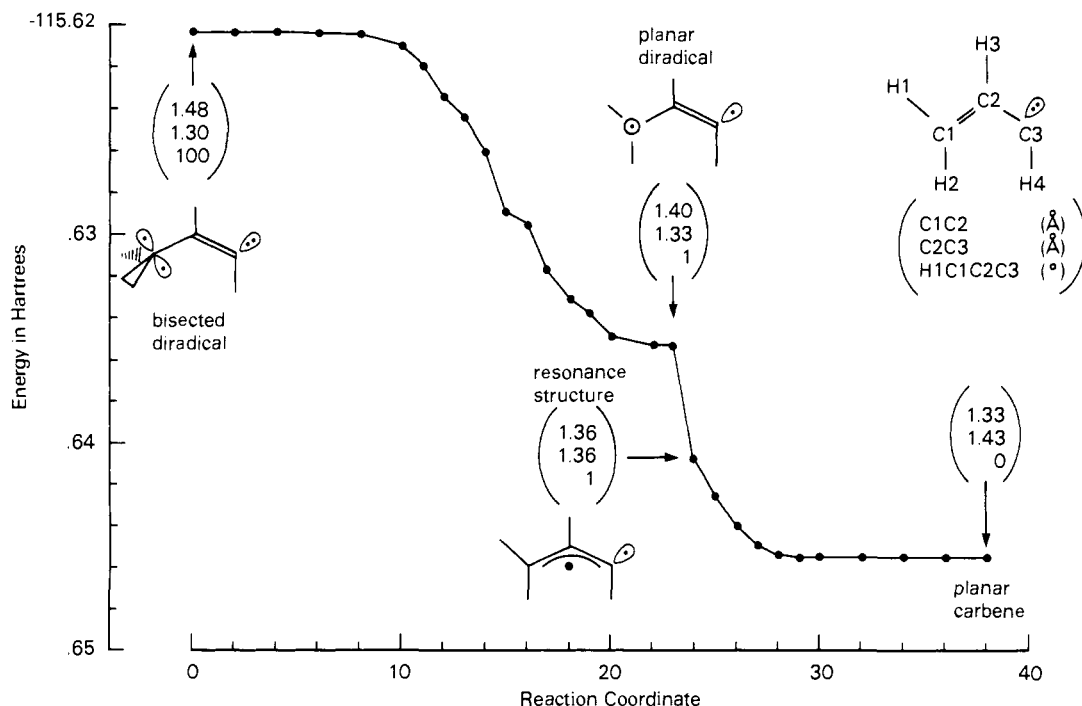


show no barriers on these paths. These paths are also believed to be reliable since the SCF(431G) energy separations between bisected and planar diradicals are in reasonable agreement with the SDQCI results (see Table VI).

**Barriers for the Cis-Trans Isomerization of Carbene and Diradicals.** Interconversions of the cis and trans isomers of planar carbenes ( $^1A'$ ,  $^3A''$ ), planar diradicals ( $^1A''$ ), and bisected diradicals ( $^3A'$ ) were also investigated. Geometries of the transition states determined by the gradient technique are listed in Table VII together with total energies and potential energy barrier heights. For carbene structures the reaction path may be described as a rotation of the H4-C3 bond about the C2-C3 bond as shown in Scheme VI, where the transition state for the isomerization is enclosed in brackets. The reaction paths for diradicals are constrained to the C1C2C3 plane because of the presence of the  $\pi$  bond between atoms C2-C3 (i.e., Scheme VII), and are similar to the inversion exhibited by the vinyl radical. The SDQCI results for the trans to cis isomerization of the  $^3A''$ ,  $^1A'$  states of the planar carbene are 4.6 and 8.4 kcal/mol. The barrier heights for the



**Figure 4.** Energy profile for the triplet trans bisected diradical to triplet planar carbene reaction path calculated by the SCF(431G) wave function. This is an approximate maximum gradient path, and a unit of the reaction coordinate corresponds to one step in the optimization procedure. Values in parentheses are pertinent bond lengths in ångströms (C1-C2, C2-C3) and the rotation of the  $CH_2$  group expressed as an angle between two planes formed by C1C2C3 and H1C1C2.



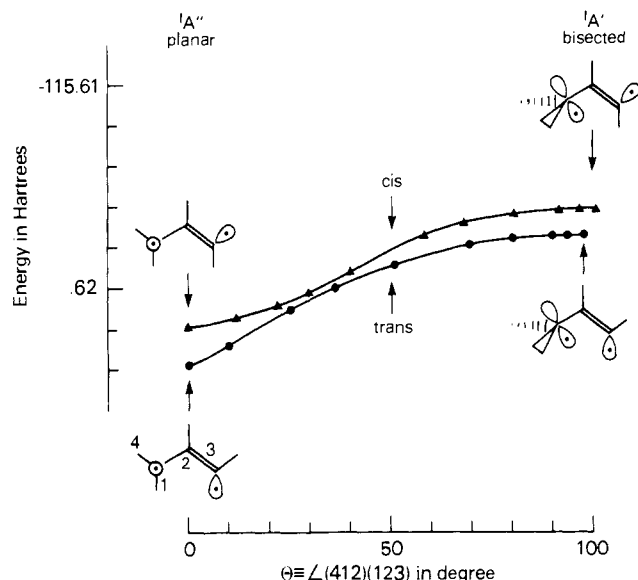
**Figure 5.** Energy profile for the triplet cis bisected diradical to triplet cis planar carbene reaction path calculated by the SCF(431G) wave function. This is an approximate maximum gradient path, and a unit of the reaction coordinate corresponds to one step in the optimization procedure. Values in parentheses are pertinent bond lengths in ångströms (C1-C2, C2-C3) and the rotation of the  $CH_2$  group expressed as an angle between two planes formed by C1C2C3 and H1C1C2.

trans-cis isomerization of the vinyl CH in the singlet and triplet planar or bisected diradicals is about 7 kcal/mol.

Davis et al.<sup>5b</sup> has reported a GVB and CI study on vinyl-methylene and the ring opening of cyclopropene. Although they used the standard bond lengths and angles for their geometries, their relative energy results for isomers are in good agreement with our SDQCI results. However, Davis et al. reported rather

different barrier heights for the cis-trans isomerizations. Their barriers at 8.38, 1.56, and 18.12 kcal/mol while ours are 4.6, 7.0, and 8.3 kcal/mol for the  $^3A''$ ,  $^1A''$ , and  $^1A'$  states, respectively. They assumed a planar path for all three isomerizations, which would explain their large barrier heights for the  $^3A''$  and  $^1A'$  states, respectively. Their low barrier for the  $^1A''$  state may be due to the fact that they did not optimize the geometry. For example,





**Figure 6.** Energy profiles for the singlet bisected diradical to planar diradical reaction paths as a function of the rotation of the  $\text{CH}_2$  group about the C1–C2 bond for the cis and trans systems determined by the SCF(431G) wave function. The rotation is expressed in terms of an angle,  $\theta$ , between the two planes formed by the three carbon atoms (123), and one of hydrogen atoms and two carbon atoms close to it (412).

**Table VII.** Geometrical Parameters and Total Energies of Transition States and Potential Energy Barriers for Cis–Trans Interconversions of Vinylmethylene Isomers<sup>a</sup>

	planar carbene $^3A''$	bisected diradical $^3A'$	planar carbene $^1A''$	planar diradical $^1A''$	bisected diradical $^1A'$
C1C2	1.328	1.492	1.327	1.464	1.493
C2C3	1.463	1.299	1.454	1.310	1.304
C1H1	1.077	1.077	1.076	1.073	1.077
C1H2	1.078	1.077	1.074	1.073	1.077
C2H3	1.081	1.089	1.087	1.085	1.087
C3H4	1.076	1.059	1.096	1.059	1.060
C1C2C3	124.2	126.5	130.9	125.5	126.3
H1C1C2	121.8	119.0	122.2	120.5	118.9
H2C1C2	121.0	119.0	120.4	120.1	118.9
H3C2C3	116.8	118.1	109.5	118.6	117.9
H4C3C2	131.1	180.0	109.4	180.0	180.0
H1C1C2C3	0.1	102.8	2.9	0.0	102.9
H2C1C2C3	-0.1	-102.8	-5.0	0.0	-102.9
H3C2C3C1	-0.5	0.0	-4.8	0.0	0.0
H4C3C2C1	90.0	0.0	85.5	0.0	0.0
Total Energies (hartrees) <sup>b</sup>					
SCF(431G)	0.64039	0.60778	0.59271	0.61054	0.60238
SCF(DZP)	0.83123	0.79910	0.79454	0.80247	0.79451
SDCI(DZP)	0.18516	0.15768	0.16065	0.16064	0.15271
SDQCI(DZP)	0.22602	0.19950	0.20458	0.20169	0.19471
Potential Barriers (kcal/mol) for Trans–Cis Interconversions					
SCF(431G)	3.2	8.1	7.9	8.2	9.4
SCF(DZP)	3.2	8.7	8.2	9.0	9.7
SDCI(DZP)	4.2	7.1	8.5	7.4	7.9
SDQCI(DZP)	4.6	6.7	8.4	7.0	7.2
Potential Barriers (kcal/mol) for Cis–Trans Interconversions					
SCF(431G)	3.2	7.8	5.6	7.1	8.6
SCF(DZP)	3.3	8.3	6.1	7.6	8.9
SDCI(DZP)	4.2	6.6	6.5	5.7	7.9
SDQCI(DZP)	4.6	6.3	6.5	5.3	8.2

<sup>a</sup> The SCF(DZP) geometries are given; all energies are calculated at these geometries except SCF(431G) energies which are calculated at the SCF(431G) geometries. <sup>b</sup> Only fractional parts are given; integer parts are -115 and -116 for SCF and CI, respectively.

the angle H4C3C2 is  $136^\circ$  in our optimized geometry while they used  $120^\circ$ .

**Structure of Vinylmethylene.** ESR experiments<sup>1</sup> on vinylmethylene suggested a triplet ground state with an allylic like

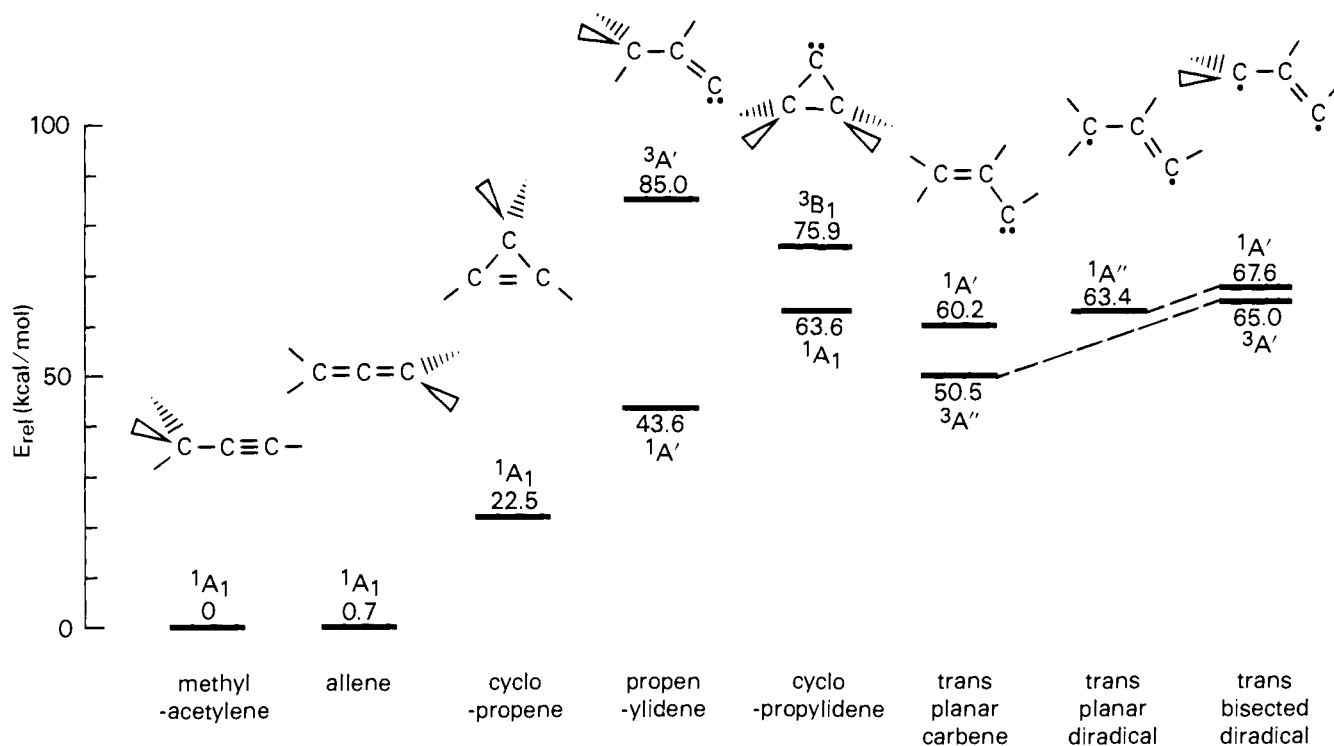
structure (equal C–C bond lengths) and a triplet–singlet energy separation of less than 1 kcal/mol. Our SDQCI results predicted a carbene structure for the triplet state, but the possibility of an allylic like ground-state structure cannot be precluded since the SDCI wave function employed in this study does not take into account a resonance energy, which could make an allylic structure more stable. In fact, our results give some indication that favors the allylic structure. The  $^3A''$  state at the TPD( $^1A''$ ) geometry is only 2 kcal/mol above the lowest  $^3A''$  state at TPC( $^3A''$ ), and the SCF(431G) study showed no barrier for the triplet TBD  $\rightarrow$  TPC path. For these observations we estimate the  $^3A''$  state energy at a structure with equal C–C bond lengths (allylic) to be 1 kcal/mol above that at the TPC structure. If we take 4 kcal/mol as the resonance energy differences between the allylic and carbene structures, which was estimated by Davis et al.,<sup>5b</sup> then the allylic structure would have a lower energy than either the carbene or diradical structures. Indeed, a MCSCF study on vinylmethylene,<sup>10</sup> detailed results of which will be reported in the next paper of this series, predicted an allylic like structure with a lower energy. This was also confirmed by a recent work of Feller et al.<sup>5d</sup> The triplet–singlet separation was determined to be 10 kcal/mol which is close to 12 kcal/mol estimated by Davis et al. but larger than a value of 0.2 kcal/mol reduced from the ESR experiment.<sup>1a</sup> We note, however, that while the triplet states are all lower in energy than the singlet states at the geometries considered, both states have the same energy at TPC( $^1A'$ ) geometry. This indicates that an intersystem crossing may occur in the vicinity of this point. So far we have discussed trans vinylmethylene, but cis vinylmethylene has a similar potential surface feature, and a similar comment should apply.

For singlet vinylmethylene the energy difference between the carbene (TPC) and diradical (TPD) structures is also small, about 3 kcal/mol. The lowest states, however, have different symmetries and orbital configurations. A pathway connecting these two structures must have a  $C_1$  symmetry, and the question as to whether or not these two structures represent true local minima must be answered by MCSCF calculations which include at least these two configurations. We may mention that a MCSCF study did reveal a significantly different feature for the potential surface of singlet vinylmethylene.<sup>10</sup>

**D. Relative Energies of Isomers.** The SDQCI results for relative energies of the stable  $\text{C}_3\text{H}_4$  isomers are summarized in Figure 7. Since trans and cis vinylmethylenes have essentially the same energies, only the results for trans vinylmethylene are shown. Bisected diradicals are included for reference although these isomers are found to be unstable with respect to the  $\text{CH}_2$  rotation as discussed above.

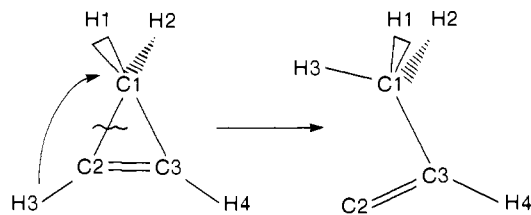
The singlet isomers can be divided into two groups. The first group includes the most stable closed-shell isomers, methylacetylene, allene, and cyclopropene. The second group consists of those relatively unstable isomers whose energies are in a range of 60 to 63 kcal/mol except propenylidene which has a relative energy of 44 kcal/mol. The fact that propenylidene has a relatively low energy compared with the other isomers in the second group may have an important implication on possible mechanisms for the cyclopropene–methylacetylene interconversion.

From a structural point of view, one would assume that the lowest energy path for the rearrangement of cyclopropene to methylacetylene would proceed via bisected diradicals. This is a direct pathway involving ring opening and then a 1,2 shift of hydrogen. Since we expect a small barrier, if any, for the ring closing, the barrier for this direct pathway depends on the barrier for the 1,2 hydrogen shift in the bisected diradical to methylacetylene rearrangement. Therefore, the energy of the transition state for this direct pathway must be higher than that of bisected diradicals. However, the fact that propenylidene lies 24 kcal/mol below the bisected diradicals may offer an alternative route, that is, an indirect pathway: cyclopropene  $\rightarrow$  propenylidene  $\rightarrow$  methylacetylene. We shall present an argument that this pathway may be competitive in energy to the direct pathway mentioned above. First, the 1,2 hydrogen shift in the propenylidene  $\rightarrow$  methylacetylene rearrangement is similar to that in the  $\text{CCH}_2$



**Figure 7.** Summary of the energy levels for possible C<sub>3</sub>H<sub>4</sub> isomers calculated in the SDQCI(DZP) approximation. The SCF(DZP) geometries are used and the energies in kcal/mol are given relative to that of the <sup>1</sup>A<sub>1</sub> state of methylacetylene, the most stable isomer. For vinylmethylene the energy levels for trans and cis structures are essentially the same, and only those for the trans are shown.

#### Scheme VIII



→ HCCH rearrangement which is known to have a small barrier if any.<sup>19</sup> This implies that the barrier height for the indirect pathway depends on the barrier for the cyclopropene → propenylidene rearrangement. There is some indication that this barrier may not be too high.

Lohr et al.<sup>20</sup> reported a theoretical study of the C<sub>2</sub>H<sub>3</sub>N energy surface. They found that the 2*H*-azirine to acetonitrile rearrangement proceeds via methyl isocyanide with a barrier of 44 kcal/mol for the 2*H*-azirine to methyl isocyanide rearrangement. The latter rearrangement is quite similar to that of cyclopropene to propenylidene; e.g., as shown in Scheme VIII, a synchronous 1,2-hydrogen shift for H<sub>3</sub> to C<sub>1</sub> occurs with the cleavage of the bond C<sub>1</sub>C<sub>2</sub>. If we take a barrier of 44 kcal/mol for the rearrangement of cyclopropene to propenylidene, then the energy of its transition state would be about 67 kcal/mol which is comparable with that of bisected diradicals (67.6 kcal/mol). Thus, this

indirect pathway may well be competitive with the more direct pathway mentioned above.

#### IV. Summary

The SCF and CI calculations have been presented for a number of reasonable isomers on the C<sub>3</sub>H<sub>4</sub> singlet and triplet surface. The results are summarized below.

1. The accuracy in the calculated relative energies is assessed as  $\pm 2$  kcal/mol from comparison of the relative energies of the most stable isomers with the experimental values.
  2. Among the isomers with a divalent carbon, only vinylmethylene has a triplet ground state while cyclopropylidene and propenylidene have a singlet ground state.
  3. Although the present calculation predicts that the triplet state of vinylmethylene has a planar carbene structure, consideration of resonance energy favors an allylic structure to be lower in energy.
  4. The singlet potential energy surfaces for trans and cis vinylmethylenes have a similar feature but are separated by a potential energy wall of about 8 kcal/mol.
  5. On the singlet surface propenylidene lies lower than vinylmethylenes, in particular the bisected diradicals. This suggests an indirect pathway for the cyclopropene → methylacetylene rearrangement which proceeds via propenylidene, and it could be lower in energy than the direct pathway via bisected diradicals.
- The results for the isomers presented here will be used as a starting point for further studies of interconversions on the C<sub>3</sub>H<sub>4</sub> surface which will be subsequently reported.

**Acknowledgment.** We thank Dr. K. Morokuma for pointing out a similarity between the cyclopropene to propenylidene and 2*H*-azirine to methyl isocyanide rearrangement.

(19) Osamura, Y.; Schaefer, F. H., III; Gray, S. K.; Miller, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 1904.

(20) Lohr, L. L., Jr.; Hanamura, M.; Morokuma, K. *J. Am. Chem. Soc.* **1983**, *105*, 5541.