Molecular Orbital Theory of the Electronic Structure of Organic Compounds. 28. Geometries and Energies of Singlet and Triplet States of the C_3H_2 Hydrocarbons

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Abstract: Single determinant ab initio molecular orbital theory has been applied to the study of the structures and relative energies of all possible singlet and triplet isomers of formula C_3H_2. Within the manifold of closed shell singlets, the 2π electron aromatic cyclopropenylidene is found to be the most stable. Some 17 kcal/mo higher in energy is the acyclic system, vinylidenecarbene. The predicted equilibrium geometry of the most stable triplet isomer, propargylene, is not linear as was earlier supposed, but rather of C_2 symmetry. The calculations allow the rationalization of the observed EPR zero-field parameters in terms of such a structure while providing details which are not available from resonance studies. The next most stable triplet form is vinylidenecarbene (24 kcal/mol above propargylene). The calculated energies of cyclic triplet isomers are far higher. Finally comparison is drawn between the relative energies of the most stable form of each of the singlet and triplet manifolds. By an indirect approach, which utilizes the difference between the calculated and experimental singlet-triplet splitting in methylene, we have estimated that the lowest energy singlet isomer, cyclopropenylidene, is about 13 kcal/mol more stable than the best triplet form, propargylene, and hence must be considered the ground state of C_3H_2.

In recent years considerable attention has been given to the application of simple levels of ab initio molecular orbital theory to questions of structure and stability of small hydrocarbons,[2] and positively charged hydrocarbon ions.[2a,3] Much of the earlier work was comparative in tenor, directed at establishing an overall level of confidence, against which one might render judgment on the theory's predictions in those instances where experimental data were unavailable. The considerable success with which these ventures have met compels us now to detail our collective studies on one such set of hydrocarbons, compounds of formula C_3H_2, on which quantitative structural and energetic data are all but completely lacking. Although only one of these hydrogen deficient species, the triplet state of prop-2-ynylidene (propargylene), has come under direct spectroscopic scrutiny, indirect "chemical" evidence suggesting the existence of derivatives of at least two others (propadienylidene and cyclopropenylidene) has emerged during the past decade. In addition, cyclopropyne, parent to the cycloalkyne series, has long been sought experimentally, though at present all such quests have proven unsuccessful.

Here we will be concerned primarily with the theoretical prediction of detailed geometrical structures and of relative isomer stability. The manifold of C_3H_2 isomers is, in at least one respect, more complicated than a number of previous systems investigated, for not only must we contend with closed shell species but also with the possibility of low-lying triplet arrangements. Thus, we shall be concerned not only with assigning which of the possible C_3H_2 isomers is the most stable singlet, but in addition shall be interested in the theory's prediction of the lowest energy member within the triplet manifold. Although the single determinant ab initio molecular orbital methods employed in the present work appear to be quite capable of properly ordering the stabilities of isomers within a given spin manifold, they are not as likely to be successful in choosing which of the lowest energy singlet or triplet species is actually the ground state of C_3H_2. In particular, it is anticipated that correlation effects, which are completely ignored within the framework of single determinant theory, will be smaller for triplet states than for singlets.

Quantum Mechanical Methods

Single determinant ab initio molecular orbital theory was used throughout. For singlet states, the closed-shell spin-restricted Hartree-Fock (RHF) procedure[4] was employed, electrons being assigned to molecular orbitals in pairs. For triplet states, wave functions were obtained by the spin-unrestricted (UHF) procedure[5] with two more α electrons than β electrons. These are not pure triplet functions, but have some contamination from functions of higher spin multiplicity. As a consequence total energies computed at the UHF level will generally be lower than those obtained using a restricted Hartree-Fock procedure.

We have employed the STO-3G minimal basis set[6] for the optimization of equilibrium geometries. The actual procedure is to select some starting geometry with a specified symmetry constraint and then to vary the remaining geometrical parameters until the energy is minimized.[7] For some structures, it was found that release of the symmetry constraint led to further energy lowering toward some other structure, and full refinement was not then carried out. The resulting structures and the corresponding symmetry constraints are listed in Table I.

To assess relative isomer stabilities more accurately, single molecular orbital calculations at the extended 4-31G basis set level[8] were then performed on each of these (STO-3G) equilibrium geometries. However, even at the 4-31G level, relative isomer energies are still subject to considerable error, in particular with regard to comparisons made between acyclic and small ring molecules. Therefore, in order to provide a still more accurate assessment of the relative stabilities of the C_3H_2 isomers, we have carried out a limited number of single calculations using the 6-31G* polarization basis set.[9] Again the equilibrium geometries specified by the minimal basis set STO-3G method were employed. The complete set of energy data are to be found in Tables II and III for closed shell singlet and triplet species, respectively. All calculations have been

Table I. Equilibrium Geometries[a]

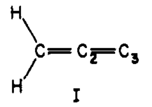
Molecule	Symmetry constraint	Parameter	Singlet	Triplet
Propadienylidene (I)	C_{2v}	$r(C_1{=}C_2)$	1.304	1.386
		$r(C_2{=}C_3)$	1.282	1.256
		$r(C_1\text{-}H)$	1.092	1.084
		$\angle(HCH)$	114.7	117.4
Propenediylidene (IIa)	C_s	$r(C_1{=}C_2)$	*b*	1.412
		$r(C_2\text{-}C_3)$		1.403
		$r(C_2\text{-}H)$		1.087
		$r(C_3\text{-}H)$		1.084
		$\angle(C_1C_2C_3)$		122.6
		$\angle(HC_2C_3)$		119.7
		$\angle(HC_3C_2)$		129.1
Propenediylidene (IIb)	C_s	$r(C_1{=}C_2)$	*b*	1.413
		$r(C_2\text{-}C_3)$		1.404
		$r(C_2\text{-}H)$		1.089
		$r(C_3\text{-}H)$		1.083
		$\angle(C_1C_2C_3)$		125.8
		$\angle(HC_2C_3)$		119.9
		$\angle(HC_3C_2)$		129.0
Prop-2-ynylidene (IIIa)	C_s	$r(C_1C_2)$	1.186	*c*
		$r(C_2\text{-}C_3)$	1.435	
		$r(C_1\text{-}H)$	1.067	
		$r(C_3\text{-}H)$	1.120	
		$\angle(C_1C_2C_3)$	175.2	
		$\angle(HC_1C_2)$	179.7	
		$\angle(HC_3C_2)$	105.6	
Prop-2-ynylidene (IIIb)	C_2	$r(C\text{-}C)$	*d*	1.303
		$r(C\text{-}H)$		1.076
		$\angle(CCC)$		167.1
		$\angle(HCC)$		145.7
		$\angle(HCCC)$		144.5
Propanediylidyne (IV)	C_{2v}	$r(C\text{-}C)$	*e*	1.547
		$r(C\text{-}H)$		1.097
		$\angle(CCC)$		109.2
		$\angle(HCH)$		108.6
Cyclopropyne (V)[f]	C_{2v}	$r(C\text{-}C)$	1.249	1.284
		$r(C\text{-}C)$	1.544	1.543
		$r(C\text{-}H)$	1.105	1.088
		$\angle(HCH)$	110.0	113.4
Cyclopropenylidene (VI)[f]	C_{2v}	$r(C{=}C)$	1.314	1.302
		$r(C\text{-}C)$	1.442	1.469
		$r(C\text{-}H)$	1.078	1.077
		$\angle(HC{=}C)$	147.2	146.8

[a] STO-3G level, bond lengths in Å, bond angles in deg. [b] Collapses without activation to cyclopropenylidene (VI). [c] On release of the C_s constraint, this structure collapses without activation to the C_2 structure IIIb. [d] On release of the C_2 constraint, this structure collapses without activation to the C_s structure IIIa. [e] Collapses without activation to cyclopropyne (V). [f] Theoretical structural data for singlet molecules from ref 12.

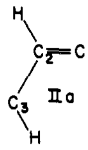
carried out using the GAUSSIAN 70 series of computer programs.[11]

Results and Discussion

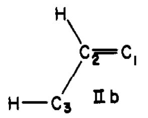
We have endeavored to explore all possible isomers of C_3H_2 (closed shell singlet and triplet) in which each hydrogen is attached to a unique carbon. No evidence was found for structures with bridging hydrogen atoms. For systems with an acyclic carbon chain C_1-C_2-C_3, possible positions of attachment of the two hydrogens are: (i) both at the same end (propadienylidene (I)); (ii) one in the middle, one at the end (propenediylidene (IIa, IIb)); (iii) one at each end (prop-2-ynylidene (IIIa, IIIb)), (iv) both in the middle (propanediylidyne (IV). For cyclic structures, the possibilities are: (v) at the same position (cyclopropyne (V)); (vi) at different positions (cyclopropenylidene (VI)). We shall discuss the structures and relative energies for the singlet and triplet potential surfaces



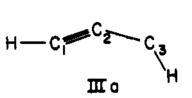
I



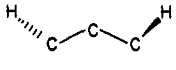
IIa



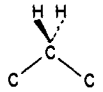
IIb



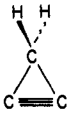
IIIa



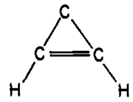
IIIb



IV



V



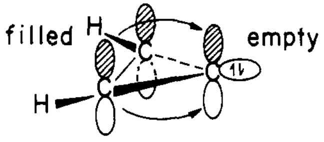
VI

in turn, postponing a comparative discussion of one with the other to the end.

Singlet Isomers

The results, given in Table II, suggest that cyclopropenylidene (VI) is the most stable singlet isomer of C_3H_2. This conclusion is based on results at the 6-31G* level. With the 4-31G basis the energies of propadienylidene (I) and cyclopropenylidene (VI) lie closer together. However, the greater energy lowering of the strained cyclic structure with the addition of d functions is in line with corresponding findings for isomers of C_3H_4 and C_3H_6[12] and is clearly important.

The geometrical structure for cyclopropenylidene (VI) shows considerable evidence of electron delocalization away from the π orbital of the double bond and into the vacant p function at the carbene center. As a consequence the two single linkages have contracted (by 0.051 Å from their value in cyclopropene) while the formal double bond has lengthened considerably (by 0.037 Å from that in cyclopropene). The enhanced stability of the resulting 2π electron cycle is evidenced by the energy of the *isodesmic* bond separation reaction[13]



$(^1A_1)$

$$+ \ 2CH_4 \ + \ CH_2(^1A_1) \longrightarrow 2CH_3{-}CH(^1A') \ + \ CH_2{=}CH_2 \qquad (1)$$

$$\Delta E(6\text{-}31G^*) = +5.5\,\text{kcal/mol}$$

ΔE of the corresponding process for cyclopropene

$$+ \ 3CH_4 \longrightarrow 2CH_3{-}CH_3 \ + \ CH_2{=}CH_2 \qquad (2)$$

$$\Delta E(6\text{-}31G^*) = -50.4\,\text{kcal/mol}$$

on the other hand, indicates the considerable strain normally present in a three-membered ring. The unusually high stability of cyclopropenylidene, relative to its bond separation products, reminds us of a related system, the isoelectronic cyclopropenyl cation.[3a] Here the calculated energy required for bond separation (reaction 3) is actually negative though of much smaller magnitude than that noted for cyclopropene (reaction 2).

$$+ \ 2CH_4 \ + \ CH_3^+ \longrightarrow 2CH_3{-}CH_2^+ + CH_2{=}CH_2 \quad (3)$$

$$\Delta E(6\text{-}31G^*) = -13.9\,\text{kcal/mol}$$

The second most stable singlet isomer is propadienylidene (I, trivial name vinylidenecarbene). According to the

Table II. Energy Data for Singlet C_3H_2 Species

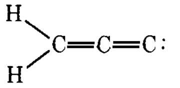
	STO-3G	4-31G		6-31G*	
Molecule and state	E, hartrees	E, hartrees	ΔE, kcal/mol	E, hartrees	ΔE, kcal/mol
Cyclopropenylidene (VI)	−113.178 04[a]	−114.424 27[a]	0.0	−114.618 49	0.0
Propadienylidene (I)	−113.137 93	−114.425 43	−0.7	−114.591 15	17.2
Prop-2-ynylidene (IIIa)	−113.124 97	−114.400 88	14.7		
Cyclopropyne (V)	−112.998 83[a,b]	−114.283 88[a,b]	88.1		

[a] Theoretical energy data from ref 12. [b] The molecular orbitals have been allowed to become complex.

Table III. Energy Data for Triplet C_3H_2 Species

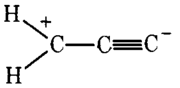
	STO-3G	4-31G		6-31G*	
Molecule and state	E(hartrees)	E, hartrees	ΔE, kcal/mol	E, hartrees	ΔE, kcal/mol
Prop-2-ynylidene (IIIb)	−113.207 88	−114.476 90	0.0	−114.631 59	0.0
Propadienylidene (I)	−113.178 66	−114.438 49	24.2	−114.593 59	23.8
Propenediylidene (IIa)	−113.127 88	−114.390 77	54.0		
Propenediylidene (IIb)	−113.122 15	−114.360 36	73.1		
Cyclopropenylidene (VI)	−113.092 72	−114.347 06	81.4		
Cyclopropyne (V)	−113.083 35	−114.325 32	95.1		
Propanediylidyne (IV)	−113.026 82	−114.272 08	128.6		

RHF/6-31G* energies, this lies some 17 kcal/mol above cyclopropenylidene (VI). The STO-3G calculated geometry is well represented by the valence structure



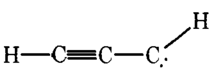
$^1A_1$

where the lengths of the double linkages have changed only slightly from the value in, say, allene (1.288 Å at the STO-3G level). These geometric distortions are small, but in a direction which suggests involvement of zwitterionic forms such as:

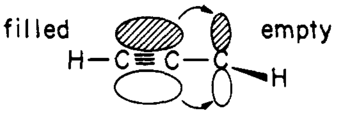


The molecule has two π electrons. Regarded as a singlet carbene, it would have a formally vacant π atomic orbital on the carbene center. However, the two electrons in the neighboring π double bond will move toward this vacancy, giving additional stability in terms of the structure $H_2C^+{-}C{\equiv}C^-$ This high polarity is reflected in the large dipole moment (4.0 D at the 6-31G* level with CH_2 at the positive end) for this isomer.

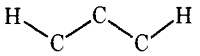
The third most stable closed shell singlet isomer is prop-2-ynylidene (trivial name propargylene) which is found to distort to an asymmetric structure well represented as ethynylmethylene.



Here, electron donation from the valence π orbital of the triple bond into the vacant p function at the carbene center results in lengthening of the former (multiple) linkage from its value



in, say, acetylene (1.168 Å at the STO-3G level) accompanied by a shortening of the connecting single bond (from an STO-3G value of 1.537 Å in a molecule like ethylidene[14]). Similar and somewhat larger geometrical effects have already been noted in the isoelectronic propargyl cation,[3a] due, in this instance, to interaction between the filled π orbital of acetylene and the vacant lobe at the carbonium center. An alternative, C_{2v} symmetry, form of singlet propargylene was also considered.

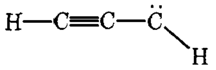


Upon release of the symmetry constraint it was noted to undergo collapse to the C_s structure. However, it is possible that a local minimum of C_{2v} symmetry might exist for an open shell singlet species.

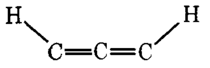
The remaining singlet structure is cyclopropyne (V) which has a much higher energy and is likely to be very unstable. At the 4-31G level it is 88 kcal/mol above cyclopropenylidene. No 6-31G* calculation was carried out on V, but, since both V and VI are three-membered rings, a similar large energy separation between them would be expected at this level.

Triplet Isomers

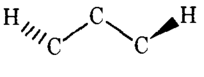
On the triplet C_3H_2 surface, the results, given in Table III, indicate that prop-2-ynylidene (IIIa, trivial name propargylene) is the most stable form. Rather than being represented as an ethynyl group attached to methylene



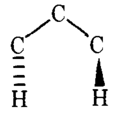
the theoretical geometry seems to be better interpreted in terms of a diradical valence structure.



The lowest energy structure found for propargylene is one of C_2 symmetry. Here the carbon skeleton is close to linear (∠CCC = 167.1°), while the terminal hydrogens are attached with bond angles of 145.7°. One hydrogen rises out of the plane formed by the three carbons, the other descends below it. Finally, these two hydrogens are oriented so as to be nearly mutually perpendicular (dihedral angle 71.1°), the molecule taking on a W as opposed to U shaped geometry.

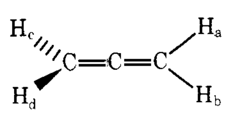


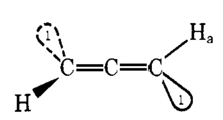
W shaped



U shaped

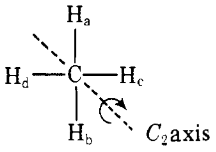
Another way in which to visualize the theoretical equilibrium geometry of triplet propargylene is to consider it as having been

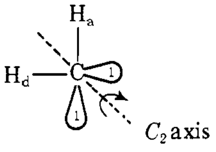




allene triplet propargylene

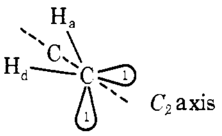
derived from allene by removal of a vicinal pair of hydrogens. The C_2 axis present in both systems is easily recognized by looking straight down the C=C=C moiety.



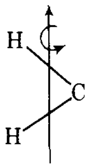


allene triplet propargylene

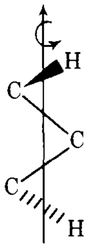
This element of symmetry is not destroyed by the further geometrical distortions undergone by propargylene (i.e., a closing of the dihedral angle between the terminal hydrogens, and a movement of the central carbon along the C_2 axis).



Experimentally, triplet propargylene was originally believed to possess a linear or nearly linear skeleton, based on the analysis of the EPR zero-field splitting parameters.[15] In particular the observation that the anisotropy parameter, E, was vanishingly small was taken as evidence that the molecule possessed cylindrical symmetry (i.e., belonged to point groups $C_{\infty v}$ or $D_{\infty h}$). It was subsequently shown for triplet methylene,[16] however, that rotation within the matrix could account for the observation of an apparent cylindrical axis in a nonlinear molecule.



Analogous considerations indicated that significant distortions of III from linearity could still allow relatively free rotation about the long axis of the molecule. Support for such distortions is found in earlier studies.[17]



In considering the zero-field parameters of III and its derivatives, the unpaired electrons were assigned to two perpendicular π systems.[17a] Each of those π systems would resemble that for the triplet ground state of vinylmethylene. The recent observation of the EPR of that species indicated nonlinear CCC and methylene carbon arrangements.[17b] Having the two HCC planes of III in an approximately perpendicular orientation was thus a possibility. When the geometry of the lowest triplet state was determined by minimizing the STO-3G energy the twisted W structure was the result. It was clear that such a structure is likely to experience only a small barrier to rotation about the long axis. Then, the measured asymmetry parameter, E_{obsd}, equals $E_f V/W_2$, where E_f is the parameter expected with no motion, V is the twofold barrier to rotation due to interaction of the triplet with the matrix, and W_2 is the second excited rotational level for motion about the long axis.[16] Consideration now turns to these three terms which determine E_{obsd}.

W_2 is inversely proportional to the moment of inertia about the long axis, I. The carbon atoms, because of their substantial mass and almost linear arrangement, are close to the axis. They therefore make only a small contribution to I. The hydrogen atoms are further away but their low mass again leads to a small contribution to the moment. The rotational energy levels will be rather widely spaced. From the geometry we determine that $W_2 \approx 40$ cm^{-1}.

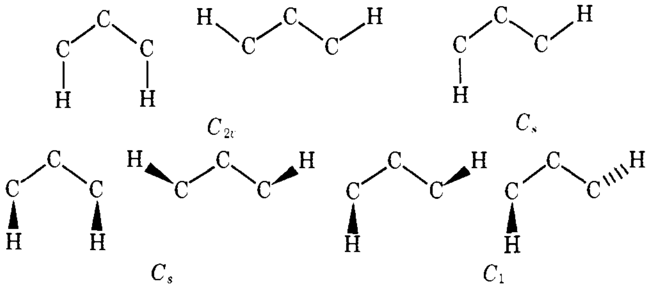
We do not have the information necessary to obtain an accurate value for the barrier to rotation, V. The shape of the cavity may resemble that of a dumbbell with the swinging hydrogens providing most of the barrier. A value similar to that observed with methylene[16] seems reasonable, ~10 cm^{-1}.

E_f is expected to be much smaller than the 0.05 cm^{-1} for methylene because of several factors. Little contribution to the electron asymmetry arises from the central carbon as there is only a small spin density at that atom. Also, with an angle of 167° the in-plane hybrid is almost a pure p orbital and shows almost no asymmetry with respect to the perpendicular C_2 π orbital. Given the spin density at C_1 or C_3 and the HCC angle of 146° we might expect the contribution to E_f at one of the end carbons to be ~0.01 cm^{-1}. However, the dihedral angle of 71° between the two HCC planes leads to extensive cancellation between the two ends of the molecule. The distribution of unpaired electrons appears to be approximately the same in two perpendicular directions and E_f is small, about ~0.001 cm^{-1}.

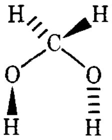
When rotation is considered, E_{obsd} for IIIb should be 2×10^{-4} cm^{-1}. The widths of the EPR spectral lines are only able to give an upper limit to E_{obsd}, ~0.002 cm^{-1}.[15a] The expected value is then considerably less than can be detected with the experiments reported hitherto and the available data are therefore compatible with IIIb.

The detection of an E of ~10^{-4} cm^{-1} by EPR studies in rigid matrices is likely to be difficult and even if observed could be due to site variations or asymmetries. A gas-phase resonance study would appear to be required for definitive results.

A number of other structural possibilities have been considered for triplet propargylene, but all were found to be of higher energy, and, including the U shaped molecule of C_2 symmetry, unstable with respect to torsion of one or the other hydrogen about the carbon skeleton. In particular, planar forms of C_{2v} and C_s symmetries and nonplanar geometries belonging to point groups C_s and C_1 were all found to collapse, without activation to the C_2 structure.

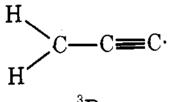


The similarity of the overall (two-dimensional) rotational potential of triplet propargylene to that of methanediol[18] is worthy of note. In both cases rotation of the terminal hydrogens around the heavy atom skeleton results in but a single minimum (or more precisely stated a pair of minimum energy forms related by the twofold symmetry axis). The equilibrium structure for the diol



does, however, have the hydroxy hydrogens placed in a manner which is quite different from the arrangement of the terminal CH's found in propargylene.

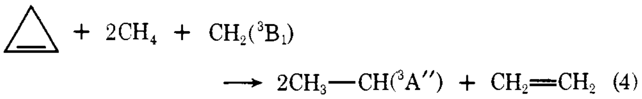
The second most stable triplet isomer is propadienylidene or triplet vinylidenecarbene. This is about 24 kcal/mol less stable than propargylene (a difference that is little changed by polarization functions). Unlike the corresponding singlet, triplet vinylidenecarbene is best viewed in terms of a diradical representation,



$^3B_1$

with one carbon-carbon linkage sizably longer than a normal double bond, the other somewhat shorter.

The remaining triplet structures including the cyclic forms V and VI are all much less stable than III or I. It is noteworthy that the effect of the 3π electrons in cyclic conjugation in triplet cyclopropenylidene is clearly one of energetic destabilization, in striking contrast to the sizable stabilization afforded to the singlet species on account of its doubly occupied π electron cycle. Indeed, ΔE of (4) is actually more negative than that



$$\Delta E(4\text{-}31G) = -84.3\,\text{kcal/mol}$$

corresponding to the process of bond separation in cyclopropene.

Relative Energies of Singlet and Triplet Isomers

As already noted in the introductory section, Hartree-Fock theory does not give satisfactory energy differences between singlet and triplet isomers, because correlation corrections are generally larger for closed shell singlets. This is evident for CH_2 where the UHF/6-31G* theory gives the triplet state 31 kcal/mol below the singlet,[19] whereas the best available experimental evidence indicates a separation of about 10 kcal/mol.[20] Since satisfactory calculations of full correlation energies for C_3H_2 are beyond our scope at present, we can only estimate singlet-triplet differences by introducing an additional hypothesis.

For this purpose, we shall treat vinylidenecarbene (I) as an analogue of methylene and assume that the correction to be made to UHF/6-31G* singlet-triplet energy differences is the same for both. In other words, we assume that the energy of the reaction

$$\text{H}_2\text{C{=}C{=}C(singlet)} + \text{H}_2\text{C(triplet)} \longrightarrow \text{H}_2\text{C{=}C{=}C(triplet)} + \text{H}_2\text{C(singlet)} \quad (5)$$

is given correctly at the UHF/6-31G* level. Using the methylene results of Hariharan and Pople,[19] this energy is +29.3 kcal/mol. Then, given a 10 kcal/mol experimental singlet-triplet energy gap for methylene, the theory predicts that singlet vinylidenecarbene is more stable than the triplet by about 20 kcal/mol. On the other hand, a direct comparison of the UHF/6-31G* energies gives the triplet lower by 1.5 kcal/mol. The value arrived at by (5) is consistent with studies of derivatives of vinylidenecarbene by Hartzler,[21] who concluded from their stereospecific addition to olefins, and in light of the Skell-Woodworth hypothesis,[22] that they possessed singlet ground states. More recent and varied studies have repeatedly confirmed these trends.

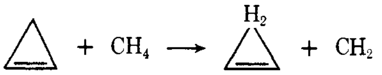
Table IV. Proposed Heats of Formation of C_3H_2 Isomers

Isomer	$\Delta H_f°$ (298 K)
Singlets	
Cyclopropenylidene (VI)	113
Propadienylidene (I)	130
Triplets	
Prop-2-ynylidene (IIIb)	126
Propadienylidene (I)	150

If we accept the relative singlet energies from Table II and the relative triplet energies of Table III (at the 6-31G* level), we may now make comparisons between the two sets by lowering all singlet levels by about 21 kcal/mol. Thus, we predict that the lowest energy isomer of C_3H_2 is singlet cyclopropenylidene (VI), this being about 13 kcal/mol more stable than the lowest triplet isomer (propargylene (III)).

Heats of Formation

In conclusion, we make tentative proposals for the absolute heats of formation of the various singlet and triplet isomers. These will be based on the further hypothesis that the energy of the (singlet) isodesmic reaction



is given correctly by Hartree-Fock theory with the 6-31G* basis. Again using the results of this paper and ref 19, this energy is 74.2 kcal/mol. Using values of −16, 102, and 69 kcal/mol for heats of formation of methane, singlet methylene, and cyclopropene, respectively, we deduce that the corresponding value for singlet cyclopropenylidene is 113 kcal/mol. Combining this with the above discussion of relative energies, we propose the values listed in Table IV.

Note Added in Proof. Since this manuscript was written, a new experimental value of 19 kcal/mol for the singlet-triplet separation in methylene has come to our attention.[23] If correct, this new result would alter the prediction made about the corresponding separation in C_3H_2. Our treatment would still predict that C_3H_2 has a singlet ground state, but that the corresponding triplet lies only 4 kcal/mol higher in energy.

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One- and Two-Configuration Hartree–Fock Limit Predictions for the Singlet–Triplet Separation in Methylene and Silylene

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Abstract: A priori electronic structure theory has been applied to the lowest $^3B_1$, $^1A_1$, and $^1B_1$ states of CH_2 and SiH_2. Very large basis sets of contracted Gaussian functions were employed. For CH_2, the factors leading to different theoretical values of the $^3B_1$–$^1A_1$ energy separation are examined. For SiH_2, the $^1A_1$ state is predicted to lie below the $^3B_1$ state by 10 kcal/mol.

The energy difference between the $^3B_1$ and $^1A_1$ states of CH_2 has been the subject of considerable experimental and theoretical research in recent years. In 1961 Herzberg established[2a] for the first time that the triplet state was the lower lying. However, since no singlet-triplet bands of CH_2 have been analyzed, electronic spectroscopy does not yield a precise value of the separation. However, Herzberg suggested[2b] in 1966 that the singlet-triplet separation (to be called ΔE hereafter) should be less than 23 kcal/mol. Since that time, essentially all experimental values have fallen into two groups, which may be referred to as the "high" values[3-6] (8-9 kcal/mol) and the "low" values[7-9] (0-3 kcal/mol).

The three most reliable ab initio theoretical studies[10-12] reported to date all favor a high value for the singlet-triplet separation. The lowest theoretical ΔE of 9.2 kcal/mol, predicted by Staemmler,[12] was obtained using the independent electron pair approximation (IEPA) and a large contracted Gaussian basis set. Somewhat larger ΔE values (11.5[10] and 14.1[11] kcal) were obtained in the two variational studies. The present research was motivated by two theoretical suggestions made independently by Hay, Hunt, and Goddard[10] and by Bender, Schaefer, Franceschetti, and Allen.[11] The first of these is the understanding that d functions on carbon significantly lower ΔE. The second is the suggestion that the $^3B_1$ state be approximated by a single configuration wave function

$$1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1\ 1b_1 \qquad (1)$$

while a two-configuration wave function

$$c_1\,(1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1^2) + c_2\,(1a_1^2\ 2a_1^2\ 1b_2^2\ 1b_1^2) \qquad (2)$$

be used to describe the $^1A_1$ state. And, in fact, comparison with the extensive (both in terms of basis set and treatment of electron correlation[13]) theoretical treatments of Bender[11] and Staemmler[12] show these two features to be important ingredients in theoretical predictions of ΔE. In general of course the reliable prediction of electronic excitation energies requires a fairly thorough treatment of electron correlation, usually via large scale configuration interaction (CI).[14] However, a simple rationalization of the apparent transparency of the correlation problem in this specific case is possible with reference to (1) and (2). We see that while the $^3B_1$ Hartree–Fock wave function treats the nearly degenerate $3a_1$ and $1b_1$ orbitals in an equivalent manner, the corresponding single-configuration $1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1^2$ for the $^1A_1$ state ignores the $1b_1$ orbital entirely. Hence the second configuration $1a_1^2\ 2a_1^2\ 1b_2^2\ 1b_1^2$ may be required for a theoretical treatment comparable to the single-configuration description of the $^3B_1$ state.

Theoretical Details

The purpose of the present research was twofold. First, to obtain near-Hartree–Fock predictions for the methylene ΔE and therefore remove the basis set dependence of earlier theoretical work.[15] Second, comparable calculations have been carried out for SiH_2 (silylene), for which the singlet-triplet separation is currently rather uncertain. For carbon and silicon, the largest readily available Gaussian basis sets were used. The carbon (13s 8p) primitive Gaussian set of van Duijneveldt[16] was contracted to (9s 6p) so as to maintain maximum flexibility in the valence region. That is, the five s functions with largest orbital exponents α_i were grouped together according to the carbon atomic 1s orbital, and an analogous procedure followed for the three carbon p functions with largest expo-