

Methyl Substitution in Carbenes: Lack of Steric or Hyperconjugative Stabilization Effects on the CH₃CH Singlet–Triplet Splitting

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Ab initio GVB-CI (generalized valence bond theory with configuration interaction) and MCSCF (multiconfiguration self-consistent-field) calculations have been carried out on methylene and ethylidene (CH₃CH) to investigate the effects of methyl substitution on the singlet–triplet splitting of methylene. We predict that ethylidene has a singlet–triplet splitting of 3 ± 2 kcal/mol, about 6 kcal/mol less than the value for methylene. Furthermore, our investigations show that neither steric effects nor hyperconjugative singlet stabilization effects are large enough to account for this decrease in the singlet–triplet splitting. Rather, the dominant effects of the CH₃ group are to (i) decrease *p* character in the nonbonding σ orbital of the triplet state, (ii) reduce electron donation to the methylenic carbon, and (iii) induce repulsions in the triplet state between the CH₃ and the singly occupied methylenic C $p\pi$ orbital. All of these effects destabilize the triplet ground state and thus decrease the singlet–triplet splitting.

I. Introduction

The geometric and electronic structure of substituted carbenes is of importance in synthetic chemistry. The diverse reactivity of such molecules can be understood in terms of their electronic structure. The singlet state (σ^2) has both of its nonbonding electrons in a σ orbital localized on the carbenoid carbon while the triplet state ($\sigma^1\pi^1$) has one electron in that σ orbital and one in a π orbital also localized on the carbenoid carbon. As a result, the chemistry in which they participate is very different: singlet carbenes undergo one-step stereospecific reactions while triplet carbenes participate in two-step, nonspecific reactions.¹ The trends in the reactivity of carbenes can thus be better understood upon determination of their singlet–triplet splittings.

The singlet–triplet gap in a substituted carbene depends strongly on the hybridization of the σ and π orbitals of the central carbon. For both the triplet and the singlet states, the π orbital is essentially a pure *p*-like orbital while the σ orbital is a hybrid of *s*- and *p*-like atomic orbitals. Thus, σ orbitals with increased *p* character favor a triplet ground state, since both nonbonding orbitals (σ and π) lie close in energy when both have high *p* character, favoring singly occupied σ and π orbitals. On the other hand, σ orbitals with increased *s* character favor singlet coupling of the electrons, since increased *s* character substantially lowers the energy of the σ orbital relative to the π orbital, favoring a doubly occupied σ orbital.²

The hybridization of the σ orbital is in turn determined by the following factors. First, steric effects: bulky substituents favor a large bond angle. This is accomplished by increasing *s* character in the C–X bond which will result in decreased *s* character (and a concomitantly increased *p* character) in the nonbonding σ orbital, thus favoring the triplet state.² Second, charge-transfer effects: substituents that are more electronegative with respect to carbon form polar bonds to carbon with electrons transferred to the substituent. Since *p* orbitals have a lower ionization potential than *s* orbitals, such polar bonds exhibit increased *p* orbital contributions, which in turn results in decreased *p* character in the nonbonding carbon σ orbital.² As a result, the σ orbital will have increased *s* character, favoring the singlet σ^2 state. By the reverse reasoning, substituents that are more electropositive than carbon will form C–X bonds that utilize greater carbon *s* character, yielding nonbonding σ orbitals with less *s* character, thus favoring the triplet $\sigma^1\pi^1$ state.

Hyperconjugation also potentially may affect the singlet–triplet splitting. For example, valence electron pairs on the substituent X in CXY may donate electron density to the nonbonding π orbital of the central carbon. Since this π orbital in the singlet is empty, this should stabilize the singlet state, while the triplet state should be destabilized since its π orbital is already singly occupied.

Thus, the singlet state should be stabilized by substituents that are electronegative and/or have electron pairs that can be donated via hyperconjugation to the empty π orbital. The triplet state, on the other hand, should be stabilized by substituents that are bulky and/or electropositive.²

It is of interest to compare the singlet–triplet splitting in ethylidene (CH₃CH) to that of the parent carbene, methylene. Such a comparison will provide information regarding the effect of a methyl group as a substituent on the singlet–triplet splitting of methylene. Several previous ab initio studies have been reported.^{3–9} However, the previous work does not attempt to explain the physical basis for the effect of CH₃ on the ΔE_{ST} . Thus, our goal in the present work was to obtain quantitative information on the magnitude of the singlet–triplet splitting in CH₃CH and to determine the importance and contribution of each of the aforementioned factors to the observed splitting. We employ a correlation-consistent CI method shown previously to provide a balanced description of both the high and low spin states of molecules.²

Our calculations indicate that substitution of a methyl group for a hydrogen atom in CH₂ reduces the singlet–triplet splitting by approximately 6 kcal/mol, yielding a ΔE_{ST} of 3 ± 2 kcal/mol for CH₃CH. Further, we find that hyperconjugation plays a minimal role, while changes in hybridization are key factors in determining the magnitude of ΔE_{ST} . The rest of the paper is laid out as follows. Section II outlines the calculations performed, section III presents our results, section IV discusses these results in light of previous work, and section V presents concluding remarks.

II. Calculations Details

Basis Sets. The following basis sets were used: *VDZp*. For carbon, the standard Huzinaga–Dunning valence double-zeta contraction (9s5p/[3s2p])^{10,11} was augmented by a set of 3d polarization functions ($\zeta^d = 0.64$)¹³ with the 3s combination of

the d functions removed. For the hydrogens, the (4s/[2s]) Huzinaga–Dunning valence double-zeta basis (exponents scaled by 1.2)^{10,11} was augmented by a set of 2p polarization functions ($\zeta^p = 1.0$).

TZ2p. For carbon, the Huzinaga (11s7p) basis¹² was contracted to triple-zeta for both core and valence by contracting the six tightest s primitives into one, leaving the other five s primitives uncontracted, and contracting the five tightest p primitives into one, leaving the other two p primitives uncontracted. Two sets of 3d polarization functions centered at 0.64 and scaled by 2.3 ($\zeta^d = 0.971$ and 0.422) were added to the carbon valence basis, with the 3s combination of the d functions removed. For the hydrogens, the Huzinaga¹¹ unscaled (6s) basis set was contracted to triple-zeta (by contracting the four tightest primitives into one, leaving the other two primitives uncontracted) and augmented by two sets of 2p polarization functions centered at 0.91 (optimized¹³ for C–H bonds) and scaled by 2.3 ($\zeta^p = 1.38$ and 0.60).

Geometries. The geometries for CH₃CH were optimized via analytic gradient techniques^{14,15} at the GVB(2/4)-PP level¹⁶ for the triplet state and the GVB(3/6)-PP level for the singlet state with C_s symmetry imposed. Lower symmetry geometries were not explored in detail, but preliminary investigations found them to be higher in energy. The optimum values obtained are shown in Figure 1. The equilibrium geometries for CH₂ were taken from the Harding and Goddard GVB-POL-CI calculations.¹⁷

MCSCF and CI Calculations. *GVB(M/2M)-PP.* A correct prediction of the singlet–triplet splitting relies on equivalent treatment of the singlet and triplet states.² At a first-order level, this is achieved by describing the singlet state (σ^2) by a two-configuration wave function of the form $\sigma^2 - \lambda^2\pi^2$, where λ is optimized variationally. This is the simplest form of the generalized valence bond (GVB) theory¹⁶ and is denoted by GVB-(1/2)-PP, which signifies the representation of one correlated electron pair by two natural orbitals. The corresponding one-electron GVB orbitals for this case are $\phi_a = \sigma + \lambda\pi$ and $\phi_b = \sigma - \lambda\pi$, where these orbitals are singlet coupled [so-called “perfect pairing”, denoted by (PP)]. The typical GVB-PP representation of the molecular wave function in terms of natural orbitals is denoted by GVB(M/2M)-PP, where it is understood that M electron pairs are correlated using 2M natural orbitals,¹⁶ where each electron pair is explicitly singlet coupled.

In our particular case, we also describe the C–H and C–CH₃ bonds as correlated electron pairs. This results in a GVB(2/4)-PP description for the triplet state, where both bond pairs involving the central carbon are correlated, and a GVB(3/6)-PP description for the singlet state, where in addition to the two bond pairs the central carbon nonbonding electrons are correlated as well.

GVB-RCI. This is the simplest CI expansion of the GVB-PP wave function which lifts the restriction of singlet pairing of the GVB orbitals and allows the two electrons of a GVB pair to occupy the two natural orbitals in all three possible ways:² (ϕ_a)², $\phi_a^1\phi_b^1$, (ϕ_b)², corresponding to 18 configurations for the singlet and nine configurations for the triplet. The expansion coefficients are then variationally optimized. When the orbitals of the RCI wave function are optimized self-consistently, in addition to variational optimization of the CI expansion coefficients, this MCSCF (multiconfiguration self-consistent-field) wave function is denoted by GVB-RCI(opt).

GVB-RCI*SD_{σπ}. This signifies a wave function in which we allow all single and double excitations from the carbon lone pair σ and π orbitals to all unoccupied orbitals in the basis. These excitations are relative to all of the GVB-RCI configurations (the so-called “reference space”). GVB-RCI*SD_{σπ}(opt) denotes the self-consistent calculation of this wave function, where both orbital shapes and CI expansion coefficients are optimized. Any

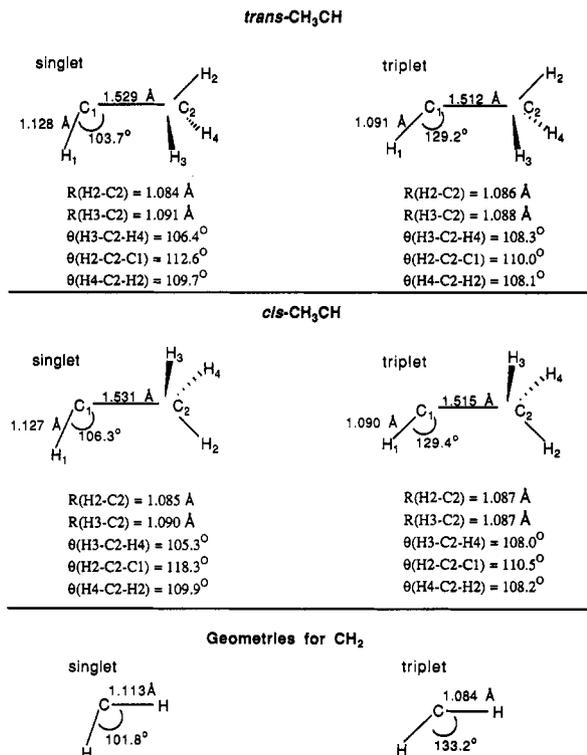


Figure 1. Equilibrium geometries for CH₃CH optimized at the VDZp/GVB-PP level for both cis and trans isomers. Geometries for CH₂ were taken from ref 17 (GVB-POL-CI calculations).

CI wave function that is not denoted as “(opt)” utilizes the GVB-PP orbitals as the CI basis and only optimizes the CI expansion coefficients.

III. Results

The optimum geometries for both cis and trans configurations, obtained at the GVB-PP level, are shown in Figure 1. For both the singlet and the triplet states, the lowest energy structure is found to be the trans configuration. For singlet CH₃CH, several configurations with C₁ symmetry that could allow for substantial hyperconjugation were studied and found to be higher in energy than the corresponding configurations with C_s symmetry. Since the lowest energy geometry for both states was found to be the trans configuration, we focus our attention on *trans*-CH₃CH.

Comparing *trans*-CH₃CH with CH₂, we see that substitution of a methyl group has only a small effect on the bond angle (2–4°) and that the C–H bond lengths only about 0.01 Å, suggesting that CH₃ does not exert much steric repulsion. This comparison, though, should not be taken too literally since the CH₂ geometries were not optimized at the same level of theory. However, a valid comparison can be made for the C–H and C–C bond lengths in CH₃CH, which appear to be sensitive to spin state. In particular, singlet CH₃CH exhibits larger bond lengths than triplet CH₃CH. Recall that the singlet states of carbenes generally utilize more p character in their bonds,² which results in smaller X–C–Y bond angles. Decreased bond angles produce greater repulsion between the substituents, which is in turn reduced by lengthening the bonds. An alternative way of stating this is to realize that the singlet CXY's increased p character in the bonds results in longer bonds simply because p-like orbitals are larger than s-like orbitals, leading to longer equilibrium bond lengths.

The total energies, as well as the singlet–triplet splittings, at the VDZp and TZ2p levels are summarized in Tables I and II, respectively. The corresponding values for CH₂ are included for comparison. It is apparent that the singlet–triplet splitting for

TABLE I: Total Energies (hartrees) and Singlet-Triplet Splittings (kcal/mol) within a VDZp Basis Set^a

calculation	total energies ^b				ΔE_{ST}^f	
	CH ₃ CH		CH ₂		CH ₃ CH	CH ₂
	¹ A'	³ A''	¹ A ₁	³ B ₁		
	Trans Structure					
GVB-PP	-77.99327 (8/8)	-78.00117 (4/4)	-38.93877 (8/8)	-38.95328 (4/4)	5.0	9.1
GVB-RCI ^c	-77.99604 (18/20)	-78.00679 (9/25)	-38.94151 (18/20)	-38.95924 (9/25)	6.7	11.1
GVB-RCI(opt) ^d	-77.99641 (18/20)	-78.00780 (9/25)	-38.94189 (18/20)	-38.96035 (9/25)	7.2	11.6
RCI*SD _{$\sigma\pi$} ^e	-78.02193 (4180/7447)	-78.02884 (3318/9030)	-38.96706 (1174/1989)	-38.98135 (2070/2874)	4.3	9.0
RCI*SD _{$\sigma\pi$} (opt)	-78.02408 (4180/7447)	-78.03110 (3318/9030)	-38.96927 (1174/1989)	-38.98409 (2070/2874)	4.4	9.3
	Cis Structure					
GVP-PP	-77.99158 (8/8)	-78.00045 (4/4)			5.6	
GVB-RCI	-77.99436 (18/20)	-78.00615 (9/25)			7.4	
GVB-RCI(opt)	-77.99472 (18/20)	-78.00718 (9/25)			7.8	
RCI*SD _{$\sigma\pi$}	-78.02018 (4180/7447)	-78.02823 (3318/9030)			5.1	

^a The corresponding number of configurations/spin eigenfunctions for each wave function is given in parentheses below each wave function. ^b 1 hartree = 627.5096 kcal/mol = 27.211 617 eV = 219 474.65 cm⁻¹. ^c Orbitals from the GVB-PP wave function were used as the CI basis. ^d The "(opt)" signifies that the shapes of the orbitals were optimized self-consistently in addition to variational optimization of CI expansion coefficients. ^e All single and double excitations from the methylenic carbon lone electrons (σ and π) to all orbitals of the CI basis were allowed. ^f $\Delta E_{ST} = E(\text{singlet}) - E(\text{triplet})$.

TABLE II: Total Energies (hartrees) and Singlet-Triplet Splittings (kcal/mol) within a TZ2p Basis Set

calculation	total energies ^a		ΔE_{ST}^b	
	¹ A'	³ A''	CH ₃ CH	CH ₂
GVB-PP	-78.00733 (8/8)	-78.01334 (4/4)	3.8	8.0 ^c
GVB-RCI	-78.01027 (18/20)	-78.01879 (9/25)	5.3	9.7 ^c
GVB-RCI(opt)	-78.01066 (18/20)	-78.01981 (9/25)	5.8	10.1 ^c
RCI*SD _{$\sigma\pi$}	-78.04117 (15715/28796)	-78.04550 (12246/33670)	2.7	7.1

^a The corresponding number of spatial configuration/spin eigenfunctions for each wave function is given in parentheses below each total energy. ^b $\Delta E_{ST} = E(\text{singlet}) - E(\text{triplet})$. ^c Taken from results by Carter and Goddard (see ref 18).

CH₃CH is 4.5 ± 0.4 kcal/mol less than that for CH₂ at all levels of calculation. Note that the highest level of theory used within the VDZp basis, the RCI*SD _{$\sigma\pi$} (opt) calculation, yielded essentially the same ΔE_{ST} as the RCI*SD _{$\sigma\pi$} . Recall that the difference between these two wave functions is simply that the latter used GVB-PP orbitals as the CI basis, while the former optimized the shapes of these orbitals in addition to variational optimization of the CI expansion coefficients. Since ΔE_{ST} appeared insensitive to this (expensive) improvement to the wave function, the other calculational series for the cis isomer and for the TZ2p basis were terminated at the RCI*SD _{$\sigma\pi$} level.

Tables III and IV provide quantitative indications of central carbon s and p contributions to the σ orbital and the C-X bond for both CH₂ and CH₃CH using Mulliken population analysis. Although such population analyses tend to be basis set dependent and do not in general provide quantitatively exact extents of charge transfer and hybridization, the fact that they are roughly invariant as the basis set size increases leads us to expect that gross relative trends should be reliable. For example, Table III shows that the hybridization of the σ orbital changes only slightly with basis set (a maximum change of 1.9%). Further examination of Table III reveals that the hybridizations of the σ orbitals in the singlet (σ^2) states of CH₂ and CH₃CH are almost identical, independent of the level of calculation. By contrast, the σ orbital of triplet CH₃-CH exhibits a nonnegligible decrease in p character, especially

TABLE III: Hybridization of the σ Orbital in CH₃CH and CH₂^a

	state	CH ₂		CH ₃ CH	
		% 2s	% 2p	% 2s	% 2p
GVB-PP	(σ^2)	62.1	37.9	63.2	36.8
(VDZp)	($\sigma^1\pi^1$)	19.0	81.0	22.0	78.0
RCI(opt)	(σ^2)	64.5	35.5	63.5	36.5
(VDZp)	($\sigma^1\pi^1$)	17.8	82.3	21.3	78.7
RCI*SD(opt)	(σ^2)	54.0	46.0	54.0	46.0
(VDZp)	($\sigma^1\pi^1$)	8.8	91.2	16.0	84.0
GVB-PP	(σ^2)	64.0	36.0	64.0	36.0
(TZ2p)	($\sigma^1\pi^1$)	19.0	81.0	23.7	76.3
RCI(opt)	(σ^2)			64.0	36.0
(TZ2p)	($\sigma^1\pi^1$)			21.7	78.3

^a Based on Mulliken population analyses (see ref 20).

at the highest level of calculation, RCI*SD _{$\sigma\pi$} (opt), where there is 7.2% less p character in CH₃CH than in CH₂. As mentioned in the Introduction, this decrease in p character will lower the energy of the σ orbital relative to the π orbital, destabilizing the triplet state and resulting in a smaller singlet-triplet splitting. Examination of Table IV indicates that the central carbon hybridization in the C-H bond is unaffected (to within 0.1%) by methyl substitution in both the singlet and triplet states. Thus, CH₃ substitution induces changes in hybridization at the methylenic carbon only in the nonbonding σ orbital and only for the triplet state. These changes suggest triplet state destabilization rather than singlet state stabilization may be responsible for the smaller singlet-triplet gap in CH₃CH.

By comparing bond populations and net charges (Table IV) for CH₂ and CH₃CH, we see that the CH₃ group donates less electrons than does H to the methylenic carbon, consistent with most electronegativity scales that place CH₃ as more electronegative than H.²³ (Note that this latter concept is in direct contrast with the conventional notion that methyl-substituted hydrocarbons are more "electron rich", with CH₃ acting as an electron donor.) Overall, however, the central methylenic carbon atom is still slightly electron withdrawing, which swamps out the electronegativity difference between H and CH₃: They both yield electrons to the central carbon atom. Electron donation would stabilize the triplet state; the fact that the CH₃ group donation is halved compared to the parent CH₂ suggests again triplet destabilization.

TABLE IV: Bond Populations, Net Charges, and Central Carbon Hybridization for CH₂ and CH₃CH^a

CXY	state	bond	bond population on carbon ^b	net charges		C-X bond		C σ^d	
				C	X ^c	% 2s	% 2p	% 2s	% 2p
CH ₂	¹ A ₁	C-H	1.07	-0.20	+0.10	27.0	73.0	54.0	46.0
CH ₂	³ B ₁	C-H	1.17	-0.30	+0.15	51.4	48.6	8.8	91.2
CH ₃ CH	¹ A'	C-H	1.04	-0.07	+0.06	27.1	72.9	54.0	46.0
CH ₃ CH	¹ A'	C-C	1.00		+0.01	31.0	69.0		
CH ₃ CH	³ A''	C-H	1.15	-0.16	+0.12	51.3	48.7	16.0	84.0
CH ₃ CH	³ A''	C-C	1.07		+0.04	52.3	47.7		

^a Based on Mulliken population analyses (see ref 20) performed at RCI*SD $\sigma\pi$ (opt) within a VDZp basis. ^b Perfect covalent bonding would lead to a bond population of 1.00. The carbon atom is the methylenic carbon. ^c For X = CH₃, we include all charge over C and the three H's. ^d Methylenic carbon nonbonding σ orbital.

TABLE V: Composition of the Methylenic π Orbital and the CH₃ Pseudo- π Orbital of CH₃CH^a

	state	% C 2p ^b	% CH ₃	% contribution from C 2p π^b
GVB-PP	(σ^2)	100.0	0.0	2.3
(VDZp)	($\sigma^1\pi^1$)	97.7	2.3	1.1
RCI(opt)	(σ^2)	100.0	0.0	2.3
(VDZp)	($\sigma^1\pi^1$)	97.8	2.2	1.0
RCI*SD(opt)	(σ^2)	100.0	0.0	2.4
(VDZp)	($\sigma^1\pi^1$)	97.7	2.3	1.0
GVB-PP	(σ^2)	100.0	0.0	2.3
(TP2p)	($\sigma^1\pi^1$)	97.3	2.7	1.0
RCI(opt)	(σ^2)	100.0	0.0	2.3
(TZ2p)	($\sigma^1\pi^1$)	97.0	3.0	0.9

^a Based on Mulliken population analyses (see ref 21). ^b C = methylenic carbon.

As mentioned earlier, hyperconjugation from the substituents may also play a role in determining the singlet-triplet splitting in substituted carbenes. Table V displays the character of the nonbonding methylenic π orbital as well as the CH₃ pseudo- π orbital of CH₃CH for both singlet and triplet states at various levels of calculation. One might imagine that another factor that would contribute to the decreased singlet-triplet splitting would be electron donation from the methyl group into the empty methylenic π orbital of the singlet CH₃CH, thereby stabilizing the singlet state relative to the triplet state. However, donation of electron density from the methyl group to the π orbital of the singlet CH₃CH is not observed at all at any level of calculation. Rather, it is the triplet state that shows a slight participation of electron density from the CH₃ radical to the π orbital. Since the π orbital in the triplet state is singly occupied, such donation will result in the destabilization of the triplet state. On the other hand, examining the CH₃ pseudo- π orbital, we see that there is a small contribution from the methylenic 2p π orbital in both the singlet and the triplet states, with a larger contribution in the singlet state. This mixing of the CH₃ and the methylenic " π " orbitals produces a bonding combination whose energy is lower than that of the pure CH₃ orbital and an antibonding combination that has a higher energy than the pure methylenic π orbital. The result is a singlet state that is slightly stabilized (with only the "bonding" orbital occupied) and a triplet state (with two electrons in the "bonding" and one electron in the "antibonding" combinations) that could be either stabilized or destabilized. Whether the triplet state is stabilized or destabilized is not obvious, since it depends on how much the methylenic π orbital is raised in energy upon mixing with the CH₃ orbital. This suggests yet another (small contributing factor to the observed decrease in the singlet-triplet splitting.

IV. Discussion

The optimum geometries for CH₃CH, shown in Figure 1, are in good agreement with the Hartree-Fock gradient-optimized geometries of Kohler and Lischka, who reported *trans* structures with bond angles of 106.2° and 129.4° for the singlet and the triplet states, respectively.⁵ Similar results were obtained by Ha

and co-workers.⁶ A recent HF*SD CI investigation by Gallo and Schaefer⁹ reported bond angles of 105.3° and 131.2° for the singlet and triplet CH₃CH, respectively, although their geometry for the singlet state has C₁ symmetry. We do not expect that the very slight distortions (e.g., 0.006 Å in a C-H bond length⁹) that yielded a C₁ rather than a C_s structure for the singlet (found by both Luke et al.⁸ and Gallo and Schaefer⁹) will undermine the conclusions of this study, since the gross structural trends are in agreement with previous work. In particular, the minute changes in the bond angles going from CH₂ to CH₃CH found by us and previous workers strongly suggest that CH₃ induces negligible steric effects in this system.

The results for the singlet-triplet splitting of CH₃CH are summarized in Tables I and II. Our best unadulterated values for the singlet-triplet splitting of CH₃CH are 2.7 and 5.8 kcal/mol, corresponding to our results within the triple-zeta plus double-polarization basis set for the RCI*SD $\sigma\pi$ and RCI(opt) levels of calculation, respectively. The effects of basis set incompleteness at the TZ2p level have been evaluated for CH₂ previously by Carter and Goddard.¹⁸ Increasing the basis from TZ2p to an extremely extended TZ3p2fn basis set (triple-zeta with three d functions, two f functions, and one set of s and p diffuse functions) was found to further reduce the RCI(opt) ΔE_{ST} by 1 kcal/mol. The zero-point energy difference between the singlet and triplet states has been calculated (CISD calculations) by Gallo and Schaefer⁹ to reduce ΔE_{ST} by 0.5 kcal/mol. Thus, corrections for basis set incompleteness and zero-point energy differences reduce these calculated values for ΔE_{ST} by 1.5 kcal/mol, leading to values for ΔE_{ST} of 1.2 and 4.3 kcal/mol. One arrives at a similar estimate independently by comparing the ΔE_{ST} values for CH₃CH and CH₂. At all levels of calculation (Tables I and II), ΔE_{ST} for CH₃CH is 4.5 \pm 0.4 kcal/mol lower than that of CH₂. Since the experimental ΔE_{ST} for CH₂ without zero-point energy is 9.1 \pm 0.2 kcal/mol,²² the ΔE_{ST} for CH₃CH should be (9.1 \pm 0.2) - (4.5 \pm 0.4) = 4.6 \pm 0.6 kcal/mol or 4.1 \pm 0.6 kcal/mol after including zero-point energy corrections. Based on these three independent values (1.2, 4.3, and 4.1 kcal/mol), our best estimate for ΔE_{ST} (CH₃CH) is 3 \pm 2 kcal/mol.

Our prediction for the singlet-triplet splitting of CH₃CH differs from results obtained by Luke et al.,⁸ who reported a ΔE_{ST} of 10.7 kcal/mol using unrestricted Hartree-Fock (UHF) and Moller-Plesset perturbation theory through fourth order (MP4) with a 6-31G* (essentially VDZp) basis set. However, this may simply be due to residual spin contamination in UHF theory,¹⁹ as well as basis set incompleteness. Ha and co-workers also reported a ΔE_{ST} of 10 kcal/mol derived from an HF*SD-CI wave function within a DZp basis.⁶ This led them to suggest that the singlet-triplet splitting is virtually unaffected by the replacement of the hydrogen atom with a methyl group.⁶ However, it has been noted² that the singles and double CI expansion, HF*SD-CI, tends to artificially stabilize the triplet by allowing a greater extent of electron correlation for the triplet than it does for the singlet, thus overestimating the singlet-triplet gap for a triplet ground state. On the other hand, Kohler and Lischka⁵ reported a ΔE_{ST} of 5.6 kcal/mol using CEPA (correlated electron pair approximation) theory within a near-TZ2p-quality basis set,

and Gallo and Schaefer⁹ also predicted a value of 5.6 kcal/mol from HF*SD CI calculations including Davidson's correction and zero-point energies within a TZ2pf basis set, in good agreement with our results. (They actually reported a value of 5.2 kcal/mol; however, we note that their value for the zero-point energy correction is in error by a factor of 2 according to their reported vibrational frequencies.)

Tables III and IV summarize the s and p characters in the σ orbital and the C-X bond pairs of CH₃CH and CH₂. We observe very similar hybridizations for both the nonbonding σ orbital and the C-H bonds of singlet CH₃CH relative to those of singlet CH₂. This suggests that replacement of the hydrogen by a methyl group does not have an appreciable effect on the σ orbital in the singlet state; it neither stabilizes nor destabilizes the σ orbital in the singlet state. On the other hand, comparison of the triplet states reveals a significant decrease in p character in the nonbonding σ orbital of CH₃CH relative to that of CH₂. This decrease in the p character of the σ orbital is of course concomitant with increased s character, which consequently lowers the σ orbital in energy and widens the energy gap between σ and π orbitals, thus destabilizing the triplet state. Furthermore, the bond populations and net charges (Table IV) suggest that CH₃ donates less electrons than H to the methylenic carbon, which also destabilizes the triplet state of CH₃CH relative to CH₂.

Table V summarizes the character of the methylenic π orbital and the CH₃ pseudo- π orbital of CH₃CH at various levels of calculation. No electron donation from the methyl group to the empty methylenic π orbital of the singlet CH₃CH is observed. On the other hand, slight donation of electron density from the methyl group to the methylenic π orbital in the triplet CH₃CH occurs. Since this orbital is partially occupied in the triplet state, this will have a small destabilizing effect. Examination of the CH₃ pseudo- π orbital reveals a small contribution from the methylenic carbon p π in both the singlet and the triplet states (larger in the singlet). As discussed in the previous section, this will stabilize the singlet slightly, while the triplet state could be either stabilized or destabilized by this mixing of orbitals. Note, however, that the minimal degree of hyperconjugation exhibited in both the methylenic carbon p π orbital and the CH₃ pseudo- π orbital is such that it cannot be the dominant reason for the decrease in the singlet-triplet gap upon CH₃ substitution.

We therefore conclude that the observed decrease in ΔE_{ST} of CH₃CH relative to CH₂ is a result of both a slight stabilization of the singlet state and a more pronounced destabilization of the triplet state. The stabilization of the singlet state is due to the slight mixing of the methylenic carbon p π and the CH₃ pseudo- π orbitals. The destabilization of the triplet state is due to a combination of three effects: (i) decreased p character in the σ orbital of the triplet CH₃CH lowers the energy of the σ orbital, widening the energy separation between the σ and π orbitals, which disfavors singly occupying both σ and π orbitals; (ii) decreased electron donation from CH₃ (relative to H) to the methylenic carbon; and (iii) repulsions between the singly-occupied methylenic carbon p π orbital and the CH₃ group, which disfavor occupation of the carbon p π orbital. Since these three effects are all fairly small, the ground state of CH₃CH is still a

triplet as in CH₂, but the energy gap between the singlet and the triplet states is reduced since the three effects work in concert.

V. Conclusions

Ab initio GVB-CI and MCSCF calculations have been performed on CH₃CH and CH₂ to determine quantitatively and qualitatively the effect of methyl substitution on the singlet-triplet splitting of CH₂. These calculations suggest that CH₃CH has a singlet-triplet splitting of 3 ± 2 kcal/mol, about 6 kcal/mol less than the energy gap for CH₂. We have offered explanations as to why substitution of a methyl group lowers the energy gap between the singlet and the triplet, while still favoring a triplet ground state. In particular, we have shown that neither steric effects nor hyperconjugative singlet stabilization can account for the decrease in ΔE_{ST} . Rather, subtle changes in the character of the nonbonding σ orbital, decreased charge transfer to the methylenic carbon, and hyperconjugative destabilization in the triplet state (as well as a slight hyperconjugative stabilization of the singlet state) are responsible for the decrease in the singlet-triplet splitting of CH₃CH relative to CH₂.

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