Electronic States of Trimethylenemethane[1a]

James H. Davis[1b] and William A. Goddard III*

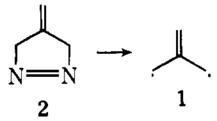
Contribution No. 5423 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125.

Received August 31, 1976

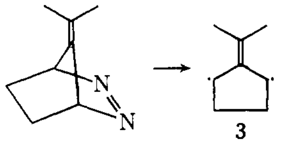
Abstract: Ab initio generalized valence bond (GVB) and configuration interaction (CI) calculations were carried out on the planar and bisected forms of trimethylenemethane. The results indicate that the ground state is the planar triplet with the planar singlet state 26 kcal/mol higher. The rotational barrier for the triplet state is 18 kcal/mol, while one component of the planar singlet prefers the bisected geometry by 7 kcal/mol. We predict the transitions for the chemically interesting states as follows: planar triplet, λ_{max} 266 nm with $f = 0.002$; bisected singlet, λ_{max} 359 nm with $f = 0.0008$; and planar singlet, λ_{max} 289 nm with $f = 0.10$. The vertical ionization potential is calculated as 8.3 eV.

I. Introduction

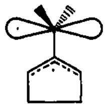
Trimethylenemethane (**1**) has been a subject of much theoretical discussion since the work of Moffitt.[2] Only recently, however, has the molecule become a subject of serious experimental and theoretical work. In 1966, Dowd[3] reported the first preparation of **1** from the pyrolysis of the pyrazoline system **2**. The early work of Dowd has been summarized in a review article[4] and will not be discussed. In 1971, Berson[5] prepared the trimethylenemethane diyl analogue **3** from the diazo compound **4**, and extensive research has been conducted since then. Early ESR experiments showed **3** to have a triplet ground state, and CIDNP studies showed that dimerization of **3** must include at least one triplet reactive species. Additional studies[6-9] have shown that at least two distinct electronic states are involved in the pyrolysis of the diazo precursor **4**. Berson has postulated that the two reactive species are a bisected singlet **5** and a planar triplet **6**.



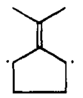
2 1



4 3



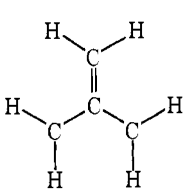
5



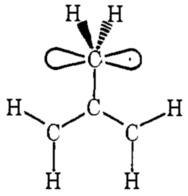
6

Previous theoretical studies on trimethylenemethane diradical **1** have led to contradictory results. Most workers agree that for the planar geometry the lowest state is a triplet state; however, calculations of the lowest planar singlet state lead to energies of 21,[10] 68,[10] and 70[11] kcal/mol from ab initio Hartree-Fock (HF) wave functions and 35 and 57 kcal/mol[12] from semiempirical Hartree-Fock wave functions. Part of the problem here is a special difficulty with spatial symmetry for the Hartree-Fock wave function of the lowest singlet state.[13]

We report here the results of ab initio configuration interaction (CI) calculations based on generalized valence bond[14] (GVB) wave functions of both the planar (**1**) and the bisected (**7**) geometries of trimethylenemethane, which eliminate the above difficulties and provide a description of the other excited states, including the transition oscillator strengths. A summary of these results was communicated earlier.[15]



1



7

II. Calculational Details

For all calculations, a contracted Gaussian basis set equivalent to a double ζ (DZ) basis was used. For carbon, Dunning's contraction[16] (3s, 2p) of Huzinaga's (9s, 5p) basis set was utilized, while for hydrogen a comparable (4s/2s) contraction was used,[16] with each Gaussian exponent multiplied by a scale factor of 1.44, corresponding to a Slater exponent of $\zeta = 1.2$.

Our objective in these studies was to establish the overall character of the states of planar and bisected trimethylenemethane. Hence we have used a geometry of each form roughly appropriate for the ground state: C-C bond lengths of 1.40 Å, CH bond lengths of 1.086 Å, and bond angles of 120°. Since these geometries are roughly appropriate for the ground state, we obtain vertical excitation energies and ionization potentials. Geometry optimization would be particularly important for the rotation barriers.

In the GVB calculations the π bond pair of the triplet state was correlated with all orbitals described as symmetry functions (for the appropriate symmetry group). For the planar configuration this led to four occupied π orbitals. In the configuration interaction (CI) calculations for the planar case, a full CI was carried out over these four orbitals plus the four remaining (virtual) π orbitals of the DZ basis. Thus the ground-state σ orbitals were used for all excited and ion states. This is adequate for the valence excited states and reasonably adequate for the lower ion states.

For the bisected configuration this GVB calculation leads to four non-closed-shell orbitals, three π and one σ. For the CI this was supplemented with three additional π and one additional σ (virtual) functions obtained by starting with the most diffuse π function on each of the three unrotated carbons plus the corresponding σ-like orbital in the rotated carbon and orthogonalizing to all original orbitals. From additional CI calculations including single excitations from the π combination of CH orbitals on the rotated carbon, we concluded that such excitations are unimportant.

All HF and GVB calculations were carried out with Bobrowicz-Wadt-Goddard program[17] using the fully self-con-

Table I. Total Energies for the Ground State of Trimethylenemethane (hartrees)

State	HF	GVB	GVB-CI
${}^3A_2$ (planar)	−154.823 62	−154.836 39	−154.873 78
${}^3B_1$ (bisected)	−154.796 19	−154.811 69	−154.844 78

sistent techniques of Hunt, Hay and Goddard.[18] The CI calculations were carried out with the Caltech CI program (Bobrowicz, Winter, Ladner, Moss, Harding, Walch, and Goddard).[17,19]

III. Results

The ground-state energies or the planar and bisected geometries of trimethylenemethane were calculated using HF, GVB, and GVB-CI wave functions. These results are shown in Table I.

The results of CI calculations on the excited states are presented in Tables II and III, where we have also listed the dominant configurations for each state. Because of the use of the GVB orbitals, the CI wave function is dominated by a few configurations.

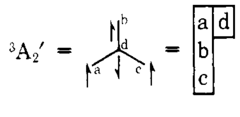
The CI results for the lower ion states of planar and bisected trimethylenemethane are shown in Tables IV and V.

In Table VI we compare our results to those of previous workers. Our numbers are in good agreement with the HF calculations of Yarkony and Schaefer.[10] (We avoided the ambiguity in the energy of the ${}^1E'$ state by carrying out CI.) The early HF calculations by Hehre et al.[11] and MINDO calculations by Dewar[12] led to excitation energies high by a factor of 2.

IV. Qualitative Description

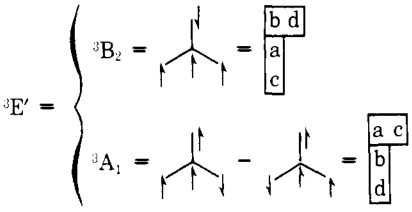
First we will consider the excited states of the planar geometry. Given four orbitals each with one electron, we can form six states (referred to as covalent or *valence* states): two singlets, three triplets, one quintet. The quintet state is expected to be of high energy and was not calculated.

The ground-state triplet, ${}^3A_2'$ can best be described as having the three outer orbitals high-spin coupled ($S = 3/2$) with the central carbon orbital low-spin coupled to all three (leading to $S = 1$) (eq 1) (see Appendix for the precise expansion of the wave function).[20] Rotating, say, the upper CH_2 group to the bisected form leads to a loss of bonding between centers b and d and hence to a higher energy (by 18.2 kcal/mol) as indicated in Figure 1.



(1)

The other two valence triplet states of the planar geometry are degenerate, ${}^3E'$, lying 107.6 kcal/mol above the ground state. These states can each be represented as the singlet coupling of two orbitals and triplet pairing of the other two (eq 2 and 3). Notice that the ${}^3B_2$ state (eq 2) has a bonding inter-



(2)

(3)

Table II. Excitation Energies and Dominant Configurations for Planar Trimethylenemethane [GVB-CI][c]

State symmetry		Excitation energy, kcal/mol	Configuration[a]								Energy lowering,[b] hartree
D_{3h}	C_{2v}		$\pi_1(a_2'')$	$\pi_2(a_2'')$	$\pi_3(e_x'')$	$\pi_4(e_y'')$	$\pi_5^*(a_2'')$	$\pi_6^*(a_2'')$	$\pi_7^*(e_x'')$	$\pi_8^*(e_y'')$	
${}^3A_2'$	${}^3B_2$	0.0	2	0	1	1	0	0	0	0	
			1	1	1	1	0	0	0	0	0.036
			0	2	1	1	0	0	0	0	0.013
${}^1E'$	${}^1B_2$	26.4	2	0	1	1	0	0	0	0	
			1	0	2	1	0	0	0	0	0.060
			2	1	0	1	0	0	0	0	0.043
	${}^1A_1$	26.4	2	0	2	0	0	0	0	0	
			2	0	0	2	0	0	0	0	
			1	0	1	2	0	0	0	0	0.061
			2	1	1	0	0	0	0	0	0.43
${}^3E'$	${}^3B_2$	107.6	1	0	2	1	0	0	0	0	
			2	1	0	1	0	0	0	0	0.089
			1	1	1	1	0	0	0	0	0.049
			2	0	0	1	1	0	0	0	0.021
			0	1	2	1	0	0	0	0	0.015
			1	2	0	1	0	0	0	0	0.015
	${}^3A_1$	107.6	1	0	1	2	0	0	0	0	
			2	1	1	0	0	0	0	0	0.089
			1	1	0	2	0	0	0	0	0.029
			1	1	2	0	0	0	0	0	0.029
			2	0	1	0	1	0	0	0	0.021
			0	1	1	2	0	0	0	0	0.015
			1	2	1	0	0	0	0	0	0.015
${}^1A_1'$	${}^1A_1$	125.4	0	0	2	2	0	0	0	0	
			2	0	0	2	0	0	0	0	0.015
			2	0	2	0	0	0	0	0	0.015

[a] The first four orbitals are the GVB orbitals, while the last four are the remaining (virtual) π orbitals for the DZ basis. [b] The energy increase upon deleting this configuration from the wave function. [c] All configurations contributing more than 0.010 hartree = 6.275 kcal/mol are included.

Table III. Excitation Energies and Dominant Configurations for Bisected Trimethylenemethane [GVB-CI][a]

State symmetry C_{2v}	Excitation energy, kcal/mol	Configuration								Energy lowering, hartree
		$\sigma(b_2)$	$\pi_1(b_1)$	$\pi_2(b_1)$	$\pi_3(a_2)$	$\sigma_2{}^*(b_2)$	$\pi_4(b_1)$	$\pi_5(b_1)$	$\pi_6(a_2)$	
$^3B_1$	18.2	1	2	0	1	0	0	0	0	
		1	1	1	1	0	0	0	0	0.023
		1	0	2	1	0	0	0	0	0.017
$^1B_1$	20.2	1	2	0	1	0	0	0	0	
		1	1	1	1	0	0	0	0	0.025
		1	0	2	1	0	0	0	0	0.017
$^3A_2$	98.7	1	1	0	2	0	0	0	0	
		1	2	1	0	0	0	0	0	0.111
		1	1	2	0	0	0	0	0	0.026
		1	0	1	2	0	0	0	0	0.024
$^1A_2$	99.9	1	1	0	2	0	0	0	0	
		1	2	1	0	0	0	0	0	0.113
		1	1	2	0	0	0	0	0	0.026
		1	0	1	2	0	0	0	0	0.025
		1	2	0	0	0	0	1	0	0.011
$^1A_1$	139.0	2	2	0	0	0	0	0	0	
		1	2	0	0	1	0	0	0	0.043
		2	0	0	2	0	0	0	0	0.028
		2	1	1	0	0	0	0	0	0.011
$^3B_1$	155.6	1	1	1	1	0	0	0	0	
		1	1	0	1	0	0	0	0	0.025
$^1A_1$	160.1	0	2	0	2	0	0	0	0	
		0	2	2	0	0	0	0	0	0.016
		0	1	1	2	0	0	0	0	0.011

[a] Note that all energies are relative to the ground state of the *planar* geometry. All configurations contributing more than 0.010 hartree = 6.275 kcal/mol are included.

Table IV. Ionization Potentials and Dominant Configurations for Planar Trimethylenemethane [GVB-CI][a]

State symmetry		Excitation energy, eV	Configuration								Energy lowering, hartree
D_{3h}	C_{2v}		$\pi_1(a_2''$	$\pi_2(a_2'')$	$\pi_3(e_x'')$	$\pi_4(e_y'')$	$\pi_5{}^*(a_2'')$	$\pi_6{}^*(a_2'')$	$\pi_7{}^*(e_x'')$	$\pi_8{}^*(e_y'')$	
$^2E''$	$^2B_1$	8.30	2	0	0	1	0	0	0	0	
			1	0	1	1	0	0	0	0	0.028
			0	0	2	1	0	0	0	0	0.013
$^2E''$	$^2A_2$	8.30	2	0	1	0	0	0	0	0	
			1	0	2	0	0	0	0	0	0.016
			1	0	0	2	0	0	0	0	0.016
			0	0	1	2	0	0	0	0	0.013
$^4A_1''$	$^4B_1$	11.30	1	0	1	1	0	0	0	0	
			0	0	1	1	0	1	0	0	0.006
$^2A_1''$	$^2A_2$	12.41	2	1	0	0	0	0	0	0	
			2	0	0	0	1	0	0	0	0.033
			1	0	0	2	0	0	0	0	0.018
			1	0	2	0	0	0	0	0	0.018
			1	2	0	0	0	0	0	0	0.012
			0	1	0	2	0	0	0	0	0.012
			0	1	2	0	0	0	0	0	0.012
$^2E''$	$^2B_1$	14.12	1	0	1	1	0	0	0	0	
			1	1	0	1	0	0	0	0	0.060
			0	0	2	1	0	0	0	0	0.013
			2	0	0	1	0	0	0	0	0.012
			0	1	1	1	0	0	0	0	0.011
$^2E''$	$^2A_2$	14.12	1	0	2	0	0	0	0	0	
			1	0	0	2	0	0	0	0	
			1	1	1	0	0	0	0	0	0.060
			0	0	1	2	0	0	0	0	0.013
			2	0	1	0	0	0	0	0	0.012
$^2A_2''$	$^2B_1$	14.45	1	0	1	1	0	0	0	0	
			0	1	1	1	0	0	0	0	0.066

[a] The energies are relative to the ground state of the *planar* geometry. All configurations contributing more than 0.010 hartree = 6.275 kcal/mol are included.

Table V. Ionization Potentials and Dominant Configurations for Bisected Trimethylenemethane [GVB-CI][a]

State symmetry C_{2v}	Excitation energy, eV	Configurations $\sigma(b_2)$	$\pi_1(b_1)$	$\pi_2(b_1)$	$\pi_3(a_2)$	$\sigma_2^*(b_2)$	$\pi_4^*(b_1)$	$\pi_5^*(b_1)$	$\pi_6^*(a_2)$	Energy lowering, hartree
$^2B_2$	8.89	1	2	0	0	0	0	0	0	
		1	0	0	2	0	0	0	0	0.019
$^2A_2$	10.55	0	2	0	1	0	0	0	0	
		0	1	1	1	0	0	0	0	0.035
		0	0	2	1	0	0	0	0	0.016
$^4A_1$	11.65	1	1	0	1	0	0	0	0	
		1	1	0	0	0	0	0	1	0.006
$^2A_1$	11.76	1	1	0	1	0	0	0	0	
		1	1	0	0	0	0	0	1	0.006
$^2B_1$	14.03	0	2	1	0	0	0	0	0	
		0	1	0	2	0	0	0	0	0.094
		0	0	1	2	0	0	0	0	0.040
		0	1	2	0	0	0	0	0	0.013
		0	2	0	0	0	0	1	0	0.013
$^2B_2$	16.96	1	1	1	0	0	0	0	0	
		1	1	0	0	0	0	1	0	0.013

[a] Note that all energies are relative to the ground state of the *planar* geometry. All configurations contributing more than 0.010 hartree = 6.275 kcal/mol are included.

Table VI. Excitation Energy (kcal/mol) for Various Calculations of Trimethylenemethane[g]

			INDO		Dewar and Wasson[a]	Hehre, Salem, and Wilcott[b]	Yarkony and Schaefer[c]	Davidson and Borden[d]	This work
			HF	CI[f]	(MINDO/2)	HF-CI)	(HF)	(HF)	(GVB-CI)
Planar	$^3A_2'$		0.0	0.0	0.0	0.0	0.0	0.0	0.0
							(−154.825 2[h])	(−152.965 4[h])	(−154.873 78[h])
	$^1E'$	D_{3h}				70.4	68.6		26.4, 26.4
		C_{2v}[e]		25, 25	36, 57		212,-	26.2, 116.3	26.4, 26.4
	$^1A_1$		112	175			128.8	123.5	125.4
Bisected	$^3B_1$		19	64	9		16.9		18.2
	$^1B_1$			69	12	18.3	18.5		20.2

[a] Reference 12. [b] Reference 11, total energy not reported. [c] Reference 10. [d] Reference 13. This work also reported a full π-CI calculation resulting in a degenerate description of the $^1E'$ state; however, no corresponding calculation was reported for $^3A_2'$. [e] The two values correspond to the $^1B_2$ and $^1A_1$ components in sequence. [f] Full CI over the π space. [g] Total energies of the ground state are reported for the ab initio calculations. [h] Units of hartrees.

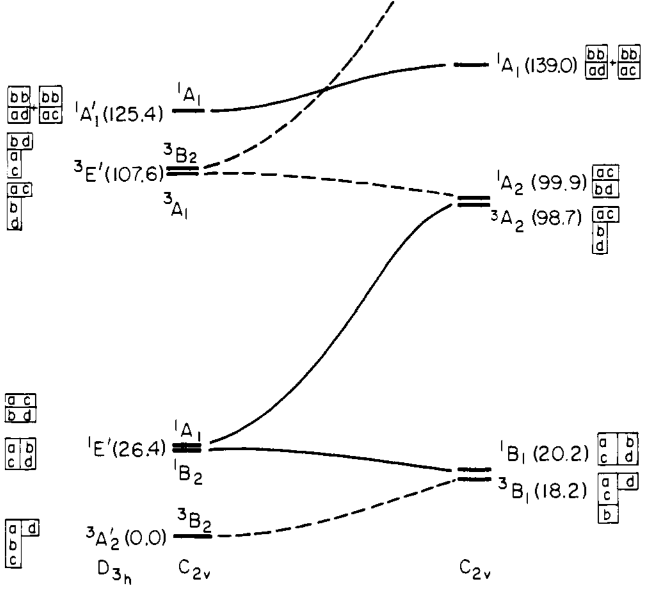
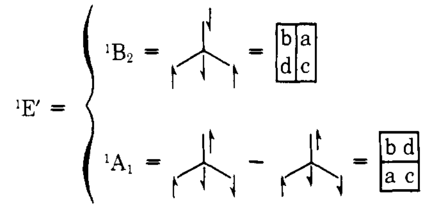


Figure 1. Electronic states of trimethylenemethane (energies in kcal/mol).

action between centers b and d, while the $^3A_1$ state (eq 3) has an antibonding interaction between these centers. As a consequence, rotation of the upper methylene group leads to a lowering of energy for the $^3A_1$ state (by 8.9 kcal) and an energy increase for the $^3B_2$ state (by 48.0 kcal).

Turning to the planar singlet states, we find two degenerate states 26.4 kcal/mol above the triplet ground state. These can be represented, respectively, as either (i) the coupling of b and d into a triplet, the coupling of a and c into a triplet, and then the coupling of these two pairs into an overall singlet state (eq 4), or as (ii) the coupling of b and d into a singlet, the coupling of a and c into a singlet, and then the coupling of these two pairs into an overall singlet state (eq 5). Both states have two



(4)

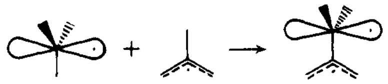
(5)

bonding and one antibonding interaction between central and terminal carbon d, and indeed we find them to be degenerate. Rotating the upper methylene group to the bisected form removes a repulsive triplet pairing for $^1B_2$ (eq 4), stabilizing this state by 6.2 kcal, but removes an attractive singlet pairing for

$^1A_1$ (eq 5), destabilizing this state by 73.5 kcal. Similar geometric effects were found for the $^3E'$ state.

The overall picture for the five valence states for planar trimethylenemethane is summarized in Figure 1. From the Jahn-Teller theorem we expect the $^1E'$ and $^3E'$ states of planar trimethylenemethane to lead to distortions removing the degeneracy. The most important effect of this will be to reduce the separation between the planar singlet and the bisected singlet.

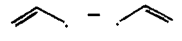
Now we will examine in more detail the excited states of the bisected trimethylenemethane. Considering the bisected trimethylenemethane to be the union of the π system of the allyl



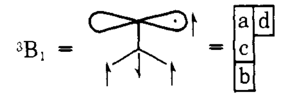
radical with the σ radical orbital of the methyl radical allows us to build up the excited states as follows.

The ground state of allyl has the form given in eq 6, corresponding to the resonance form

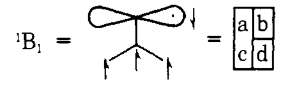
(6)



leading to $^2A_2(\pi^3)$ symmetry. Combining this with the in-plane σ p orbital ($^2B_2(\sigma)$ symmetry) leads to $^3B_1(\sigma\pi^3)$ (eq 7) and $^1B_1(\sigma\pi^3)$ (eq 8) states that should be nearly degenerate (separated by a two-center σ-π exchange integral). As expected, we find a $^3B_1$ ground state for the bisected geometry with the $^1B_1$ excited state lying 1.8 kcal/mol higher in energy. Rotating the upper methylene group to the planar form leads to a bonding interaction for $^3B_1$ (stabilizing this state) and leads to an antibonding interaction for $^1B_1$ (destabilizing this state).

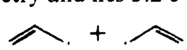


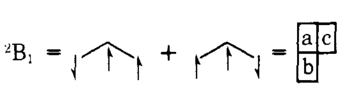
(7)



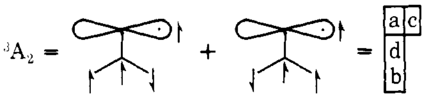
(8)

The first excited state of allyl is the antiresonant state (eq 9), which is $^2B_1$ symmetry and lies 3.2 eV[21] above the resonant state (eq 6). Combining this antiresonant form of allyl with the σ p orbital ($^2B_2$) leads to the $^3A_2$ (eq 10) and $^1A_2$ (eq 11) states, which should be ~3.2 eV above the $^{3,1}B_1$ states and nearly degenerate (separated by a two-center σ-π exchange integral). In fact we find the $^3A_2$ and $^1A_2$ states at 3.3 eV above the $^3B_1$ ground state with a triplet-singlet splitting of only 1.2 kcal/mol. Rotating the upper methylene group to the planar geometry destabilizes the $^3A_2$, while stabilizing the $^1A_2$ state.

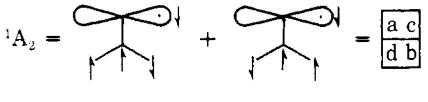




(9)



(10)



(11)

Summarizing the above discussion, we find that the states correlate as shown in Figure 1.

Additional excited states are also given in Tables II and III. Since our basis does not contain diffuse basis functions, these states must be of ionic (zwitterionic) character. For such states one would expect significant changes in the σ orbitals and hence our energies should be significantly too high.

The cation states can be easily understood in terms of the above description. Ionization of an electron from one of the outside π orbitals in the planar $^3A_2'$ ground state results in a degenerate pair of doublet states ($^2E''$) lying at 8.3 eV and a $^2A_2''$ state at 14.5 eV. Rotation of a methylene group splits the degeneracy of the $^2E''$ states, leading to a $^2B_2$ ion at 8.9 eV and a $^2A_2$ ion at 10.6 eV. The $^2B_2$ state has a $\sigma\pi^2$ configuration in which the π system is an allylic cation; the higher energy $^2A_2$ ion has a π^3 configuration with the charge localized on the rotated methylene.

Ionization of the electron from the central π orbital leads to a $^4A_2''$ state at 11.3 eV. Once again, rotating the methylene group to the bisected form raises the energy, since we decrease the delocalization.

Other ion states involving simultaneous ionization and excitation are listed in Tables IV and V.

V. Comparison with Experiment

A. Spectroscopic Data. Thus far little spectroscopic data have yet been reported (Berson and Piatz[22] are attempting to observe these transitions in the low-temperature ultraviolet spectrum). For comparison with future experimental results we have calculated the intensities of the various transitions as tabulated in Table VII.

For the planar geometry we calculated that the vertical transition energy from ground state $^3A_2'$ to $^3E'$ ($^3B_2$ and $^3A_1$) corresponds to λ_{max} 266 nm[23] with an oscillator strength of $f = 1.7 \times 10^{-3}$. For the bisected geometry we find that the first vertical transition energy from the lowest singlet state ($^1A_2 \leftarrow {^1B_1}$) corresponds to λ_{max} 359 nm with $f = 7.9 \times 10^{-4}$. For the planar geometry the first absorption of the *singlet state* is calculated as λ_{max} 289 nm with $f = 0.10$. This planar singlet state, however, may be too short-lived for sufficient population to observe the transition in absorption experiments.

On the basis of the calculated ionization potentials, Rydberg transitions are expected at ~4.6-4.9 eV (270 to 250 nm) [$^3A_2' \rightarrow {^3E''}(3s)$] and ~5.6-6.7 eV (220-200 nm)[$^3A_2' \rightarrow {^3E'}(3p)$]. Since diffuse basis functions were not included, we have not calculated these states directly.

B. Pyrolysis. The pyrolysis data of Berson[5-8] correspond qualitatively to the calculated energy surface. We expect that the pyrolysis of the diazo compound **4** gives planar excited singlet ($^1E_1$). The $^1B_2$ component quickly undergoes methylene rotation to give the bisected $^1B_1$, which in turn intersystem crosses to give the $^3B_1$ state, which quickly rotates to the $^3A_2'$ ground state. (The $^1A_1$ component can convert to the bisected geometry by rotating about another axis.) Thus, assuming intersystem crossing to be slow compared with diradical trapping, the reactive species observed by Berson should be the planar $^3A_2'$ and the bisected $^1B_1$.

A possibly significant difference between **1** and **3** is that the lowest ^1E state of **1** splits into two nondegenerate states ($^1A_1$ and $^1B_2$) of **4**. Of these, the $^1A_1$ state seems more likely formed. If $^1A_1$ is lower than $^1B_2$ for the planar geometry (only the $^1B_2$ states prefers twisting to the bisected form), the $^1A_1$ state may live long enough to do some chemistry or to convert (intersystem cross) directly to the lower triplet state. In this circumstance there could be three reactive forms of trimethylenemethane (planar $^3B_2$ and $^1A_1$ and bisected $^1B_2$). With proper substituents on **3** it may be possible to stabilize planar $^1A_1$ lower than bisected $^1B_2$ so that all the chemistry would involve the two planar states. Such possibilities could be probed

Table VII. Transition Strengths

Geometry	Transition	Transition energy, nm	Dipole matrix element, au	f
Planar	$1\ ^3A_2' \rightarrow 2\ ^3E'$	266	0.086 38	1.7×10^{-3}
	$1\ ^3A_2' \rightarrow 2\ ^3A_2'$	146[a]	−1.545 66	5.0×10^{-1}
	$1\ ^1E' \rightarrow 1\ ^1A_1'$	289	1.401 41	1.0×10^{-1}
Bisected	$1\ ^1B_1 \rightarrow {}^1A_2$	359	0.096 41	7.9×10^{-4}

[a] The upper state is $(\pi_1)^2(\pi_2)^1(\pi_4)^1$.

by observing the absorptions at 266 (planar $^3B_2$), 359 (bisected $^1B_1$), and 289 nm (planar $^1A_1$) as a function of reaction conditions and time for various substituents.

C. Photoionization. Thus far photoionization experiments have not been reported. Starting with the planar triplet state the prominent vertical photoionization potentials are calculated to be 8.3 eV to $^2E''$, 11.3 eV to $^4A_2''$, and 14.5 eV to $^2A_2''$. Other cation states involve excitation simultaneous with ionization.

Starting with the bisected singlet state $^2B_1$, the prominent IP's are 9.7 eV for ionizing the electron from the σ orbital and 8.0 and 10.9 eV for ionizing an electron from a π orbital.

Starting with the $^1A_1$ component of planar ^1E that could be stable for planar geometries (vide supra), the IP's are 7.2 and 13.0 eV (the $^1B_2$ component leads to the same IP's).

Recently Yarkony and Schaefer[24] reported HF calculations for the ion states of TMM. They find ionization potentials (HF) of 8.03, 8.99, 12.75, 13.86, and 16.62 eV for the states we find (CI) at 8.30, 11.30, 12.41, 14.12, and 14.45 eV, respectively. These differences of up to 2.5 eV are mostly due to the electron correlation effects; however, for the highest two states, our restriction of the σ core to be that of the ground state may also lead to significant error.

VI. Summary

Our calculations predict that the ground state of trimethylenemethane is the planar triplet, with the planar singlet state 26 kcal/mol higher. The rotational barrier for the triplet state is 18 kcal/mol, while one component of the planar singlet prefers the bisected geometry by 7 kcal/mol. We predict the transitions for the chemically interesting states as follows: planar triplet, $\lambda_{\max}$ 266 nm with $f = 0.002$; bisected singlet, $\lambda_{\max}$ 359 nm with $f = 0.0008$; and planar singlet, $\lambda_{\max}$ 289 nm with $f = 0.10$. The vertical ionization potential is calculated as 8.3 eV.

Appendix

The tableaux representation used in Section IV and Figure 1 describes the precise coupling of orbitals and spins for each wave function. Two orbitals in a horizontal box indicate that the orbitals are singlet coupled, while two orbitals in a vertical box indicate that the orbitals are high-spin or triplet coupled. The cases used in this paper are given below.

$$\boxed{a\ b} \equiv \mathcal{A}[\phi_a\phi_b(\alpha\beta - \beta\alpha)]$$

$$\boxed{\begin{array}{c}a\\b\end{array}} \equiv \mathcal{A}[\phi_a\phi_b(\alpha\beta + \beta\alpha)]$$

$$\begin{array}{|c|c|}\hline a & c \\ \cline{2-2} b \\ \cline{1-1}\end{array} \equiv \mathcal{A}\{\phi_a\phi_b\phi_c[\alpha\alpha\beta - \tfrac{1}{2}(\alpha\beta + \beta\alpha)\alpha]\}$$

$$\begin{array}{|cc|}\hline a & c \\ \hline \multicolumn{1}{|c|}{b} \\ \cline{1-1}\end{array} \equiv \mathcal{A}\{\phi_a\phi_c\phi_b(\alpha\beta - \beta\alpha)\alpha\}$$

$$\begin{array}{|c|c|}\hline a & c \\ b & d \\ \hline\end{array} \equiv \mathcal{A}\{\phi_a\phi_b\phi_c\phi_d[\alpha\alpha\beta\beta + \beta\beta\alpha\alpha - \tfrac{1}{2}(\alpha\beta + \beta\alpha)(\alpha\beta + \beta\alpha)]\}$$

$$\begin{array}{|cc|}\hline a & c \\ \hline b & d \\ \hline\end{array} \equiv \mathcal{A}\{\phi_a\phi_c\phi_b\phi_d(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)\}$$

$$\begin{array}{|cc|}\hline a & d \\ \hline \multicolumn{1}{|c|}{b} \\ \multicolumn{1}{|c|}{c} \\ \cline{1-1}\end{array} \equiv \mathcal{A}\{\phi_a\phi_d\phi_b\phi_c(\alpha\beta - \beta\alpha)(\alpha\beta + \beta\alpha)\}$$

$$\begin{array}{|c|c|}\hline a & d \\ \cline{2-2} \multicolumn{1}{|c|}{b} \\ \multicolumn{1}{|c|}{c} \\ \cline{1-1}\end{array} \equiv \mathcal{A}\{\phi_a\phi_b\phi_c\phi_d[\alpha\alpha\alpha\beta - \tfrac{1}{3}(\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha)\alpha]\}$$

$$\begin{array}{|c|c|}\hline a & c \\ \cline{2-2} \multicolumn{1}{|c|}{b} \\ \cline{1-1} \multicolumn{1}{|c|}{d} \\ \cline{1-1}\end{array} \equiv \mathcal{A}\{\phi_a\phi_b\phi_c\phi_d[\alpha\alpha\beta\alpha - \tfrac{1}{2}(\alpha\beta + \beta\alpha)\alpha\alpha]\}$$

References and Notes

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

(2) Cited in C. A. Coulson, *J. Chim. Phys. Physicochim. Biol.*, **45**, 243 (1948).

(3) P. Dowd, *J. Am. Chem. Soc.*, **88**, 2587 (1966).

(4) P. Dowd, *Acc. Chem. Res.*, **5**, 242 (1972).

(5) J. A. Berson, R. J. Bushby, J. M. McBride, and M. Tremelling, *J. Am. Chem. Soc.*, **93**, 1545 (1971).

(6) J. A. Berson, L. R. Corwin, and J. H. Davis, *J. Am. Chem. Soc.*, **96**, 6177 (1974).

(7) J. A. Berson, D. M. McDaniel, L. R. Corwin, and J. H. Davis, *J. Am. Chem. Soc.*, **94**, 5508 (1972).

(8) J. A. Berson, L. R. Corwin, and C. D. Duncan, *J. Am. Chem. Soc.*, **96**, 6175 (1974).

(9) J. A. Berson, D. M. McDaniel, and L. R. Corwin, *J. Am. Chem. Soc.*, **94**, 5509 (1972).

(10) D. R. Yarkony and H. F. Schaefer III, *J. Am. Chem. Soc.*, **96**, 3754 (1974).

(11) W. J. Hehre, L. Salem, and M. R. Wilcott, *J. Am. Chem. Soc.*, **96**, 4328 (1974).

(12) M. J. S. Dewar and J. S. Wasson, *J. Am. Chem. Soc.*, **93**, 3081 (1971).

(13) W. T. Borden, *J. Am. Chem. Soc.*, **97**, 2906 (1975).

(14) W. A. Goddard III, T. H. Dunning Jr., W. J. Hunt, and P. J. Hay, *Acc. Chem. Res.*, **6**, 368 (1973).

(15) J. H. Davis and W. A. Goddard III, *J. Am. Chem. Soc.*, **98**, 303 (1976).

(16) T. H. Dunning Jr., private communication.

(17) F. W. Bobrowicz, Ph.D. Thesis, California Institute of Technology, 1974.

(18) W. J. Hunt, P. J. Hay, and W. A. Goddard III, *J. Chem. Phys.*, **57**, 738 (1972).

(19) R. C. Ladner, Ph.D. Thesis, California Institute of Technology, 1971.

(20) The spin coupling represented by the arrows in eq 1 indicates the coupling qualitatively. The precise coupling is indicated by the tableaux representation.

(21) G. Levin and W. A. Goddard III, *J. Am. Chem. Soc.*, **97**, 1649 (1975).

(22) J. A. Berson, private communication.

(23) The conversion between energy units is 1 hartree = 27.2116 eV = 627.5096 kcal/mol = 149.9784 kJ/mol; taken from E. R. Cohen and B. N. Taylor, *J. Phys. Chem. Ref. Data*, **2**, 717 (1973).

(24) D. R. Yarkony and H. F. Schaefer III, *J. Am. Chem. Soc.*, in press.