Table III

	Optical transition	Obsd (cm^{-1})	Calcd (cm^{-1})
Sc_2	$1\sigma_g \rightarrow 1\sigma_u$	15 100	15 492
	$1\sigma_g \rightarrow 2\sigma_u$	21 050	19 880
	$1\sigma_g \rightarrow 2\pi_u$	29 850	29 558
Ti_2	$1\sigma_g \rightarrow 1\sigma_u$	16 020	15 355
	$1\sigma_g \rightarrow 2\sigma_u$	18 310	16 654
	$1\sigma_g \rightarrow 2\pi_u$	23 250	23 307

Matrix uv-visible and molecular orbital investigations of the first transition series diatomic molecules Sc_2 through to Zn_2 are currently underway in our laboratories and full details will be reported soon.

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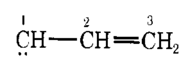
Vinylmethylene and the Ring Opening of Cyclopropene. Ab Initio Generalized Valence Bond and Configuration Interaction Studies

Sir:

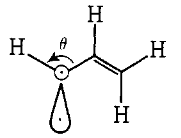
Vinylmethylenes (e.g., **1**) have been suggested as intermediates in both the ring opening of cyclopropenes[1] and in the decomposition of vinyl diazo compounds.[2] Recent ESR experiments[2] have detected two forms of **1.**

We report herein theoretical studies of the planar (**2**) and twisted (**3**) forms of vinylmethylene, along with the corresponding calculation on cyclopropene (**4**), of sufficient accuracy to be compared directly with experimental results. All calculations[3] used a "double-zeta" basis of contracted Gaussian functions[6] which was augmented with a set of d-polarization functions ($\alpha = 0.6769$) on each carbon for the final calculations. Hartree–Fock (HF), generalized valence bond (GVB),[7] and configuration interaction (CI) wave functions were used. In the initial step of the GVB calculations (referred to as GVB2) all but four electrons (three π and one σ) were in doubly occupied orbitals (that is, uncorrelated C_{1S}, CH bond, and CC σ bond pairs). In the final set of GVB calculations (referred to as GVB4), two additional pairs, corresponding to the CC sigma bonds, were correlated. With both the GVB2 and GVB4 wave functions, CI calculations were carried out allowing all configurations involving the correlated orbitals and, in addition, all double excitations from those orbitals into π virtuals. This led to from 176 to 205 spin configurations (677–1260 determinants) of appropriate spin and spatial symmetry.

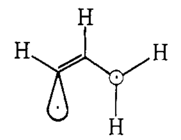


$\underset{\cdot\cdot}{\overset{1}{C}}H—\overset{2}{C}H=\overset{3}{C}H_2$

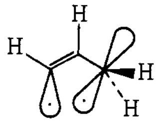
1



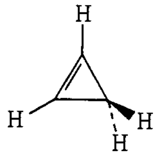
2a ($^3A''$ and $^1A''$)



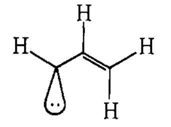
2b ($^3A''$ and $^1A''$)



3 ($^3A'$ and $^1A'$)



4 ($^1A_1$)



5 ($^1A'$)

It has generally been assumed that planar vinylmethylene can be represented by a resonance hybrid of **2a** and **2b,** much as in the allyl radical. However, the GVB calculation shows quite conclusively that in the triplet state ($^3A''$), the double bond is largely *localized* to the region between C-2 and C-3; i.e., the structure is basically that of a triplet methylene as in **2a** alone. The first $\sigma\pi$ singlet state ($^1A''$) also has a localized double bond, but in this case the GVB calculations show that it is localized in the C-1 and C-2 region; i.e., the structure is basically that of a singlet 1,3-biradical as in **2b.** This result of localized bonds is due to the nondegeneracy of the two resonance contributors (**2a** and **2b**) resulting from the exchange interactions. In allyl the two resonance contributors analogous to **2a** and **2b** are degenerate, and the mixing of the two states is strong.[8] We can represent the energy of each configuration of **2** as the sum or difference of a basic energy term, E_0, and an exchange term, $K_{\sigma\pi}$, which describes the interaction between the two unpaired electrons. The triplet state is stabilized by the exchange term as in eq 1, while the singlet state is *destabilized* by $K_{\sigma\pi}$ as in eq 2.

$$E_T = E_0 - K_{\sigma\pi} \tag{1}$$

$$E_S = E_0 + K_{\sigma\pi} \tag{2}$$

The *magnitude* of the exchange term $K_{\sigma\pi}$ is related to the proximity of the orbitals. Thus for **2a** (where the electrons are located on the same carbon), it is large (0.9 eV) but for **2b** (where the electrons are well separated) it is small (0.05 eV). Thus eq 1 shows that, in the triplet state, localized structure **2a** will be lower than **2b** by ~0.8 eV, but from eq 2 in the singlet case state **2b** will be lower than **2a** by the same amount. With such energy separations the two configurations mix (resonate) only slightly, and the wave function for each final structure is dominated by the lower-energy (localized) configuration.

ESR experiments[2] on **1** lead to D values comparable to that[8b] in :CφH and :Cφ_2 and much smaller[8a] than in CH_2. This has been interpreted as indicating nearly complete delocalization of the π system in **1.** Such extensive delocalization would be in conflict with our wave functions. We have included all important correlation effects involving the σ and π orbitals of the CCC region and consider our wave functions to be quite reliable. (We should note that at the Hartree–Fock level the π orbitals are delocalized (due to the extra ionic character forced in the wave function) but that inclusion of electron correlation leads to the localization discussed above.) For this

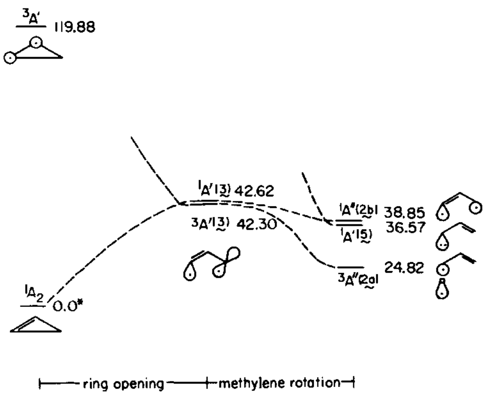


Figure 1. Electronic states of vinylmethylene (energies in kcal mol^{-1}) from GVB4-CI using double-zeta basis with d functions. CH bonds are omitted in the diagrams. The lowest energy isomerization pathway (not shown) involves simultaneous ring opening and methylene rotation. *The absolute energy is −115.940 99 hartrees.

reason we are in the process of developing the capability to evaluate the *D* values for our wave functions in order to determine whether the small delocalizations found theoretically lead to the small *D* values observed experimentally.

The other low lying singlet state of the planar geometry is the $^1A'$ state (**5**). This state is analogous to the lowest singlet state ($^1A_1$) of methylene just as the triplet state ($^3A''$) of **2a** is analogous to the triplet state ($^3B_1$) of methylene.[10] This $^1A'$-$^3A''$ separation is very sensitive to the level of calculation, and both CC σ bond correlation and d functions *must* be included in order to obtain a reliable value.[10] We find the $^1A'$ state to be 11.8 kcal above the $^3A''$ state—very close to the separation (11.0 kcal) calculated in methylene.[10] Omitting the d functions increases the excitation energy by 18 kcal mol^{-1}; omitting the correlations involving the CC σ bonds decreases the excitation energy by 4 kcal mol^{-1}.

Opening the ring of **4** without twisting the CH_2 group leads to **3** with a calculated energy increase of 42.3 kcal (bond angle to 120°). For an unstrained system, the CC bond energy would have been ~95 kcal,[11a] and thus the calculations indicate a strain energy of ~53 kcal for cyclopropene (empirical estimates are ~54 kcal).[11b] Allowing the CH_2 group to twist leads to **2** with a drop of 4.5 kcal for the singlet ($^1A''$) (partly due to the small resonance effect in **2b**) and 17.8 kcal for the triplet state ($^3A''$) (representing also the energy gain in shifting the C-1, C-2 double bond to the C-2, C-3 position in **2a**).

With regard to the mechanism for cyclopropene ring opening and reclosure, the calculations show that it is the 1,3-diradical singlet state ($^1A''$), rather than the methylene-like singlet ($^1A'$) which correlates well with cyclopropene, and we therefore suggest that $^1A''$ (**2b**) is the state most important in the isomerization.[12] We envision that the isomerization involves a simultaneous C–C bond stretching and rotation of the CH_2 group, leading directly from **4** to **2b** without passing through the higher energy configuration **3**. This "1,3-diradical" state $^1A''$ (**2b**) may also decay to the "carbene" states $^1A'$ (**5**) and $^3A''$ (**2a**), leading to products characteristic of singlet and triplet methylenes; however, ring closure must then be preceded by reconversion to $^1A''$.

On the other hand, extrusion of nitrogen from a vinyl diazo compound leads directly to $^1A'$ (**5**), which may act as a singlet carbene, or decay to $^3A''$ (**2a**), which would react as a triplet methylene. We would not expect significant formation of $^1A''$ (**2b**).

In order to examine the interconversion of syn and anti isomers of **2**, we carried out calculations at the GVB2 level and without d functions, using CCH (θ) angles of 120° (anti), 180° (linear), and 240° (syn) and equal bond lengths. Because of the restrictions, the separations between electronic states are not as accurate, but the shapes of the potential surfaces should be reliable. In the $^3A''$ state the calculations predict relative energies of 0.48, 8.76, and 0.0 kcal for these θ angles, indicating that the syn and anti forms are nearly degenerate (with syn more stable), but are separated by a relatively large inversion barrier comparable to that of triplet methylene (9 kcal).[10] In the $^1A''$ state the relative energies were 25.56, 27.12, and 26.40 kcal; here there is a small inversion barrier, as one might expect for a vinyl radical (~2 kcal mol^{-1}).[13] The $^1A'$ state gave energies of 26.64, 44.76, and 28.08 kcal, corresponding to the large barrier observed in the inversion of singlet methylene ($^1A_1$).[10] The finding of two triplet stereoisomers of vinylmethylene separated by a large barrier is consistent with the ESR experiments.[2,14]

Summarizing, our calculations predict that: (1) the allyl-type π-system is strongly distorted by the presence of the unpaired σ electron leading to a methylene-like triplet, $^3A''$ (**2a**), but a 1,3-diradical-like singlet state, $^1A''$ (**2b**); (2) the lowest-lying singlet state of vinylmethylene has the form of a singlet methylene $^1A'$ (**5**) lying 12 kcal/mol above the $^3A''$ ground state, while the diradical singlet state $^1A''$ (**2b**) lies at 14 kcal/mol; (3) the $^3A''$ ground state of **2** should exist in two geometrical forms (syn and anti) having nearly the same energy and separated by a large barrier (9 kcal); and (4) the 1,3-diradical singlet state has only a low barrier (2 kcal mol^{-1}) between the syn and anti forms while the methylene triplet and singlet states have large barriers. These results suggest that the ring opening of cyclopropene proceeds directly to a diradical planar intermediate.

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(3) The following geometries were used. Cyclopropene: experimental geometry.[4] Planar states: all angles 120° except CCH angle (θ), $R_{CH} = 1.08$ Å; with $R_{C_1-C_2} = 1.34$, $R_{C_2-C_3} = 1.54$, $\theta = 135°$ for $^3A''$, with $R_{C_1-C_2} = 1.54$, $R_{C_2-C_3} = 1.34$, $\theta = 135°$ for $^1A''$; and with $R_{C_1-C_2} = 1.503$, $R_{C_2-C_3} = 1.320$, $\theta = 105°$ for $^1A'$.[5] Twisted states: all angles 120° except θ, $R_{CH} = 1.086$, $R_{C_1-C_2} = 1.357$, $R_{C_2-C_3} = 1.514$, $\theta = 135°$.

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(11) (a) For example: $D_0(C_2H_3-C_2H_5) = \Delta H_f(C_2H_3) + \Delta\ H_f(C_2H_5) - \Delta H_f$(1-butene) = 69 + 26 − 0 = 95 kcal mol^{-1}; (b) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N.Y., 1968.

(12) For the planar configuration the $^1A'$ (**5**) state is 2.3 kcal below the $^1A''$ (**2b**) state, and an adiabatic potential surface would lead to an "avoided crossing" between the states shown correlating with $^1A''$ and $^1A'$. This would occur very near the planar geometry since, upon twisting, the $^1A'$ (**5**) state increases rapidly in energy, like the ground state of ethylene. Because of the dissimilarity between the $^1A''$ and $^1A'$ states, we believe that the Born–Oppenheimer breakdown terms will dominate the dynamics, resulting in correlation of $^1A''$ with the ground state (**4**).

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(14) Chapman[2b] has suggested that the singlet state of **2** is 0.2 kcal above the triplet state. We find that the singlet–triplet gap is 12 kcal/mol and cannot accept this interpretation. It seems that there could be several possible reasons (other than a singlet at 0.2 kcal) for the observed shifts and changes in intensity of the ESR lines: for example, changes in *D* and *E* values due

to varying population of vibrational levels as a function of temperature[15a] or rotation and oscillation in the matrix.[15b]

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

(16) John and Beverly Stauffer Foundation Fellow, 1975–1976.

(17) Camille and Henry Dreyfus Teacher-Scholar Grant Awardee, 1970–1975.

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On the Alleged Existence of Partially Oxidized $Mg[Pt(CN)_4]Cl_{0.28}{\cdot}7H_2O$ and the Attempted Preparation of the Analogous Be^{2+} and Ba^{2+} Derivatives. A Caveat[1]

Sir:

Partially oxidized tetracyanoplatinate (POTCP) conducting salts of *monovalent* cations are well known,[2a,b] and we have recently reported the unusual molecular structures of *anion* deficient $K_2[Pt(CN)_4]Br_{0.3}{\cdot}3H_2O$,[2c] KCP(Br), and *cation* deficient $K_{1.75}[Pt(CN)_4]{\cdot}1.5H_2O$,[2d] K(def)TCP. These one- and quasi-one-dimensional salts form unusual Pt–Pt "chains" having metal–metal separations not greatly in excess of that observed in platinum metal itself. In an effort to understand the effect of cation size on the structure, the conductive properties, and the Pt–Pt bond lengths, we have undertaken the synthesis and characterization of POTCP salts containing a *divalent* cation.

There exists in the literature only one recent report of a POTCP salt of a *divalent* cation, viz., *blue* $Mg[Pt(CN)_4]Cl_{0.28}{\cdot}7H_2O$,[3,4] hereafter referred to as **1**. The preparation of **1** was reportedly accomplished[3] by cocrystallizing red $Mg[Pt(CN)_4]{\cdot}7H_2O$, hereafter known as **2**, and $Mg[Pt(CN)_4]Cl_2{\cdot}xH_2O$. Initially we attempted the room temperature synthesis of the corresponding POTCP complexes of Be^{2+} and Ba^{2+} but were unable to form partially oxidized complexes. Therefore, the Krogmann and Ringwald[3] synthesis of **1** was repeated, and we did indeed obtain the "blue magnesium tetracyanoplatinate" they reported. However, this material transformed to crystalline **2** depending simply on the H_2O vapor pressure above the sample. Thus it appears that the material thought to be the only POTCP of a *divalent* cation is simply a different hydrate of $Mg[Pt(CN)_4]{\cdot}7H_2O$. We have further verified the composition of the compounds and the lack of halogen by chemical analysis,[5] x-ray fluorescence studies, and powder x-ray diffraction (vide infra). The implications of these results with respect to the formation of one-dimensional POTCP salts of Be^{2+}, Mg^{2+}, and Ba^{2+} are discussed herein.

Partial oxidation of dark-red $Be[Pt(CN)_4]{\cdot}2H_2O$, **3**, by cocrystallization of $Be[Pt(CN)_4]Br_2{\cdot}xH_2O$ and **3** at room temperature, yielded only a mixture of starting materials. Similarly, attempted partial oxidation of yellow-green-$Ba[Pt(CN)_4]{\cdot}4H_2O$, **4**, by cocrystallization of $Ba[Pt(CN)_4]Br_2{\cdot}5H_2O$ and **4** at room temperature, and alternatively

Table I. X-Ray Diffraction Powder Patterns of Magnesium Tetracyanoplatinates[a]

$Mg[Pt(CN)_4]Cl_{0.28}{\cdot}7H_2O$[3] (blue)	$Mg[Pt(CN)_4]{\cdot}xH_2O$[b] (blue)	$Mg[Pt(CN)_4]{\cdot}7H_2O$[3] (red)	$Mg[Pt(CN)_4]{\cdot}xH_2O$[c] (red-green)[16]	$Mg[Pt(CN)_4]{\cdot}xH_2O$[d] (dark-purple)
4.2 (vs)	4.2 (vs)	4.0 (vs)	4.3 (vs)	4.2 (vs)
6.0 (vs)	6.0 (vs)	6.0 (vs)	6.1 (vs)	6.0 (vs)
8.6 (vs)	8.6 (vs)	8.6 (vs)	8.6 (vs)	8.6 (vs)
		9.3 (w)	9.3 (w)	
9.6 (vs)	9.6 (vs)	9.6 (vs)	9.7 (vs)	9.6 (vs)
10.0 (vw)				
		11.1 (w)	11.2 (w)	
		11.6 (vw)	11.8 (vw)	
		12.0 (vw)		
12.1 (m)	12.2 (m)	12.3 (s)	12.3 (s)	12.2 (s)
		12.6 (vw)		
12.9 (w)	12.9 (w)	12.9 (s)	13.0 (s)	13.0 (m)
		13.1 (vw)		
13.6 (m)	13.6 (m)	13.7 (s)	13.8 (s)	13.7 (m)
14.2 (vw)	14.4 (vw)	14.2 (w)	14.2 (w)	14.1 (vw)
		14.5 (vs)	14.6 (s)	
14.6 (vw)	14.7 (vw)	14.8 (vw)	15.2 (w)	14.7 (vw)
15.0 (vw)				15.1 (vw)
15.3 (s)	15.2 (m)			
15.5 (m)	15.6 (w)			15.6 (s)
		15.8 (vs)	15.8 (vs)	
16.5 (s)	16.4 (m)			16.8 (m)
17.3 (w)	17.3 (w)			17.4 (w)
17.6 (m)	17.6 (w)			
17.9 (m)	17.9 (w)			18.0 (m)
18.3 (w)	18.4 (w)			18.5 (w)
18.7 (m)	18.7 (w)			
				19.0 (w)
19.4 (w)	19.5 (w)			
19.7 (m)	19.7 (w)			
21.6 (s)	21.6 (m)			20.0 (m)
21.8 (w)	21.9 (m)			21.9 (s)

[a] Diffraction lines are reported in degrees θ and vs = very strong; s = strong; m = medium; w = weak; vw = very weak. Argonne patterns taken with Cu $K\alpha$ radiation, λ 1.5418 Å. [b] Prepared by cocrystallizing $Mg[Pt(CN)_4]{\cdot}7H_2O$ and $Mg[Pt(CN)_4]Cl_2{\cdot}xH_2O$ (this work). [c] Red-green[16] crystals formed after the blue[b] magnesium tetracyanoplatinate was removed from the solution in which it was prepared and stored at 72% relative humidity (this work). This pattern was identical with that of $Mg[Pt(CN)_4]{\cdot}7H_2O$ prepared in this study. [d] Prepared by the addition of H_2O_2 to a solution of $Mg[Pt(CN)_4]{\cdot}7H_2O$.