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New Theoretical Evidence for the Nonlinearity of the Triplet Ground State of Methylene

Sir:

It is generally accepted[1] that the triplet ground state of the CH_2 molecule is linear. However, it is interesting to note that both Walsh,[2] in his early qualitative paper, and Herzberg,[3] in his experimental study, leave open the possibility that this state is "nearly linear." Further, early *ab initio* configuration interaction (CI) calculations by Foster and Boys[4] indicated a relatively flat surface with changing angle and an equilibrium angle of 129°. Finally, from recent valence-bond calculations, Harrison and Allen[5] predicted an angle of 138° for the ground $^3B_1$ state.

We have recently begun a relatively accurate series of quantum mechanical calculations on the low-lying states of the CH_2 radical. It was decided to first investigate the question of the geometry of the ground state.

The gaussian basis functions used in this work were Huzinaga's[6] 9s,5p set for carbon and 4s set for hydrogen. The functions were contracted to 4s,2p for carbon and 2s for hydrogen (with a scale factor of 1.2), according to Dunning's recommendations.[7]

The first step in each calculation involved the computation of the SCF wave function within the above basis. Then CI calculations were carried out including the SCF function ($1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1\ 1b_1$ in this case) plus all configurations of $^3B_1$ symmetry arising from orbital occupancies differing by one or two orbitals from the SCF function, with the restriction that the $1a_1$ orbital was always doubly occupied. An iterative natural orbital procedure[8] was then used in several subsequent CI calculations to obtain the most rapidly convergent expansion of the above type. Calculations were also routinely carried out for SCF plus single excitations only.

We carried out a much more exhaustive geometry search than previous *ab initio* investigators[4,5,9] of CH_2. The calculated total energies from our largest calculation (including 408 $^3B_1$ configurations) are given as a function of geometry in Table I. Our lowest calculated total energy lies 0.0671 hartree = 42 kcal/mol below the lowest energy previously reported, that of Harrison and Allen.[5] Force constants were obtained by fitting the expression[10]

Table I. Calculated *Ab Initio* Energies for the Ground $^3B_1$ State of CH_2[a]

	R, bohrs			
θ	1.9	2.0	2.1	2.2
90°	−38.92913	−38.94283	−38.94751	−38.94554
105°	−38.95363	−38.96588	−38.96916	−38.96583
120°	−38.96644	−38.97761	−38.97986	−38.97554
135°	−38.97045	−38.98077	−38.98222	−38.97717
150°	−38.96881	−38.97838	−38.97912	−38.97344
165°	−38.96527	−38.97413	−38.97425	−38.96799
180°	−38.96347	−38.97200	−38.97184	−38.96530

[a] The wave functions were of the configuration-interaction variety, including the SCF function plus all singly and doubly excited configurations arising from a "double-ζ" gaussian basis set. In all, 408 configurations were included.

$$2V = F_{11}r_1^2 + F_{22}r_2^2 + F_{33}R^2\alpha^2$$

where r_1 and r_2 are the stretches of the two CH bonds, α is the distortion of the equilibrium bond angle, and R is the equilibrium bond length. Table II gives the predicted geometry and force constants for each of the three types of calculation carried out.

Table II. Predicted Equilibrium Geometry and Force Constants (mdyn/Å) of CH_2

	SCF	SCF + single excitations	SCF + single excitations + double excitations	Experiment[a]
Bond distance, Å	1.080	1.080	1.096	1.03
Bond angle, deg	129.8	135.7	135.1	180
Interpolated total energy, hartrees	−38.913	−38.921	−38.984	
$F_{11} = F_{22}$	6.41	6.52	6.83	
F_{33}	0.26	0.20	0.21	

[a] See ref 3.

All the present calculations indicate that the methylene ground state is bent, with a bond distance greater than the 1.03 Å determined by Herzberg.[3] In light of the present results it is interesting to note that an alternate interpretation[3] of Herzberg's spectroscopic data suggested a bond distance of 1.071 Å and a 140° angle, in good agreement with our predictions. However, owing to the absence in the spectrum of certain subbands, Herzberg[3] concluded the above geometry to be unlikely. The fact that the potential surface is rela-

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(1) G. Herzberg, "Electronic Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1967.

(2) A. D. Walsh, *J. Chem. Soc.*, 2260 (1953).

(3) G. Herzberg, *Proc. Roy. Soc., Ser. A*, **262**, 291 (1961).

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(5) J. F. Harrison and L. C. Allen, *J. Amer. Chem. Soc.*, **91**, 807 (1969).

(6) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965).

(7) T. H. Dunning, manuscript in preparation.

(8) C. F. Bender and E. R. Davidson, *J. Phys. Chem.*, **70**, 2675 (1966).

(9) M. Krauss, *J. Res. Nat. Bur. Stand., Sect. A*, **68**, 635 (1965).

(10) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955, p 170.

tively flat in going from 135 to 180° may make a rigorous experimental determination of the geometry rather difficult. Our most stable calculated linear geometry (r = 1.083 Å) lies only 6.7 kcal/mol above the calculated equilibrium geometry. Nevertheless, on the basis of the present and previous[4,5] *ab initio* calculations and the stated[3] experimental uncertainties, we conclude that the CH_2 ground state is nonlinear with a geometry close to r = 1.096 Å, θ = 135.1°.

Since there is a great deal of current interest[11] in rapidly convergent CI expansions for molecules, Table III includes the seven most important spatial configurations in our natural orbital expansion near the minimum. We note that (1) all of these configurations involve only valence orbitals, (2) the SCF configuration dominates, (3) the second most important orbital occupancy involves six electrons outside closed shells, and (4) the single excitation $2a_1 \rightarrow 4a_1$ is very important.

Table III. The Seven Most Important Spatial Configurations in the Natural Orbital Expansion of $^3B_1$ CH_2 at θ = 135°, r = 2.1 bohr[a]

	Excitation	Spatial configuration	Coefficient
1.		$1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1\ 1b_1$	0.97914
2.	$2a_1\ 1b_2 \rightarrow 4a_1\ 2b_2$	$1a_1^2\ 2a_1\ 1b_2\ 3a_1\ 1b_1\ 4a_1\ 2b_2$	0.07269
3.	$2a_1 \rightarrow 4a_1$	$1a_1^2\ 2a_1\ 1b_2^2\ 3a_1\ 1b_1\ 4a_1$	0.06393
4.	$1b_2^2 \rightarrow 2b_2^2$	$1a_1^2\ 2a_1^2\ 3a_1\ 1b_1\ 2b_2^2$	0.05686
5.	$1b_2^2 \rightarrow 4a_1^2$	$1a_1^2\ 2a_1^2\ 3a_1\ 1b_1\ 4a_1^2$	0.05246
6.	$2a_1^2 \rightarrow 4a_1^2$	$1a_1^2\ 1b_2^2\ 3a_1\ 1b_1\ 4a_1^2$	0.05027
7.	$1b_2\ 1b_1 \rightarrow 2b_2\ 2b_1$	$1a_1^2\ 2a_1^2\ 1b_2\ 3a_1\ 2b_2\ 2b_1$	0.04725

[a] The coefficients incorporate the effects of all triplet spin eigenfunctions corresponding to the given orbital occupancy.

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(11) G. Das and A. C. Wahl, *J. Chem. Phys.*, **44**, 87 (1966).

(12) (a) Supported by a grant from the Chemical Applications Department of the UCC Computer Utility Network; (b) supported in part by the Petroleum Research Fund and the Research Corporation; to whom correspondence should be addressed.

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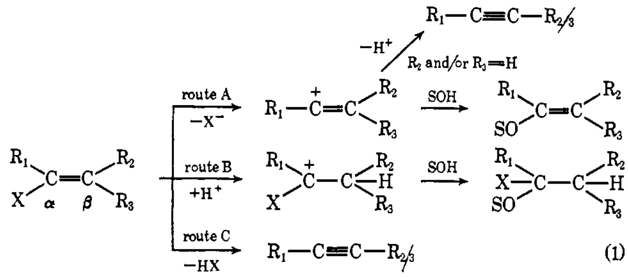
Vinyl Cations from Solvolysis

Sir:

In a recent communication Schubert and Barfknecht commented[1] regarding the solvolyses of vinyl halides which are proposed to occur by the SN1 mechanism (eq 1, route A) that "plausible under some, but not all, of the conditions used is hydrolysis *via* protonation of the alkene" (eq 1, route B). From studies on the hydrolysis of α-bromo-p-aminostyrene (**1a**) in aqueous buffers and perchloric acid they concluded that for **1a** "the vinyl carbonium ion mechanism for this compound is definitely incorrect and that hydrolysis most probably occurs *via* acid catalyzed hydration."[1] For compounds having a *trans*-hydrogen atom at the double bond in respect to the leaving group X a third mechanism must be considered. In this mechanism, especially under neutral or alkaline conditions, the corresponding acetylene beside route A can also be formed by a concerted elimination of HX (route C). In contrast an acetylene formation is not possible *via* route B. Table I shows predictions for reaction *via* the electrophilic addition–elimination route (for both Markovnikov and anti-Markovnikov additions) or *via* the vinyl cation intermediate, for 20 different phenomena. The experimental data for the systems **1–12** so far investigated are given in the last two columns. It is clear that the data are compatible only with the SN1 route, except for reactions of **5** in HCOOH,[2] of **1a** in acidic media,[1] and of **1b** in unbuffered AcOH.[3] In the latter three cases the addition–elimination route was already suggested and it is significant that the same substrates in nonacid media (*i.e.*, **5** in MeOH–H_2O,[4] **1a** in 80% EtOH,[5] and **1b** in buffered AcOH[3]) react (according to Table I) only *via* route A. As an example of a concerted elimination (route C) in nonacidic solvent compound **8** shall be given. Besides route C, route A can be made responsible for the acetylene formation; examples are **1c**, **4**, **5**, **7**; in the case of **9** the acetylene formation can only be explained through route A.



(1)

1, R_1 = YC_6H_4; R_2 = R_3 = H
1a, Y = p-NH_2; X = Br
1b, Y = p-MeO; X = Br
1c, Y = H; X = OSO_2Ar
2, R_1 = Ar_1; R_2 = Ar_2; R_3 = Ar_3; X = Cl, Br, I, OSO_2Ar, OSO_2F, OSO_2CF_3
3, R_1 = Ar_1; R_2 = Ar_2; R_3 = ArS; X = OSO_2Ar
4, R_1 = CH:CMe_2; R_2 = R_3 = H or Me; X = Br
5, R_1 = R_2 = Me; R_3 = H; X = OSO_2Ar, OSO_2CF_3
6, R_1 = R_2 = Ph; R_3 = morpholyl; X = Cl, Br
7, R_1 = cyclopropyl; R_2 = R_3 = H; X = Cl, I
8, R_1 = R_3 = Me; R_2 = H; X = OSO_2Ar, OSO_2CF_3
9, R_1 = cyclopropyl; X = I
9a, R_2 = Me; R_3 = H
9b, R_2 = H; R_3 = Me
10, Ar–CX:C:CPh_2; X = Cl
11, R_1 = Me; R_2 = R_3 = Ph; X = OSO_2CF_3
12, R_1 = t-Bu; R_2 = R_3 = H; X = OSO_2CF_3

While **1a** solvolyzes in acidic media *via* addition–elimination,[1] extrapolation to pH of Schubert's k_{obsd} data[1] in water gives $k^{50°}$ = 1.4 10^{-7} $\sec^{-1}$ (and lower values at higher pH), by using Grob's data[5] $k_1^{50°}$ = 0.035 $\sec^{-1}$ in basic 80% ethanol. The difference of at least five orders of magnitude in rate is a real discrepancy, which at present is difficult to explain.[6]

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(1) W. M. Schubert and G. W. Barfknecht, *J. Amer. Chem. Soc.*, **92**, 207 (1970).

(2) See Table I, footnote *oo*.

(3) See Table I, footnote *aa*.

(4) See Table I, footnote *u*.

(5) See Table I, footnote *p*.

(6) This difference is even higher if account is taken of the difference in the two solvents. It was suggested by Professor W. M. Schubert (private communication) that this is due to formation of sufficient amount of unneutralized protons, so that Grob's data really reflect addition mechanism by these protons. On the other hand, Schubert and Barfknecht[1] did not consider the possibility of electrophilic acceleration of the solvolysis by protons, *via* protonation on the bromine, which should contribute to SN1 solvolysis even under acidic conditions.