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

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

The energy difference between the 3B_1 and 1A_1 states of CH_2 has been the subject of considerable experimental and theoretical research in recent years. In 1961 Herzberg established^{2a} for the first time that the triplet state was the lower lying. However, since no singlet-triplet bands of CH_2 have been analyzed, electronic spectroscopy does not yield a precise value of the separation. However, Herzberg suggested^{2b} in 1966 that the singlet-triplet separation (to be called ΔE hereafter) should be less than 23 kcal/mol. Since that time, essentially all experimental values have fallen into two groups, which may be referred to as the "high" values³⁻⁶ (8–9 kcal/mol) and the "low" values⁷⁻⁹ (0–3 kcal/mol).

The three most reliable ab initio theoretical studies¹⁰⁻¹² reported to date all favor a high value for the singlet-triplet separation. The lowest theoretical ΔE of 9.2 kcal/mol, predicted by Staemmler,¹² was obtained using the independent electron pair approximation (IEPA) and a large contracted Gaussian basis set. Somewhat larger ΔE values (11.5¹⁰ and 14.1¹¹ kcal) were obtained in the two variational studies. The present research was motivated by two theoretical suggestions made independently by Hay, Hunt, and Goddard¹⁰ and by Bender, Schaefer, Franceschetti, and Allen.¹¹ The first of these is the understanding that d functions on carbon significantly lower ΔE . The second is the suggestion that the 3B_1 state be approximated by a single configuration wave function

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

while a two-configuration wave function

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

be used to describe the 1A_1 state. And, in fact, comparison with

the extensive (both in terms of basis set and treatment of electron correlation¹³) theoretical treatments of Bender¹¹ and Staemmler¹² show these two features to be important ingredients in theoretical predictions of ΔE . In general of course the reliable prediction of electronic excitation energies requires a fairly thorough treatment of electron correlation, usually via large scale configuration interaction (CI).¹⁴ However, a simple rationalization of the apparent transparency of the correlation problem in this specific case is possible with reference to (1) and (2). We see that while the 3B_1 Hartree-Fock wave function treats the nearly degenerate $3a_1$ and $1b_1$ orbitals in an equivalent manner, the corresponding single-configuration $1a_1^2 2a_1^2 1b_2^2 3a_1^2$ for the 1A_1 state ignores the $1b_1$ orbital entirely. Hence the second configuration $1a_1^2 2a_1^2 1b_2^2 1b_1^2$ may be required for a theoretical treatment comparable to the single-configuration description of the 3B_1 state.

Theoretical Details

The purpose of the present research was twofold. First, to obtain near-Hartree-Fock predictions for the methylene ΔE and therefore remove the basis set dependence of earlier theoretical work.¹⁵ Second, comparable calculations have been carried out for SiH_2 (silylene), for which the singlet-triplet separation is currently rather uncertain. For carbon and silicon, the largest readily available Gaussian basis sets were used. The carbon (13s 8p) primitive Gaussian set of van Duijneveldt¹⁶ was contracted to (9s 6p) so as to maintain maximum flexibility in the valence region. That is, the five s functions with largest orbital exponents α_i were grouped together according to the carbon atomic 1s orbital, and an analogous procedure followed for the three carbon p functions with largest expo-

Table I. Summary of Near-Hartree-Fock Results for CH₂ and SiH₂^f

Theoretical description	State	Total energy, hartrees	Bond distance, Å	Bond angle, deg	Singlet-triplet separation ΔE , kcal/mol
NPF	³ B ₁ CH ₂	-38.920 07	1.071	130.2	
NPF-OC	¹ A ₁ CH ₂	-38.869 85	1.100	106.1	31.5
NPF-TC	¹ A ₁ CH ₂	-38.885 05	1.105	104.4	22.0
PF	³ B ₁ CH ₂	-38.934 78	1.070 (1.08 ^a)	129.5 (134 ± 2 ^b)	
PF-OC	¹ A ₁ CH ₂	-38.895 24	1.095	103.7	24.8
PF-TC	¹ A ₁ CH ₂	-38.917 48	1.097 (1.11 ^c)	102.9 (102.4 ^c)	10.9 (~9 ^d)
NPF	³ B ₁ SiH ₂	-289.989 25	1.485	118.2	
NPF-OC	¹ A ₁ SiH ₂	-289.994 29	1.533	94.1	-3.2
NPF-TC	¹ A ₁ SiH ₂	-290.005 79	1.536	93.8	-10.4
PF	³ B ₁ SiH ₂	-290.019 27	1.471	117.6	
PF-OC	¹ A ₁ SiH ₂	-290.027 65	1.509	93.5	-5.3
PF-TC	¹ A ₁ SiH ₂	-290.048 90	1.508 (1.521 ^e)	94.3 (92.1 ^e)	-18.6

^a G. Herzberg and J. W. C. Johns, *J. Chem. Phys.*, **54**, 2276 (1971). ^b Reference 11. ^c G. Herzberg and J. W. C. Johns, *Proc. R. Soc. London, Ser. A*, **295**, 107 (1966). ^d References 3-6. ^e Reference 25. ^f Calculations with no polarization functions (NPF) do not include d functions on the heavy atom (C or Si) or p functions on hydrogen. Calculations carried out including these polarization functions are labeled PF. For the ¹A₁ state both one-configuration (OC) and two-configuration (TC) SCF results are reported. Experimental values are given in parentheses.

nents. In a similar fashion, for silicon Veillard's (12s 9p) set¹⁷ was contracted to (9s 6p). For both C and Si, three sets (six functions each) of d-like functions were added as polarization functions. The chosen orbital exponents were 1.6, 0.8, and 0.3 for carbon and 1.2, 0.6, and 0.2 for silicon. For each hydrogen atom, a (6s) primitive set was contracted to (4s) and two sets of p functions ($\alpha = 1.4, 0.25$) were added. Thus the final basis sets may be labeled C(13s 8p 3d/9s 6p 3d), Si(12s 9p 3d/9s 6p 3d), and H(6s 2p/4s 2p). Based in part on Clementi and Popkie's study¹⁸ of the water molecule with many basis sets, we estimate that the present basis for CH₂ should yield total energies within 0.003 hartree of the true Hartree-Fock limits. For silylene, such an estimate is more treacherous, but the primary error arises from the inability¹⁷ (by 0.005 67 hartree) of the present Si atom basis to precisely reproduce the Si atom Hartree-Fock energy. Nevertheless, we expect this SiH₂ basis to describe rather well the valence region of the molecule and hence the singlet-triplet separation.

All computations were carried out on the Harris Slash Four minicomputer¹⁹ using the Ohio State-Cal Tech-Berkeley version²⁰ of POLYATOM.²¹ Typical times for CH₂ using the complete basis set were: integrals, 61.5 min; SCF procedure for two-configuration description of the ¹A₁ state, 80.2 min for six iterations. Note that a total of 65 contracted Gaussian functions were used with the complete basis sets for both CH₂ and SiH₂.

Results

The present theoretical results are summarized in Table I. In each calculation, the geometry was predicted by variation of the total energy with respect to both bond distance and bond angle. After the minimum was qualitatively located, nine adjacent points on the two-dimensional potential surface were used to determine the analytical form

$$V = \sum_{i=0}^2 \sum_{j=0}^2 a_{ij} r^i \theta^j$$

This form was then used to predict the precise equilibrium geometry, and a final calculation was carried out at that point in (r, θ) space. The goodness of the fit was measured by the difference between the predicted actual total energies at the minimum.

Note that the methylene total energies reported here are significantly lower than any one- and two-configuration results reported earlier¹⁵ in the literature. Previously the lowest reported energies were those of Staemmler,¹² whose energies lie

0.004 and 0.005 hartree higher than those in Table I. For CH₄, our results confirm at essentially the Hartree-Fock limit the points emphasized in our introductory section, namely that both polarization functions and a two-configuration treatment of the ¹A₁ state are required for a reliable prediction of ΔE . More quantitatively, comparison of lines 3 and 6 suggests that polarization functions lessen ΔE by 11.1 kcal. Similarly comparison of lines 5 and 6 suggests that going from a single configuration to a two-configuration description of the ¹A₁ state lowers the predicted ΔE by 13.9 kcal. Clearly, however, the two effects are coupled since their sum is 25.0 kcal/mol, while the difference between lines 2 and 6 is only 20.6 kcal.

Although the reactions of silylene have attracted considerable interest²²⁻²⁴ during the past few years, the singlet-triplet separation is quite uncertain. Although a number of careful spectroscopic studies²⁵⁻²⁷ have been reported for SiH₂, no transitions involving triplet electronic states have been identified. Although one's natural tendency is thus to assume a singlet ground state for silylene, Dubois, Herzberg, and Verma²⁵ caution against precluding the possibility of a triplet ground state. However, it must be noted that Skell and Goldstein²⁸ demonstrated in 1964 that dimethylsilylene has a singlet ground state. And a very recent experimental nuclear recoil study by Zeck, Su, Gennaro, and Tang²⁹ seems to establish for SiH₂ itself the existence of a singlet ground state.

While it now seems clearly established that for SiH₂ the ¹A₁ state lies below the ³B₁ state, the value of the singlet-triplet separation ΔE has not been determined experimentally. At least two theoretical values of ΔE have been presented. The first, 46 kcal/mol, is that of Jordan,³⁰ who carried out semi-empirical calculations for the singlet and triplet state. A very different result, 4.8 kcal/mol, was obtained by Wirsam,³¹ who carried out ab initio calculations with a Gaussian basis set of moderate size. For comparison, Wirsam finds a total energy at the predicted ³B₁ equilibrium geometry of -289.9066 hartrees, or 0.1127 hartree higher than that obtained in the present research.

Table I shows that all four of our calculations predict silylene to have a singlet ground state. The same trends as in CH₂ (with respect to basis set and number of singlet configurations) are seen here. Thus, we expect the bottom line ΔE value of -18.6 kcal/mol to be of accuracy comparable to the 10.9 kcal prediction for CH₂.

The structure of singlet silylene is known from the experiments of Herzberg and co-workers.²⁵⁻²⁷ Our predicted Si-H bond distance (last line, Table I) is 0.013 Å shorter than ex-

Table II. Orbital Energies (in hartree atomic units) and Mulliken Populations from Near-Hartree-Fock Wave Functions for the 3B_1 States of CH_2 and SiH_2

		Orbital energies	
		CH_2	SiH_2
			1a ₁ -68.7924
			2a ₁ -6.1392
			1b ₁ -4.2447
			3a ₁ -4.2444
	1a ₁	-11.2442	1b ₂ -4.2440
	2a ₁	-0.8567	4a ₁ -0.6694
	1b ₂	-0.6015	2b ₂ -0.5002
	3a ₁	-0.4766	5a ₁ -0.4122
	1b ₁	-0.4033	2b ₁ -0.3033
		Mulliken Populations	
3B_1	C	6.16	Si 13.47
	H	0.92	H 1.26
1A_1	C	6.13	Si 13.38
	H	0.94	H 1.31

periment, while the predicted bond angle is 2.2° too large. Errors of this magnitude are about what should be expected at the Hartree-Fock limit of theory. The structure of 3B_1 SiH_2 is not known, and we predict $r_e(SiH) = 1.471 \text{ \AA}$ and $\theta_e(HSiH) = 117.6^\circ$. Perhaps most interesting is the sizable reduction (21.9°) with respect to methylene of the triplet bond angle. A smaller reduction (8.6°) in bond angle is found in going from singlet CH_2 to singlet SiH_2 , as is the case in the better known $H_2O \rightarrow H_2S$ progression. Although the structure of 3B_1 SiH_2 is not known from experiment, two prior theoretical predictions are available. Jordan's semiempirical studies³⁰ predicted a bond angle of 137.8° , a value we consider too large. Wirsam's ab initio structure for triplet silylene is $r_e(SiH) = 1.55 \text{ \AA}$, $\theta_e(HSiH) = 123.5^\circ$.

Among other molecular properties computed, the predicted dipole moments (at the respective equilibrium geometries) are of particular interest: (CH_2) $\mu({}^3B_1) = 0.58 \text{ D}$, $\mu({}^1A_1) = 1.71 \text{ D}$; (SiH_2) $\mu({}^3B_1) = -0.19 \text{ D}$, $\mu({}^1A_1) = 0.10 \text{ D}$, where a positive dipole moment implies A^-H^+ polarity. One must not, of course, directly compare the singlet and triplet dipole moments, since they refer to very different geometries. In general one expects triatomic molecules AH_2 with smaller bond angles to have larger dipole moments, since the dipole moment becomes identically zero for $\theta = 180^\circ$.

In Table II are listed orbital energies and Mulliken populations. Inspection of the orbital energies provides an immediate rationalization of why CH_2 has a triplet ground state while that for SiH_2 is a singlet. Namely, the separation between the highest a₁ and b₁ orbitals is 0.0733 hartree for CH_2 but much greater, 0.1089 hartree, for SiH_2 . Thus in SiH_2 , the 5a₁ orbital would prefer to be doubly occupied, while in CH_2 there is some triplet "pairing energy" which is large enough to counterbalance this tendency and singly occupy both orbitals. Furthermore, the difference $(0.1089 - 0.0733) = 0.0356$ hartree = 22.3 kcal is reasonably close to the predicted difference $[10.9 - (-18.6)] = 29.5$ kcal between the singlet-triplet separations for CH_2 and SiH_2 .

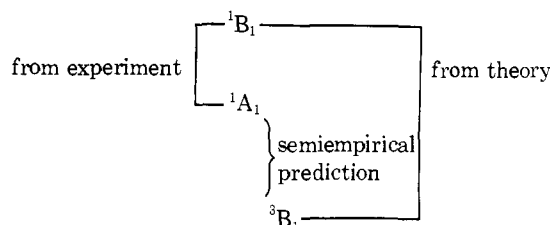
Discussion and Additional Results

After the present paper had been completed and accepted for publication, we became aware of the laser photodetachment experiments of Lineberger and co-workers.³² The shocking (relative to previous experimental work) result of their direct (employing no thermochemical data) measurements is a value of 19.5 ± 0.7 kcal for the CH_2 singlet-triplet separation. In addition two new theoretical singlet-triplet separations have

appeared and are slightly higher than the 14.1 kcal result of Bender, Schaefer, Franceschetti, and Allen. Using a double ζ plus polarization Slater basis set and a straightforward all single and double excitations CI procedure, Pakiari and Handy³³ predict $\Delta E = 15.4$ kcal/mol. Second, Pople, Binkley, and Seeger³⁴ predict 15.3 kcal using third-order unrestricted Moller-Plesset perturbation theory. Thus it seems likely that the earlier Bender result¹¹ (14.1 kcal) was in fact 5 kcal less than the exact value, rather than 6 kcal too high, as previously assumed.

With the above in mind, it now appears that a two-configuration description of the 1A_1 state is in fact heavy handed relative to the one-configuration 3B_1 result. More precisely, the correct ΔE value (19.5 kcal) appears to lie $\sim 60\%$ of the "distance" from the two-configuration 1A_1 result (10.9 kcal) to the one-configuration result (24.8 kcal). Thus it appears that neither of these simple theoretical prescriptions provides a particularly accurate ΔE prediction.

For this reason we have reverted to an approach used perhaps for the first time by Huo, Freed, and Klemperer³⁵ in their research on diatomic BeO. This semiempirical scheme was discussed by Harrison in his review article,¹⁵ but discarded when it appeared inconsistent with the "experimental" ΔE value of 8-9 kcal. One assumes that although the 3B_1 - 1A_1 separation in CH_2 is not reliably predicted, the 3B_1 - 1B_1 separation may be treated more easily. In fact this is plausible since both the 3B_1 and 1B_1 states arise from electron configuration (1) and the correlation energies of these two states might be nearly equal. Since the 1A_1 - 1B_1 separation is known experimentally^{2b} to be $7100 \text{ cm}^{-1} = 20.3$ kcal, we have a diagram of the type



To complete the above cycle, we carried out a geometry optimization for the 1B_1 state of CH_2 , yielding $r_e = 1.065 \text{ \AA}$, $\theta_e = 141.2^\circ$, and $E = -38.87106$ hartrees using our largest basis set. Comparison with the analogous 3B_1 total energy yields a 3B_1 - 1B_1 separation of -40.0 kcal/mol and in turn a ΔE value of 19.7 kcal. The fact that this result lies within Lineberger's experimental error is especially significant since our theoretical predictions are at the Hartree-Fock limit.

A similar analysis is possible for SiH_2 since the 1A_1 - 1B_1 separation T_0 is known experimentally to be 15540 cm^{-1} or 44.4 kcal/mol. For the 1B_1 state near-Hartree-Fock calculations were carried out, yielding $r_e = 1.468 \text{ \AA}$, $\theta_e = 123.5^\circ$, and $E = -289.96440$ hartrees. The theoretical 3B_1 - 1B_1 separation is thus 34.4 kcal and allows a semiempirical prediction of -10.0 kcal for $\Delta E({}^1A_1$ - ${}^3B_1)$. In light of the CH_2 results this value would appear to have a measure of reliability. Finally, we note that Dubois, Herzberg, and Verma have spectroscopically determined the 1B_1 SiH_2 equilibrium geometry to be $r_0(SiH) = 1.485 \text{ \AA}$, $\theta_0 = 122^\circ$, in good agreement with the present ab initio predictions.

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Nuclear Magnetic Resonance and Conformational Studies on Amylose and Model Compounds in Dimethyl Sulfoxide Solution

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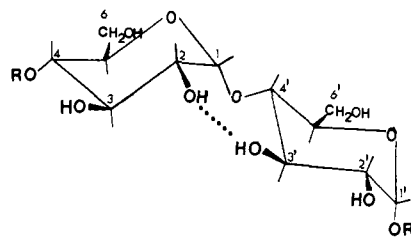
Abstract: The 220-MHz NMR spectra of maltose, cyclohexaamylose, cycloheptaamylose, and amylose were obtained in DMSO- d_6 at several temperatures up to 85 °C. Upfield migration of the signals attributed to the HO(2) and HO(3') hydroxyl protons was measured and interpreted in terms of an intramolecular hydrogen bond from OH(3') to OH(2) in all compounds. Analysis of the pertinent coupling constants provides identification of the local environments of donor and acceptor hydroxyl groups by assigning to them a range of $\chi(3')$ torsional (dihedral) angles. Energetically favorable conformations for amylose which satisfy these criteria are defined by steric maps and are discussed. The interpretation of the data in terms of intramolecular hydrogen bonding between contiguous residues leads to the conclusion that the same conformation is perpetuated along the amylose chain and implies substantial right-handed helical character in this solvent.

High-resolution nuclear magnetic resonance (NMR) spectroscopy has been used extensively to determine the conformational characteristics of polypeptides,^{1,2} oligopeptides,^{3,4} and cyclic peptides.⁵⁻¹⁴ Among the pertinent information provided by NMR for such molecules are the presence or absence of intramolecular hydrogen bonded groups deduced from the behavior of the chemical shift with respect to temperature or deuterium exchange and values for the torsional angles on the backbone or side groups deduced from the vicinal coupling constants. Such data have also been used with potential energy calculations to propose a most probable solution conformation for such molecules.^{11,15}

In this work, we have sought to determine whether similar NMR techniques will yield information on the solution conformation of some carbohydrates. To avoid complicated spectra arising from compounds containing different sugars and dissimilar linkages, we chose oligo- and polysaccharides which contain only 1 \rightarrow 4' linked α -D-glucose as the repeating unit: maltose, cyclohexaamylose, cycloheptaamylose, and amylose.

At present, the short-range conformational characteristics

of amylose and related compounds with the repeating sequence I are inferred from the crystalline conformations of maltose¹⁶



and β -methyl maltopyranoside.¹⁷ Both of these studies reveal an intramolecular hydrogen bond between OH(2) and OH(3') and the latter study¹⁷ showed specifically that the OH(2) hydroxyl group is the donor in this interaction. (In this paper, O(2), HO(2), and OH(2) denote respectively the oxygen atom, the hydroxyl hydrogen atom, and the hydroxyl group as an entity.) The crystal structure of cyclohexaamylose and its potassium acetate complex¹⁸ showed a similar intramolecular interaction. A secondary structure is also proposed from X-ray