The Prototypical Zinc Carbene and Zinc Carbyne Molecules ZnCH₂ and HZnCH: Triplet Electronic Ground States

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The title molecules have been examined using *ab initio* quantum mechanical methods and it is shown by a comparison of the theoretical and experimental IR spectra that the species prepared are triplet electronic ground states separated by about 80 kJ mol⁻¹; the theoretical molecular structures display a zinc–carbon single bond for the carbene and a zinc–carbon double bond for the carbyne.

In 1987 Chang *et al.*[1] reported in this journal the isolation and characterization of $ZnCH_2$ by Fourier transform infrared matrix isolation spectroscopy. Zinc carbenes are of general interest[2] and thus the synthesis and examination of the prototype molecule $ZnCH_2$ is of some importance. The experiments of Chang *et al.*[1] were carried out by codepositing zinc atoms with diazomethane and argon onto a rhodium plated copper mirror at 12 K, and generating $ZnCH_2$ with visible light. Perhaps their most fascinating observation is the carbene → carbyne rearrangement that takes place during UV photolysis [eqn.(1)].

$$ZnCH_2 \rightarrow HZnCH \qquad (1)$$

The pioneering experimental work by the Rice University group[1] leaves open a number of important questions concerning the observed $ZnCH_2$ and HZnCH species. Foremost among these are (*a*) the electronic ground states of both species; (*b*) their detailed molecular structures; and (*c*) the energy difference between these two isomers. In the present communication we attempt to supplement the experimental work of Chang *et al.* by providing answers to these question from theory.

The methods used here were self-consistent-field (SCF) theory and configuration interaction including all Hartree–Fock interacting single and double excitations (CISD). A double zeta plus polarization (DZP) basis set[3] was used throughout. In the CISD treatment, the ten lowest energy SCF molecular orbitals were held doubly occupied in all configurations and the twelve highest virtual orbitals deleted. The largest CISD wave function was for the closed shell ¹A state of $ZnCH_2$ and included 45 685 configurations. DZP CISD stationary point geometries were located using analytic gradient methods.[4]

In searching for the lowest energy molecular structures of $ZnCH_2$ and HZnCH, about a dozen different electronic states

were investigated. The predicted equilibrium geometries for the three lowest-lying structures are seen in Fig. 1. The electronic ground state of $ZnCH_2$ turns out to be the $^3B_1$ state arising from electron configuration x (with Zn 1s, 2s, 2p, 3s, 3p and C 1s electrons taken implicitly). Predicted to lie only 49.6 kJ mol⁻¹ higher (Davidson corrected[5] DZP CISD) is the closed-shell singlet state **y**. Among HZnCH structures considered, the lowest is the $^3\Sigma^-$ state arising from electron configuration **z**. This zinc carbyne ground state is predicted to lie 86.0 kJ mol⁻¹ above the $^3B_1$ $ZnCH_2$ global minimum. Such a ΔE value for chemical reaction (1) is easily consistent with the observation of Chang *et al.*[1] that the HZnCH species is observed under UV photolysis to 360 nm, *i.e.* 333 kJ mol⁻¹.

$$7a_1^2 8a_1^2 1a_2^2 3b_2^2 3b_1^2 9a_1^2 4b_2^2 10a_1^2 11a_1 4b_1$$

x

$$9a'^2 3a''^2 10a'^2 11a'^2 4a''^2 12a'^2 5a''^2 13a'^2 14a'^2$$

y

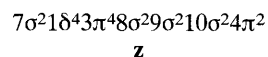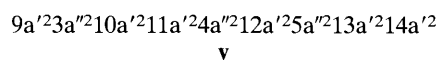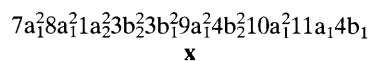$$7\sigma^2 1\delta^4 3\pi^4 8\sigma^2 9\sigma^2 10\sigma^2 4\pi^2$$

z

Table 1 compares the theoretical and experimental vibrational frequencies for the triplet electronic ground states of $ZnCH_2$ and HZnCH. The agreement is sufficiently satisfactory to conclude that the electronic states being considered theoretically are indeed the states that have been observed in the laboratory. However, it would be of interest to see if higher level theoretical studies reduce the CH_2 wagging frequency for the $^3B_1$ state of $ZnCH_2$. An illustration of the IR spectrum of HZnCH is given by Chang *et al.*[1] and the peak heights associated with the three assigned fundamentals fall in the order of the IR intensities predicted from theory in Table 1.

Table 1 Theoretical and experimental (ref. 1) vibrational frequencies for the zinc carbene and zinc carbyne systems

Symmetry	Description	$^3B_1$ ZnCH₂ (DZP SCF) ω/cm⁻¹	Intensity/ km mol⁻¹	Experiment ν/cm⁻¹
b₂	C–H asym. stretch	3315	20	3047
a₁	C–H sym. stretch	3227	42	2956
a₁	CH₂ scissor	1475	5	1341
b₁	CH₂ wag	621	84	525
b₂	CH₂ rock	569	6	544
a₁	Zn–C stretch	562	42	514
		HZnCH (DZP SCF)		Experiment
σ	C–H stretch	3393	2	—
σ	Zn–H stretch	1972	119	1924
σ	Zn–C stretch	660	60	648
π	*cis* bending	452	127	469
π	*trans* bending[a]	162i	45	—

[a] Although this linear structure is a transition state at the DZP SCF level of theory, it is a genuine minimum at the higher DZP CISD level of theory.
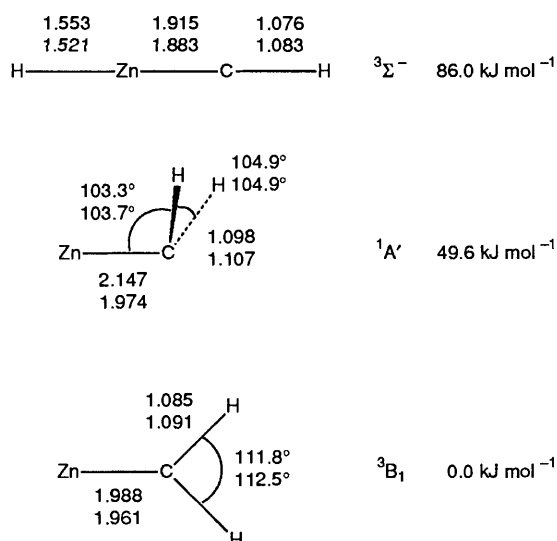
$$H\text{———}Zn\text{———}C\text{———}H \quad {}^3\Sigma^- \quad 86.0 \text{ kJ mol}^{-1}$$

1.553 1.915 1.076
1.521 1.883 1.083

$${}^1A' \quad 49.6 \text{ kJ mol}^{-1}$$

104.9°
103.3° H 104.9°
103.7°
1.098
Zn———C 1.107
2.147
1.974

$${}^3B_1 \quad 0.0 \text{ kJ mol}^{-1}$$

1.085 H
1.091
111.8°
Zn———C 112.5°
1.988
1.961
H

Fig. 1 Theoretical predictions of the equilibrium geometries of the three lowest energy structures of the $ZnCH_2$ system. Bond distances are in Å. The upper entries are DZP SCF optimized values, the lower entries are DZP CISD.

There are several interesting features of the molecular structures in Fig. 1. First is the pyramidal (about carbon) structure of the closed shell singlet state. This would be the structure preferred by the interaction of Zn with the empty p orbital of carbenes with singlet ground states. Secondly, the zinc–carbon distance is shortest (1.883 Å) for the linear carbyne structure, and is 0.078 Å longer for the global minimum ${}^3B_1$ $ZnCH_2$ state. Higher levels of theory (e.g., addition of f functions on the zinc atom) are expected to shorten these zinc–carbon bond distances by roughly 0.02 Å. Experimental single bond distances[6] for zinc alkyls fall in the range 1.93–1.96 Å. We suggest that the 'carbyne' incorporates a Zn=C double bond, while the 'carbene' incorporates a Zn–C single bond. Further experiments on these fascinating systems would be most welcome.

Note added in proof: the dideuteriated and ${}^{13}C$ substituted vibrational frequencies were also computed and the frequency

shifts (from $ZnCH_2$ to $Zn^{13}CH_2$ and $ZnCD_2$, and from $HZnCH$ to $HZn^{13}CH$ and $DZnCD$) agree well with experiment. The ${}^{13}C$ shifts are reproduced to within 1 cm^{-1} of experiment except for the wag in $Zn^{13}CH_2$, which the normal mode analysis of Chang *et al.*[1] also missed by 4 cm^{-1}. The $ZnCD_2$ and $DZnCD$ shifts are much larger, and hence agreement is less quantitative.

A referee noted that the $ZnCH_2$ molecule should be a radical ion pair formed by formal transfer of an electron from Zn to CH_2, giving the carbene anionic character. This is partially supported by the DZP SCF Mulliken charges of +0.43 on Zn and −0.66 on C.

References

1 S.-C. Chang, R. H. Hauge, Z. H. Kafafi, J. L. Margrave and W. E. Billups, *J. Chem. Soc., Chem. Commun.*, 1987, 1682.

2 See, for example, J. Burdon and R. C. Price, *J. Chem. Soc., Chem. Commun.*, 1986, 893.

3 The basis set chosen was as follows: (a) for zinc Zn(14s11p6d/10s8p3d) from the primitive gaussian basis of A. J. H. Wachters, *J. Chem. Phys.*, 1970, 52, 1033, following contraction No. 15 of D. M. Hood, R. M. Pitzer and H. F. Schaefer, *J. Chem. Phys.*, 1979, 71, 705. Throughout this work, all six d-like functions were included. (b) For carbon and hydrogen the standard C(9s5p1d/4s2p1d), H(4s1p/2s1p) sets of S. Huzinaga, *J. Chem. Phys.*, 1965, 42, 1293 and T. H. Dunning, *J. Chem. Phys.*, 1970, 53, 2823 were used. Polarization function orbital exponents were $\alpha_d(C) = 0.75$, $\alpha_p(H) = 0.75$. Hydrogen atom s functions were scaled by a factor of $(1.2)^2 = 1.44$.

4 H. F. Schaefer and Y. Yamaguchi, *Robert S. Mulliken Issue*, *J. Mol. Struct.*, 1986, 135, 369.

5 E. R. Davidson, in *The World of Quantum Chemistry*, eds. R. Daudel and B. Pullman, Reidel, Dordrecht, Holland, 1974, pp. 17–30.

6 A. Almenningen, T. U. Helgaker, A. Haaland and S. Samdal, *Acta Chem. Scand., Ser. A*, 1982, 36, 159.