POTENTIAL ENERGY SURFACES FOR CHEMICAL REACTIONS

Progress Report March 15, 1988, through ¹⁹⁸⁹ Present

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"Potential Energy Surfaces for Chemical Reactions"

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A. Publications Supported by the U. S. Department of Energy (Since - Proposal of 9/30/87).

- 1 R. S. Grev and H. F. Schaefer, "Cyclopolsilanes: Structure, Strain, and the Form of the SOMO in their Radical-Anions", *J. Amer. Chem. Soc.* **109**, 6569 (1987).
- 3 R. S. Grev and H. F. Schaefer, "Hetero-Substituted Cyclopolsilanes: Unusual Structures and a New Model of Bonding in 1,3-Disubstituted Four-Membered Rings", *J. Amer. Chem. Soc.* **109**, 6577 (1987).
- 4 G. E. Scuseria and H. F. Schaefer, "The Nuclear Quadrupole Moment of ^{14}N . A Theoretical Prediction from Full Valence Shell and Full Configuration Interaction Atomic Wavefunctions", *J. Chem. Phys.* **87**, 4020 (1987).
- 5 W. D. Allen and H. F. Schaefer, "An Examination of the $2\ ^1\text{A}_1$ States of Formaldehyde and Ketene Including Analytic Configuration Interaction Energy First Derivatives for Singlet Excited Electronic States of the Same Symmetry as the Ground State", *J. Chem. Phys.* **87**, 7076 (1987).
- 6 Y. T. Chang, Y. Yamaguchi, W. H. Miller, and H. F. Schaefer, "An Analysis of the Infrared and Raman Spectra of the Formic Acid Dimer $(\text{HCOOH})_2$ ", *J. Amer. Chem. Soc.* **109**, 7245 (1987).
- 7 B. S. Thies, R. S. Grev, and H. F. Schaefer, "Dimethyldisilyne: A Fleeting Observed Species Incorporating a Triple Bond?", *Chem. Phys. Lett.* **140**, 355 (1987).
- 8 D. A. Clabo, W. D. Allen, R. B. Remington, Y. Yamaguchi, and H. F. Schaefer, "A Systematic Study of Molecular Vibrational Anharmonicity and Vibration-Rotation Interaction by Self-Consistent-Field Higher-Derivative Methods. Asymmetric Top Molecules", *Chem. Phys.* **123**, 187 (1988).
- 9 B. Kim, H. S. Johnston, D. A. Clabo, and H. F. Schaefer, "Vertical Electronic Spectrum of NO_3 : $^2\text{A}_2'$, $^2\text{E}''$ ($^2\text{A}_2$, $^2\text{B}_1$), and $^2\text{E}'$ States", *J. Chem. Phys.* **88**, 3204 (1988).
- 10 B. F. Yates, D. A. Clabo and H. F. Schaefer, "Cyclic Isomers of Singlet Si_4H_4 Related to Tetrasilacyclobutadiene", *Chem. Phys. Lett.* **143**, 421 (1988).

- 11 G. E. Scuseria and H. F. Schaefer, "Variational Studies of the Importance of Triple and Quadruple Excitations on the Barrier Height for $F + H_2 \rightarrow FH + H$ ", *J. Chem. Phys.* **88**, 7024 (1988).
- 12 T. J. Lee, J. E. Rice, W. D. Allen, R. B. Remington, and H. F. Schaefer, "How Bent Can a Benzene Be? The Molecular Structure, Infrared Spectrum and Energetics of [6] Paracyclophane", *Chem. Phys.* **123**, 1 (1988).
- 13 W. D. Allen and H. F. Schaefer, "Reaction Paths for the Dissociation of $\tilde{a}^3A'' CH_2CO \rightarrow \tilde{X}^3B_1 CH_2 + \tilde{X}^1\Sigma^+ CO$ ", *J. Chem. Phys.* **89**, 329 (1988).
- 14 B. H. Besler, G. E. Scuseria, A. C. Scheiner, and H. F. Schaefer, "A Systematic Theoretical Study of Harmonic Vibrational Frequencies: The Single and Double Excitation Coupled Cluster (CCSD) Method", *J. Chem. Phys.* **89**, 360 (1988).
- 15 B. F. Yates, H. F. Schaefer, T. J. Lee and J. E. Rice, "The Infrared Spectrum of $F \cdot H_2O$ ", *J. Amer. Chem. Soc.* **110**, 6327 (1988).
- 16 W. Thiel, G. E. Scuseria, H. F. Schaefer, and W. D. Allen, "The Anharmonic Force Fields of HOF and F_2O ", *J. Chem. Phys.* **89**, 4965 (1988).
- 17 H. F. Schaefer, "A History of *Ab Initio* Computational Quantum Chemistry: 1950-1960", *Tetrahedron Computer Methodology* **1**, 97 (1988).
- 18 T. P. Hamilton and H. F. Schaefer, "Silaktene: A Product of the Reaction Between Silylene and Carbon Monoxide?" *J. Chem. Phys.* **90**, 1031 (1989).
- 19 H. F. Schaefer, "The Infrared Spectra of Polyatomic Molecular Ions: A Profitable Alliance Between Theory and Experiment", pages 109-129 in *Ion and Cluster-Ion Spectroscopy and Structure*, Editor J. P. Maier (Elsevier, Amsterdam, 1989).
- 20 H. F. Schaefer, "Computers and Molecular Quantum Mechanics: 1965-1988, A Personal Perspective", to appear in *Computational Atomic and Nuclear Physics at One Gigaflop*, Editors C. Bottcher, M. R. Strayer, and J. B. McGrory.
- 21 G. E. Scuseria and H. F. Schaefer, "The Photodissociation of Formaldehyde: A Coupled Cluster Study Including Connected Triple Excitations of the Transition State Barrier Height for $H_2CO \rightarrow H_2 + CO$ ", *J. Chem. Phys.*, **90**, 3629 (1989).
- 22 T. P. Hamilton and H. F. Schaefer, "The Reaction of Methane with Molecular Oxygen: A Semi-Quantitative Estimate of the Activation Energy", *J. Chem. Phys.*, **90**, 6391 (1989).
- 23 B. F. Yates and H. F. Schaefer, "Tetrasilacyclobutadiylidene: The Lowest Energy Cyclic Isomer of Singlet Si_4H_4 ?" *Chem. Phys. Lett.* **155**, 563 (1989).
- 24 H. F. Schaefer, "The Third Age of Quantum Chemistry," *Chimia* **43**, 1 (1989).
- 25 Y. Xie, G. E. Scuseria, B. F. Yates, Y. Yamaguchi, and H. F. Schaefer, "Methylnitrene ($CH_3-\dot{N}$): Theoretical Predictions of its Molecular Structure and Comparison with the Conventional C-N Single Bond in Methylamine (CH_3-NH_2)," *J. Amer. Chem. Soc.* **111**, 5181 (1989).
- 26 Y. Xie, B. F. Yates, Y. Yamaguchi, and H. F. Schaefer, "The π -Bonded Complex Between Aluminum and Ethylene," *J. Amer. Chem. Soc.* **111**, 6163 (1989).

- 27 G. E. Scuseria and H. F. Schaefer, "The Unimolecular Triple Dissociation of Glyoxal: Transition State Structures Optimized by Configuration Interaction and Coupled Cluster Methods", *J. Amer. Chem. Soc.* **111**, 7761 (1989).
- 28 Y. Xie, B. F. Yates, and H. F. Schaefer, "The Wealth of Energetically Low-Lying Isomers for Very Simple Organometallic Systems. The Aluminum-Acetylene ($\text{Al-C}_2\text{H}_2$) System", *J. Amer. Chem. Soc.*
- 29 N. L. Allinger, R. S. Grev, B. F. Yates, and H. F. Schaefer, "The Syn Rotational Barrier in Butane", *J. Amer. Chem. Soc.*
- 30 G. E. Quelch, Y. Xie, B. F. Yates, Y. Yamaguchi, and H. F. Schaefer, "The HO_2^+ Molecular Ion. A Comparison of Theoretical Methods for the Prediction of Anharmonic Vibrational Frequencies", *Molecular Physics*.
- 31 T. P. Hamilton and H. F. Schaefer, "Vinylidene Radical Cation (H_2CC^+): A Sizeable Barrier to Unimolecular Rearrangement to the Acetylene Radical Cation", *J. Phys. Chem.*
- 32 C. P. Blahous, Y. Xie, and H. F. Schaefer, "The Infrared Spectrum of Trimethylenemethane. Predictions of In-Plane Vibrational Frequencies from Extensively Correlated Wave Functions", *J. Chem. Phys.*
- 33 G. E. Quelch, R. S. Grev, and H. F. Schaefer, "Concerning the Interaction of Atomic Silver with a Silicon Monoxide Ligand", *J. Chem. Soc. (London), Chemical Communications* 1498 (1989).
- 34 Y. Xie and H. F. Schaefer, "The Bitetrahedral Molecule C_8H_6 : The Shortest Possible C-C Bond Distance for a Saturated Hydrocarbon?", *Chem. Phys. Lett.* **161**, 516 (1989).

B. The Bitetrahedral Molecule C_8H_6 : The Shortest Possible C-C Bond Distance for a Saturated Hydrocarbon?

Ermer, Bell, Schäfer, and Szeimies (hereafter designated EBSS) have recently reported the remarkable crystal structures of the two esters

Both molecules are coupled bicyclo[1.1.0]butane derivatives and are found to have extremely short carbon-carbon central bonds, $1.445(3) \text{ \AA}$ for 1 and $1.440(2) \text{ \AA}$ for 2. The central C-C distance found for 2 is "the shortest non-cyclic (unbent) CC single bond between saturated tetravalent C atoms observed so far". As discussed by EBSS, the origin of these extremely short C-C bonds lies with the six abnormally widened CCC angles adjacent to the central carbon-carbon single bond.

In their paper EBSS hypothesize that the observed length of the central C-C bond in 2 may be regarded as an upper limit of that in the bitetrahedral molecule

3

The purpose of the present research is to test the hypothesis of EBSS using *ab initio* quantum mechanical methods. Such theoretical methods have been established as very reliable for the prediction of hydrocarbon equilibrium geometries and are a genuinely

viable alternative when experiments are not possible (as seems likely to be the case for bitetrahedryl 3 for some years). As a pertinent example of the above, we note that the four theoretical methods used here predict the prototype C-C single bond length in ethane to be 1.538 Å (MBS), 1.537 (DZ), 1.531 (DZ+d), and 1.530 (DZ+P), all very close to the observed 1.535 Å.

Four distinct basis sets were used in this research in conjunction with the single configuration self-consistent-field (SCF) method. The smallest was the STO-3G minimum basis set (MBS) of Hehre, Stewart, and Pople. Intermediate in size was the standard double zeta (DZ) set of Huzinaga and Dunning, designated C(9s5p/4s2p), H(4s/2s). The next largest basis set employed was the double zeta plus d (DZ+d) set, in which a set of six d-like functions (with orbital exponent $\alpha = 0.75$) was added to each of the eight carbon atoms. The largest basis set, double zeta plus polarization (DZ+P), adds a set of p functions ($\alpha = 1.0$) to the DZ+d set and thus includes 158 contracted gaussian functions. This final basis may be labeled C(9s5p1d/4s2p1d), H(4s1p/2s1p). All four theoretical methods should provide reasonable structural predictions with the reliability increasing in the order MBS $\rightarrow$ DZ $\rightarrow$ DZ+d $\rightarrow$ DZ+P.

The theoretical predictions for the equilibrium geometry of bitetrahedral 3 are given in the Figure. Beyond any question theory confirms the general prediction by EBSS that the central C-C bond distance is very short. The four *ab initio* methods predict $r_e(\text{C-C}) = 1.449$ (MBS), 1.428 (DZ), 1.443 (DZ+d) and 1.444 (DZ+P). However it is difficult to precisely compare the theoretical central C-C distance in bitetrahedryl 3 with that determined by crystallography (1.440(2) Å) for compound 2. The most reliable *ab initio* prediction of $r_e = 1.444$ Å (DZ+P SCF) is probably uncer-

tain by $\pm 0.01 \text{ \AA}$, while the distance in the crystal ($1.440 \text{ \AA}$) could differ by $\pm 0.02 \text{ \AA}$ from the true equilibrium distance r_e for compound 2 in the gas phase. Thus all one can say is that the central C-C distances for 2 and 3 are both extremely short and about equal.

At the highest level of theory (DZ+P SCF) the six equivalent central CCC bond angles are predicted to be 144.6° . This corresponds to a bond angle widening relative to tetrahedrality of $144.6^\circ - 109.5^\circ = 35.1^\circ$. For the experimental structure of 2 the bond angle widening is significantly less, 21.4° . By the arguments of EBSS, one would expect the central C-C distance for bitetrahedral 3 to be intermediate between $1.440 \text{ \AA}$ (2, widening angle 21.4°) and the value 1.384 observed for diacetylene

which has a formal angle widening of $180^\circ - 109.5^\circ = 71.5^\circ$.

First Entry	—	DZ+P SCF
Second Entry	—	DZ+d SCF
Third Entry	—	DZ SCF
Fourth Entry	—	STO-3G SCF