30

the synthesis of trichothecins. The results of these studies will be reported in due course.

Table I. CI Results for 1,2,4,5-Tetramethylenebenzene

state	UHF optimized[a,b]	ROHF optimized[a,c]
	SD-CI/STO-3G[e]	
$^3B_{1u}$	-379.773 01	-379.826 71
^1A_g	-379.783 08	-379.778 38
^5A_g	-379.760 39	

state	SDTQ-CI energy[a]	rel energy[d]
	SDTQ-CI/STO-3G[e]	
^1A_g	-379.863 47	0.0
$^3B_{1u}$	-379.851 72	7.4
^5A_g	-379.773 90	56.2
	SDTQ-CI[4s,2p][f]	
^1A_g	-384.366 65	0.0
$^3B_{1u}$	-384.341 94	15.5

[a] Energy in hartrees. [b] SD-CI energy at STO-3G UHF optimized geometry. The ^1A_g calculation uses a two-configuration reference state. [c] SD-CI energy at STO-3G ROHF/TCSCF optimized geometry. The ^1A_g calculation was done as in footnote b. [d] Energy relative to ^1A_g state in kcal/mol at SDTQ-CI level. [e] STO-3G basis set at STO-3G optimized geometry, using UHF geometry for ^1A_g and ROHF geometry for $^3B_{1u}$ (see text). [f] Dunning-Huzinaga (9s,5p)[4s,2p] basis set at STO-3G optimized geometry.
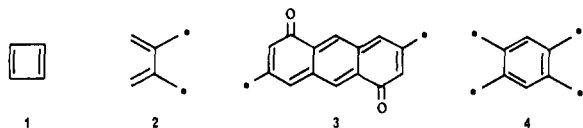
Ab Initio Study of 1,2,4,5-Tetramethylenebenzene: A Disjoint Non-Kekulé Molecule with a Possible Singlet Ground State

Paul M. Lahti,[1] Angelo Rossi,*[2] and Jerome A. Berson*[1]

Departments of Chemistry, Yale University
New Haven, Connecticut 06511
University of Connecticut, Storrs, Connecticut 06268

The application[3] of Hund's first rule, not only to its original domain in atomic spectroscopy[4] but also to conjugated non-Kekulé molecules, has been discussed widely.[5-7] Hückel[6] was the first to point out that a violation might occur in the specific case of the Schlenk–Brauns hydrocarbon, because theory then available showed the singlet and triplet states to be of nearly equal energy. Borden and Davidson[7] later discerned theoretically that this property should inhere in the whole class of "disjoint" biradicals, of which an important subgroup comprises alternant systems with equal numbers of starred and unstarred π-centers.[7,8] Higher level ab initio SCF-MO-CI calculations confirm this idea by predicting singlet ground states for two disjoint systems, square cyclobutadiene (1)[5d,h,9] and tetramethyleneethane (2).[7,10] However,

the only available experimental test shows the disjoint non-Kekulé molecule 3 to have a triplet ground state,[11] and, although an ab initio calculation currently is not practical, INDO/S-CI calcu-

lations do concur with the experimental finding.[12] In order to explore further the consequences of disjoint character, we have undertaken an ab initio study of a disjoint system of intermediate size, 1,2,4,5-tetramethylenebenzene (4). INDO/S-CI calculations[12] predict a singlet ground state by 9 kcal/mol. So far, this is the largest system for which our previously reliable semiempirical method[12] has been tested against higher level theory.

Geometry optimization of 4 was carried out using restricted open-shell Hartree–Fock (ROHF) and unrestricted Hartree–Fock (UHF) wave functions for the $^3B_{1u}$ state, two-configuration SCF (TSCF) wave functions for the ^1A_g state, and UHF wave functions for the ^5A_g state; the STO-3G basis set[13] was used to optimize the geometries to less than 2.0 millihartrees/bohr using the program GAMESS.[14] Planarity was imposed during the optimization since our objective was to examine disjoint character. The final geometries are shown in the supplementary material. Only the ^5A_g state has an "aromatic" geometry. The geometries of the ^1A_g TCSCF and $^3B_{1u}$ ROHF states, as expected,[15,16] are essentially identical and resemble partially localized pentadienyl radicals joined at inactive sites. The $^3B_{1u}$ UHF geometry has longer exocyclic methylene bond lengths than does the triplet ROHF geometry, but the UHF geometry is still approximately that of joined pentadienyl radicals. UHF wave functions are known to give variationally better geometries than ROHF wave functions for many open-shell species, due to the better correlation in UHF wave functions,[15] which helps to avoid doublet instability in the triplet wavefunction.[5g] However, the UHF/STO-3G-optimized $^3B_{1u}$ state of 4 has a spin-squared expectation value ($\langle S^2 \rangle$) of 3.14, indicating substantial spin contamination, since a pure triplet should have $\langle S^2 \rangle = 2.00$. As a result, the UHF geometry presumably reflects the optimum for some mixture of spin states, not for the "pure" $^3B_{1u}$ state. Therefore both UHF and ROHF geometries were used in configuration interaction (CI) calculations described below. The geometry of lowest CI energy would under these circumstances be variationally preferable, though probably not optimal due to the approximate nature of the wave functions used for optimization.

CI calculations were then carried out on the appropriate geometries for the states of 4, using STO-3G (spin-pure) ROHF MO's for multiplet states and TCSCF MO's for ^1A_g. We carried

(1) Yale University.

(2) University of Connecticut.

(3) For a particularly relevant example, see Hund, F., as cited by Müller, E.; Bunge, W. Ber. 1936, 69, 2168.

(4) Hund, F. Z. Phys. 1925, 33, 345.

(5) Cf. inter alia: (a) Coulson, C. A. "Valence"; Oxford University Press: Oxford, 1952; p 99. (b) Dewar, M. J. W. "Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969; p 234. (c) Longuet-Higgins, H. C. J. Chem. Phys. 1950, 18, 265. (d) Kollmar, H.; Staemmler, V. Theor. Chim. Acta 1978, 48, 223. (e) Salem, L.; Rowland, C. Angew. Chem., Intl. Ed. Engl. 1972, 11, 92. (f) Syrkin, Y. K.; Dyatkina, M. E. "Structure of Molecules and the Chemical Bond"; Butterworths: London, 1950; p 135. (g) Borden, W. T. "Diradicals"; Academic Press: New York, 1982; Chapter 1. (h) Borden, W. T.; Davidson, E. R.; Hart, P. J. J. Am. Chem. Soc. 1978, 100, 388.

(6) Hückel, E. Z. Phys. Chem., Abt. B 1936, 34, 339.

(7) Borden, W. T.; Davidson, E. R. J. Am. Chem. Soc. 1977, 99, 4587.

(8) (a) Ovchinnikov, A. A. Theor. Chim. Acta 1978, 47, 297. (b) Misurkin, I. A.; Ovchinnikov, A. A. Russ. Chem. Rev. (Engl. Transl.) 1977, 46, 967.

(9) Buenker, R. J.; Peyerimhoff, S. D. J. Chem. Phys. 1968, 48, 354.

(10) Dixon, D. A.; Foster, R.; Halgren, T.; Lipscomb, W. N. J. Am. Chem. Soc. 1978, 100, 1359.

(11) Seeger, D. E.; Berson, J. A. J. Am. Chem. Soc. 1983, 105, 5146.

(12) Lahti, P. M.; Rossi, A.; Berson, J. A. J. Am. Chem. Soc. 1985, 107, 2273.

(13) Hehre, W. J.; Stewart, R. F.; Pople, J. A. J. Chem. Phys. 1969, 51, 2657.

(14) Dupuis, M.; Spangler, D.; Wendolowski, J. J. QCPE 1981, 1, 91.

(15) Paldus, J.; Veillard, A. Mol. Phys. 1978, 35, 445.

(16) Kato, S.; Morokuma, K.; Feller, D.; Davidson, E. R.; Borden, W. T. J. Am. Chem. Soc. 1983, 105, 1791.

out CI over the complete set of 10 π orbitals, using up to doubly (SD-CI) or quadruply (SDTQ-CI) excited configurations from the ground state.[17] Table I shows the results. Of particular interest is that the SD-CI $^3B_{1u}$ state has a lower energy at the ROHF geometry by 32 kcal/mol, while the ^1A_g state is lower at the triplet UHF geometry by 4 kcal/mol. Using the geometries that correspond to the lowest SD-CI energies calculated for each state, we find that **4** has a singlet ground state at the SDTQ-CI/STO-3G level, with the $^3B_{1u}$ and ^5A_g states 7 and 56 kcal/mol, respectively, higher in energy. The ^1A_g ground state is a biradical, as shown by the major terms in its CI wave function (eq 1) and

$$\psi_{CI} = 0.697(b_{2u})^2 - 0.529(b_{3g})^2 \qquad (1)$$

by the natural orbital occupancies of the frontier MO's, 1.078 and 0.922, respectively.

We then carried out SDTQ-CI/[4s,2p] calculations over the first 12 π orbitals obtained using the Dunning–Huzinaga (9s,5p)/[4s,2p] contracted Gaussian basis set,[18] with the geometries that gave the lowest SDTQ-CI/STO-3G energies for the ^1A_g and $^3B_{1u}$ states. At this level, the ^1A_g state remains the ground state by 15 kcal/mol below the $^3B_{1u}$ state.[19]

Since use of proper MCSCF wave functions is not yet practically possible for so large a system as **4**, the geometries obtained from UHF and ROHF wave functions for the states are uncertain, especially for the singlet and triplet states. As a result, there is uncertainty in the singlet–triplet gap. Although the geometry for the triplet state is not optimal because of spin contamination by a higher quintet state, and consequently the energy values of the individual states might change in a calculation based on a spin-pure triplet geometry, it seems unlikely that this would result in a drastic selective stabilization of the triplet. Therefore, the calculations suggest that a singlet is either the ground state or a very low-lying excited state of **4**, in confirmation of qualtiative prediction based on disjoint HMOs and in accord with the INDO/CI result.[12] This species now becomes an attractive synthetic target as an experimental test of theory.

Supplementary Material Available: Diagram of optimized geometries for 1,2,4,5-tetramethylenebenzene (3 pages). Ordering information is given on any current masthead page.

(17) The CI calculations were carried out using the MELD package of routines developed by Professor E. R. Davidson's group.

(18) Dunning, T. H.; Hays, P. J. In "Modern Theoretical Chemistry"; Schaeffer, H. F.; III, Ed.; Plenum Press: New York, 1977; Vol. 3, Chapter 1.

(19) The $^1B_{1u}$ state, at the same level of calculation, lies much higher in energy than the two lowest states.

Observation of an Unusually Low CO Stretching Frequency on Fe(100)

D. W. Moon, S. L. Bernasek,* D. J. Dwyer,† and J. L. Gland†

Department of Chemistry, Princeton University Princeton, New Jersey 08544

We report here our observation with high-resolution electron energy loss spectroscopy (HREELS) of an unusually low CO

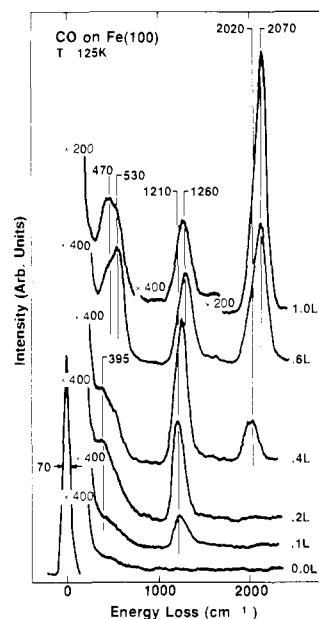†Exxon Research and Engineering Corporate Research Laboratory, Clinton Township, Annandale, NJ 08801.

Figure 1. Vibrational spectra for CO chemisorbed on Fe(100) at 125 K for various exposures. Primary beam energy, 5.0 eV.

stretching frequency (1210 cm^{-1}) for a chemisorbed CO molecular state (α_3) on Fe(100). This chemisorbed state is the precursor state for CO dissociation. Our recent studies of CO adsorption on Fe(100) using X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD)[1] showed that CO adsorbs molecularly in three sequentially filled states (CO(α_1), CO(α_2), and CO(α_3)), and that CO dissociation is correlated with the most tightly bound molecular state, CO(α_3). The stretching frequency for this CO(α_3) state is 1210 cm^{-1} indicating a substantially weakened C–O bond relative to the gas-phase molecule, which has a stretching frequency of 2143 cm^{-1}. Along with the very recently reported observation for CO on Cr(110)[2] (1150–1330 cm^{-1}), it is the lowest CO stretching frequency reported to date for CO adsorbed on any single-crystal metal surface.[3,4] Since all the previously observed CO molecular states on iron surfaces have substantially higher vibrational frequencies (1530–2070 cm^{-1}),[5,6] this report demonstrates a striking example of the geometric effect of the adsorption site on the CO bond weakening upon chemisorption.

The experiments reported here were performed in a stainless steel UHV system with a base pressure of 3×10^{-10} torr equipped with a 127° cylindrical sector HREELS and TPD. The same Fe(100) crystal and cleaning procedures used for our previous XPS and TPD studies[1] were used. CO TPD spectra were identical with those observed previously for the clean Fe(100) surface. HREELS spectra as a function of CO exposure are shown in Figure 1. For CO exposure up to 0.2 langmuir at 125 K, one loss peak clearly dominates at 1210 cm^{-1}. There is also a weak peak at 395 cm^{-1}. Above 0.3 langmuir CO exposure, a loss peak appears at 2020 cm^{-1} which increases in intensity with CO exposure. This second peak shifts to 2070 cm^{-1} at 1.0 langmuir CO exposure. With the appearance of the second peak at 2020 cm^{-1}, the loss peak at 1210 cm^{-1} shifts to 1260 cm^{-1}. Initially the intensity of the loss peak at 1210 cm^{-1} increases with CO exposure. However, with increasing CO exposure above 0.4 langmuir, the 1210-cm^{-1} loss peak intensity decreases as the loss peak at 2020 cm^{-1} increases in

(1) Moon, D. W.; Dwyer, D. J.; Bernasek, S. L. *Surf. Sci.*, in press.

(2) Shinn, N. D.; Madey, T. E. *Phys. Rev. Lett.*, in press.

(3) Yates, J. T., Jr.; Madey, T. E.; Campuzano, J. C. "The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis"; King, D. A., Woodruff, D. P. Eds., in press.

(4) Hoffman, F. M.; de Paola, R. A. *Phys. Rev. Lett.* **1984**, *52*, 1697.

(5) Seip, U.; Tsai, M.-C.; Christmann, K.; Küppers, J.; Ertl, G. *Surf. Sci.* **1984**, *139*, 29.

(6) Erley, W. J. *Vac. Sci. Technol.* **1981**, *18*, 472.