with a recent theoretical study of diazetine fragmentation, which reveals that the preferred mechanism is unsymmetrical and involves a diradicaloid with a pair of coupled electrons, one each residing approximately at C and N.[25]

Finally, we note that since the kinetic method employed in this study only produces information about how unequally the two C–N bonds are ruptured in the transition state, the question of the nature of the pathway followed after the saddle point must be regarded as still open.[26]

Acknowledgment. I am grateful to the Danish Natural Science Research Council and to the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung for generous support of the work and to Professors M. G. Ettlinger (University of Copenhagen) and J. F. M. Oth (ETH, Zürich) for valuable suggestions and Dr. N. Bernth (TI, Tåstrup) for helpful discussions.

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[23] Opposing isotope effects have previously been reported for the thermal decomposition of (α-phenylethyl)azomethane. The α effects were interpreted in terms of a two-step cleavage. See: Seltzer, S.; Dunne, F. T. *J. Am. Chem. Soc.* **1965**, *87*, 2628–2635. See also: von Gustorf, E. K.; White, D. V.; Leitich, J.; Henneberg, D. *Tetrahedron Lett.* **1969**, 3113–3116. Collins, C. J.; Benjamin, B. M.; Kabalka, G. W. *J. Am. Chem. Soc.* **1978** *100*, 2570–2571.

[24] If hyperconjugative effects were operative, the β-isotope effect should be normal ($k_H/k_D > 1$). See, e.g.: DeFrees, D. J.; Hehre, W. J.; Sunko, D. E. *J. Am. Chem. Soc.* **1979**, *101*, 2323–2327.

[25] Crans, D.; Snyder, J. P., private communication. The work is quoted in the recent review of Engel (Engel, P. S. *Chem. Rev.* **1980**, *80*, 113) on the mechanism of the thermal and photochemical decomposition of azoalkanes.

[26] A true intermediate could intervene on the potential surface. Further possibilities are potential surfaces that sustain "twixtyl"[27] and "continuous diradical"[28] species.

[27] Hoffmann, R.; Swaminathan, S.; Odell, B. G.; Gleiter, R. *J. Am. Chem. Soc.* **1970**, *92*, 7091–7097.

[28] von Doering, W. E.; Sachdev, K. *J. Am. Chem. Soc.* **1974**, *96*, 1168–1187; **1975**, *97*, 5512–5520.

Small Ring Cyclic Allenes: An ab Initio Study of the Structure of 1,2-Cyclohexadiene

Michael W. Schmidt,[1a] Richard O. Angus, Jr.,[1b] and Richard P. Johnson*[1b]

Department of Chemistry, Iowa State University and Ames Laboratory, USDOE, Ames, Iowa 50011

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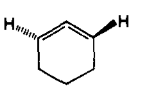
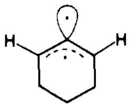
Allenes incorporated in small rings are constrained to bent, near planar geometries.[2] The archetypes of this series, 1,2-cyclohexadiene (**1**) and 1,2-cycloheptadiene were the subjects of recent experimental investigations by Balci and Jones,[3] which provided clear evidence that both are chiral but that **1** racemizes easily, competitive with trapping by cycloaddition with diphenylisobenzofuran. These results seemed to contradict earlier conclusions that 1,2-cyclohexadiene may contain a planar zwitterionic structure such as **3** or **4**.[4-6] Zwitterion **3**, which corresponds to the lowest closed-shell state at this geometry, found support in an INDO study by Dillon and Underwood on C_{2v} planar allene.[6]



1



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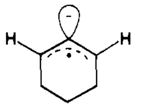

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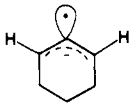

4

We report here results of ab initio MCSCF calculations on 1,2-cyclohexadiene, which support the contention that its equilibrium geometry is strongly bent and chiral (C_2 symmetry) but can easily racemize through a species best described as diradical **2**. Zwitterions **3** and **4** are *electronically excited states* of **2**.[7,8]

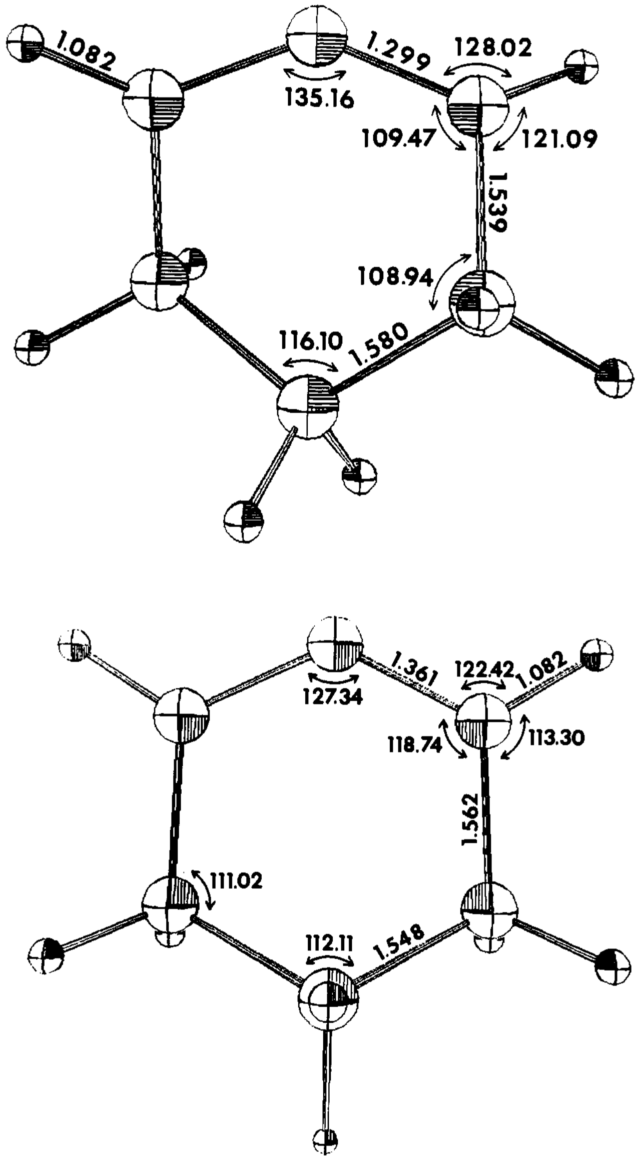

Figure 1. STO-3G geometries for **1** (C_2, top) and **2** (C_s, bottom).

Table I. Computational Results for C_2 and C_s **1**,2-Cyclohexadiene[a]

species	state	basis	type	energy	rel energy[b]
1 (C_2)	1^1A	STO-3G	RHF	−228.95597	0.0
		3-21G	RHF	−230.46297	0.0
		3-21G and STO-3G[e]	RHF	−229.74932	0.0
		3-21G and STO-3G[e]	FORS[c]	−229.81769	0.0
2 (C_s)	1^1A″	STO-3G	ROHF	−228.96296	−4.4
		3-21G	ROHF	−230.45734	3.5
		3-21G and STO-3G[e]	ROHF	−229.74613	2.0
		3-21G and STO-3G[e]	FORS[d]	−229.79679	13.1
2 (C_s)	1^3A″	3-21G and STO-3G[e]	ROHF	−229.74941	
3 (C_s)	1^1A′	STO-3G	RHF	−228.79919	

[a] All calculations performed at the STO-3G optimized geometry for the 1^1A or 1^1A″ states. [b] E(molecule) − E(1) by using comparable basis and level of theory (in kcal/mol). [c] Twelve configuration MCSCF. [d] Eight configuration MCSCF. [e] See footnote 14.

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[1] (a) Iowa State University and Ames Laboratory; (b) Iowa State University.

[2] Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978.

[3] Balci, M.; Jones, W. M. *J. Am. Chem. Soc.* **1980**, *102*, 7607.

[4] Moore, W. R.; Moser, W. R. *J. Am. Chem. Soc.* **1970**, *92*, 5469. For recent investigations, see ref 5.

[5] (a) Bottini, A. T.; Hilton, L. L.; Plott, J. *Tetrahedron* **1975**, *31*, 1997. (b) Bottini, A. T.; Corson, F. P.; Fitzgerald, R.; Frost, K. A., II *Ibid.* **1972**, *28*, 4883.

[6] Dillon, P. W.; Underwood, G. R. *J. Am. Chem. Soc.* **1974**, *96*, 779.

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Limiting structures for 1,2-cyclohexadiene (**1** and **2**) contain twisted or planar bent allene moieties with overall C_2 or C_s molecular symmetry. Initial MNDO calculations[9] predicted **1** to be 1.5 kcal/mol lower than **2**. Calculations at various levels of ab initio theory were then performed. Geometries were optimized at the SCF level within appropriate (C_2 or C_s) symmetry contraints for the 1^1A state of **1** and the $1^1A''$ state of **2**, by using an analytical gradient procedure and an STO-3G basis set;[10] results are shown in Figure 1. The allenic hydrogens are bent in opposite directions 30° out of the plane defined by the allenic carbons, with significant rehybridization at C_1 and C_3. Energies and resulting energy differences are given in Table I. At the STO-3G level, **2** is predicted to be 4.4 kcal/mol below **1**. This basis set has some well-known deficiencies with respect to π bonding,[11] and although we expect geometries to be reliable, absolute energies are suspect. Calculations with the more flexible 3-21G basis set[12] reversed this ordering, predicting **2** to be 3.5 kcal/mol above **1**. Although this qualitatively agrees with experiment, it seemed unlikely that single-determinant SCF calculations could accurately predict the energy difference between the closed shell **1** and open shell species **2**, the latter having one less electron pair. To assess this difference, we applied the full optimized reaction space (FORS) approach of Ruedenberg and co-workers.[13] These MCSCF calculations include configurations generated by distributing the four electrons intimately involved in the inversion, within the π MO's and the in-plane hybrid at C_2.[14] As expected, the FORS-MCSCF calculations recovered more correlation energy for **1** (1.86 eV) than for **2** (1.38 eV), increasing their difference to 13.1 kcal/mol. We thus conclude that 1,2-cyclohexadiene should have a chiral equilibrium geometry.

The origins of the energy difference between **1** and **2** are of some interest. The C_1–C_2 length in **1** is significantly shorter than that in **2**, which suggests some recovery of π bonding in **1**. Increased π bonding in **1**, relative to **2**, is due to interaction of the nonbonding allyl-like MO of **2** with the σ sp^2 hybrid on C_2, as C_1 and C_3 are rehybridized. However, this rehybridization also results in a loss of π bonding in the lowest lying allyl-like MO, due to nonplanarity. The net energy gain in **1** over **2** at the SCF level is thus rather minimal, and the ultimate barrier is due primarily to correlation energy differences, as shown through MCSCF calculation.

Calculations also were performed for the lowest C_s closed shell state ($1^1A'$, corresponding to **3**) and the C_s triplet ($1^3A''$). With an STO-3G basis, the zwitterion **3** ($1^1A'$) is predicted to be 4.46 eV higher in energy than **1** ($1^1A''$). The triplet diradical proved only slightly lower (2.06 kcal/mol) than the singlet, which implies that the triplet lies ca. 11 kcal/mol above closed-shell **1**, if electron correlation were included.

In conclusion, these calculations should resolve some important theoretical questions concerning the structure of 1,2-cyclohexadiene, including its experimentally demonstrated chirality.[3] The ground-state potential surface has a well-defined minimum corresponding to **1**, closely connected to diradical **2**, while zwitterions **3** and **4** are excited states. We speculate that **1** might be trapped and observed under matrix isolation conditions.[15]

Acknowledgment. The present work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by Ames Laboratory, U.S. Department of Energy, operated by Iowa State University under Contract W-7405-Eng-82, with the research support of the Director of Energy Research, Office of Basic Energy Science, WPAS-KD-01-03-01-2.

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[7] R. P. Johnson and B. Lam, to be submitted for publication. MCSCF calculations on C_{2v} planar allene show an open-shell diradical corresponding to **2** to be the singlet ground state, with zwitterions such as **3** and **4** much higher in energy; cf. ref 8.

[8] A C_{2v} bent diradical has been predicted to correspond to the barrier to rotation in allene: Seeger, R.; Krishnan, R.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1977**, *99*, 7103.

[9] Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1976**, *99*, 4907.

[10] Dupuis, M.; Spangler, D.; Wendoloski, J. J. NRCC Software Catalog, 1 Prog. No. QG01, GAMESS, 1980; Vol. 1.

[11] (a) Newton, M. D. In "Applications of Electronic Structure Theory"; Schaefer, H. F., III, Ed., Plenum Press: New York, 1977; Chapter 6, p 223. (b) As pointed out to us by Professor Joel Liebman, greater stabilization (45–50 kcal/mol) accrues on introduction of the extended basis set on carbons 1–3 than on carbons 4–6. This is due to the fact that the STO-3G basis underestimates the stability of π bonds more than that of σ bonds. Similar trends are observed in comparison of literature values for ethane vs. ethylene. Optimization with an extended basis set undoubtedly would improve our geometry somewhat, but we doubt that changes in total energy would be significant.

[12] Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

[13] Feller, D. F.; Schmidt, M. W.; Ruedenberg, K. *J. Am. Chem. Soc.* **1982**, *104*, 960 and references therein.

[14] The full 3-21G basis proved too large for the MCSCF calculations, thus for these calculations, the split valence 3-21G basis was used only on the three carbons and two hydrogens of the allene moiety, while the minimal STO-3G basis was applied for the C_3H_6 skeleton. This combined basis is denoted 3-21G and STO-3G.

[15] See, for example: West, P. R.; Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1982**, *104*, 1779.

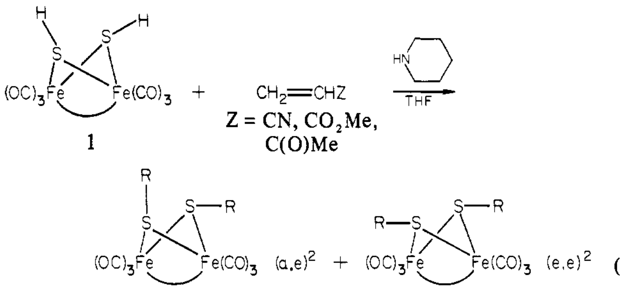
Construction of Bridging Organosulfur Ligands in Hexacarbonyldiiron Complexes via Proximity-Induced Reactions of Bis(μ-mercapto)bis(tricarbonyliron) with α,β-Unsaturated Substrates

Dietmar Seyferth* and Gary B. Womack

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received August 19, 1982

We have reported that bis(μ-mercapto)bis(tricarbonyliron), **1**, undergoes base-induced addition to terminally unsubstituted α,β-unsaturated substances such as acrylonitrile, methyl acrylate, and methyl vinyl ketone (eq 1).[1] Since this apparently general reaction has the potential of being a useful synthetic route in organosulfur chemistry,[3] we have examined base-induced reactions of **1** with other olefinic and with acetylenic α,β-unsaturated systems. We report our preliminary findings at this time since some novel and potentially useful reactions have been discovered in which cyclic bridging organosulfur ligands have been formed as a result of the proximity of the two μ-HS functions in the molecule.[4]



1

Z = CN, CO_2Me, C(O)Me

(1)

R = CH_2CH_2Z

Like the terminally unsubstituted α,β-unsaturated systems, those with only one substituent (e.g., *trans*-3-penten-2-one, 2-cyclo-

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[1] Seyferth, D.; Henderson, R. S. *J. Organomet. Chem.* **1981**, *218* C34.

[2] Shaver, A.; Fitzpatrick, P. J.; Steliou, K.; Butler, I. S. *J. Am. Chem. Soc.* **1979**, *101*, 1313.

[3] Note the useful sulfur ligand release reactions (to give disulfides, sulfides and mercaptans) reported by Russian workers: Nametkin, N. S.; Tyurin, V. D.; Kukina, M. A. *J. Organomet. Chem.* **1978**, *149*, 355.

[4] In (μ-EtS)$_2$Fe$_2$(CO)$_6$ (a,e isomer) the S···S distance is 2.93 Å: Dahl, L. F.; Wei, C. H. *Inorg. Chem.* **1963**, *2*, 328.

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