A Theoretical Study of the Thermal Degenerate Rearrangement in Methylenecyclobutane

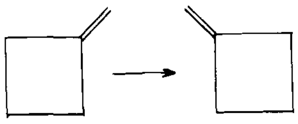
P. N. Skancke,*,† N. Koga, and K. Morokuma*

Contribution from the Institute for Molecular Science, Myodaiji, Okazaki 444, Japan.

Received June 6, 1988

Abstract: Ab initio molecular orbital calculations, using 3-21G through 6-31G* basis sets and including electron correlation through CASSCF and MP4, have been applied in a study of the thermal degenerate rearrangement of methylenecyclobutane (**1**). Our calculations indicate that the process goes through an intermediate stabilized by π-electron delocalization in the allylic moiety. The intermediate nearly has C_s symmetry, with very low barrier to rotation of the migrating CH_2 group. The transition state between **1** and the intermediate is found to have a CCCC dihedral angle of 67° and one CH_2 group perpendicular to the CCH_2 group within the allylic moiety. The CASSCF calculations with the UHF-based zero point energy correction give a barrier height of 49 kcal/mol. Exploratory calculations on the conversion of spiropentane to methylenecyclobutane suggest that the process is initiated by a peripheral bond fission in spiropentane.

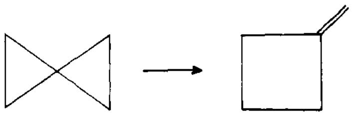
The occurrence of a thermally induced degenerate rearrangement of methylenecyclobutane (**1**) was demonstrated by Doering and Gilbert[1] after having been previously alluded to by Chesick.[2] They uncovered an intramolecular isomerization by observing changes in IR and NMR spectra and by confirming an unaltered mass spectrum of dideuteriomethylenecyclobutane upon heating at 342 °C for 47 h.[1] The conversion was determined to be a reversible first-order reaction having an activation energy of 49.5 ± 1.0 kcal/mol. This value being larger than the binding energy for the C(2)–C(3) bond in the ring (~42 kcal/mol)[3] indicates that biradicals may be present in the isomerization process, suggesting that the autoisomerization **1** → **1′** is a two-step process with a biradical intermediate.



1 **1′**

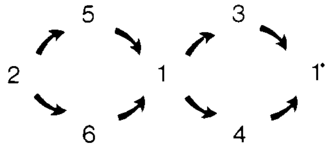
In an impressive series of papers Baldwin and Fleming[4] studied deuterium scrambling and racemization in the optically active α-*d*-1-ethylidene-2-methylcyclobutane. They found the rate constant for scrambling to be substantially higher than for racemization (~8 × 10^{-5} s^{-1} versus ~5 × 10^{-5} s^{-1}) and they interpreted this difference in terms of a substantial amount of antarafacial allylic participation in the 1,3-sigmatropic rearrangement. A re-evaluation of the rate constants by Gajewski[5] for racemization and deuterium scrambling in α-*d*-1-ethylidene-2-methyl-*trans*-3,4,4-trideuteriocyclobutane led to a reassessment of the mechanisms for the reactions involved. It was concluded that the adjusted rate constants could be accounted for by complete suprafacial allylic participation in the transient biradical and that about one-third of the ring closures implied inversion of the migrating center. The major part of the products was formed through a ring closure with random orientation of the migrating group. The structure and the nature (TS or intermediate) of the biradical involved in the automerization have not been described previously.

A degenerate thermal rearrangement does not take place in spiropentane (**2**). The main product by pyrolysis of **2** is **1**, with allene and ethylene as minor products.[6] For the activation energy of the first-order process **2** → **1** there are two experimental values, viz. 57.6[6] and 55.5 kcal/mol. These values are about 10 kcal/mol higher than the bond dissociation energy of the peripheral carbon–carbon bond in **2**,[3] thus indicating the presence of a biradical also in the process **2** → **1**.



2 **1**

Scheme I



The relative thermodynamic stabilities of **1** and **2** can be deduced from experimental data on heats of formation. From a recent compilation[7] of such data we find $\Delta H_f(\mathbf{1})$ = 29.1 kcal/mol and $\Delta H_f(\mathbf{2})$ = 44.3 kcal/mol, both values referring to the vapor phase.

Several experimental studies of the thermal reactions of **2** and of derivatives of **2** have been made.[1,6,8-12] But the detailed pathway for the structural isomerization to **1** is not known. However it has been shown that by attaching an isopropenyl group to **2** the rearrangement occurs with peripheral bond cleavage.[11] Preference of initial peripheral bond rupture may be rationalized in terms of a free rotation of the methylene groups leading to an (E,E) orientation that would make the central carbon able to direct engagement in allylic stabilization by subsequent cleavage of the radial bond. This sequence of bond fissions would thus lead to the transient species **3** or **4** (vide infra).

The systems **1** and **2** represent local minima on the potential surface for C_5H_8. The interconversions mentioned above may go through metastable intermediates or go as one-step processes through a single transition state. To our knowledge these reactions have not been previously studied by ab initio methods.

Recently we have carried through a theoretical study of thermal rearrangements in bicyclo[2.1.0]pent-2-ene,[13] and we consider the

---

[†] Permanent address: Department of Chemistry, The University of Tromsö, P.O. Box 953, N-9001 Tromsö, Norway.

(1) Doering, W. von E.; Gilbert, J. C. *Tetrahedron, Suppl.* **1966**, *7*, 397.
(2) Chesick, J. P. *J. Phys. Chem.* **1961**, *65*, 2170.
(3) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981.
(4) Baldwin, J. E.; Fleming R. H. *J. Am. Chem. Soc.* **1972**, *94*, 2140; **1973**, *95*, 5249, 5256, 5261.
(5) Gajewski, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 5254.
(6) Flowers, M. C.; Frey, H. M. *J. Chem. Soc.* **1961**, 5550.
(7) Pedley, J. B.; Rylance, J. *Sussex-N.P.L. Computer Anal. Thermochem. Data*; University of Sussex, 1977.
(8) Burkhardt, P. J. *Diss. Abstr.* **1962**, *23*, 1524.
(9) Gilbert, J. C. *Tetrahedron* **1969**, *25*, 1459.
(10) Flowers, M. C.; Gibbons, A. R. *J. Chem. Soc., Perkin Trans. II* **1972**, 548, 555.
(11) Gajewski, J. J. *J. Chem. Soc., Chem. Commun.* **1967**, 920.
(12) Gajewski, J. J. *J. Am. Chem. Soc.* **1970**, *92*, 3688.

0002-7863/89/1511-1559$01.50/0

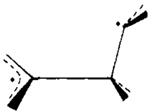
present study to be a continuation of our efforts to elucidate mechanisms in thermal reactions of hydrocarbons.

The purpose of the present work is to scrutinize the parts of the potential surface for C_5H_8 that link the systems referred to above. The stable species of interest in these processes are connected in Scheme I.

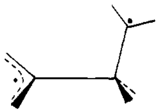
In the degenerate process **1** → **1′** we label as **3** the transient species that occurs if the reaction proceeds with retention at the migrating center and as **4** the corresponding one with inversion at this center. For symmetry reasons **3** and **4**, both having C_s symmetry, are stationary points on the potential surface, being transition states (TS) in one-step processes or intermediates in case of two-step reactions. In the latter case there should be TS's of C_1 symmetry between **1** and **3**, **1** and **4**, and **3** and **4**, respectively.

In the reaction **2** → **1** we label as **5** the transient species encountered if the process is initiated by a peripheral ring opening of **2** and as **6** the corresponding one if it starts by a radial bond cleavage. In the process **2** → **1** we may anticipate either C_{2v} or C_s symmetry for **5** depending on the mutual orientation of the terminal CH_2 groups (EE, EF, or FF form). For **6** it is assumed that C_s symmetry is preferred. If the reactions via **5** and **6** are two-step processes, we also have four inequivalent TS's for the path **2** → **1**.

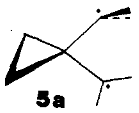
Referring to the symmetry assumptions presented above, we studied initially the following transient species in addition to the parent compounds, with the assumed symmetry as indicated.



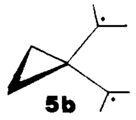
3



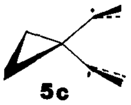
4



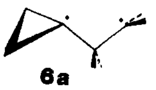
5a



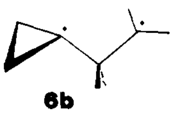
5b



5c



6a



6b

Hartree–Fock Calculations

Preliminary Hartree–Fock calculations on the lowest singlet states of **1**–**6** were performed with the 3-21G basis set using the program GAUSSIAN82.[14] The structures were completely optimized with analytical first and second derivatives. In order to treat the species with closed and open shell structures in a consistent way, we have used the unrestricted Hartree–Fock (UHF) method. Geometrical structures in which odd electrons are localized somewhat far away from each other are often reasonably well predicted by the singlet UHF method.[15] In subsequent sections of the presentation we will discuss the energetics and wave functions of the systems as obtained by Complete-Active-Space SCF (CASSCF) and Unrestricted Møller–Plesset (UMP) methods.

A selection of parameters from the completely optimized geometries at this level of calculation are shown in Figure 1. For **1** and **2** UHF calculations gave restricted (R) HF solutions, whereas for **3** and **4** having open-shell states $^1A''$ and $^1A'$ respectively, UHF wave functions were calculated. The Mulliken atomic spin densities obtained for **3** and **4**, and shown in Table I, reveal an extensive spin polarization in these species. This is in accordance with the observation that their $\langle S^2 \rangle$ values increased from about 1.25 to around 1.70 after annihilation of the triplet contamination, indicating a contribution of higher spin states to the UHF wave function. In order to make an estimate of the possible influence of these high-spin contaminations on the equilibrium geometries of **3** and **4**, these species were reoptimized using the RO(open-shell)HF approximation as implemented in GAUSSIAN86,[16] and by applying the same basis set (3-21G). The results of these optimizations, shown in brackets in Figure 1, confirm that the predicted UHF geometries are not significantly influenced by the spin contaminations. The only noticeable difference between the UHF and ROHF optimized structures is

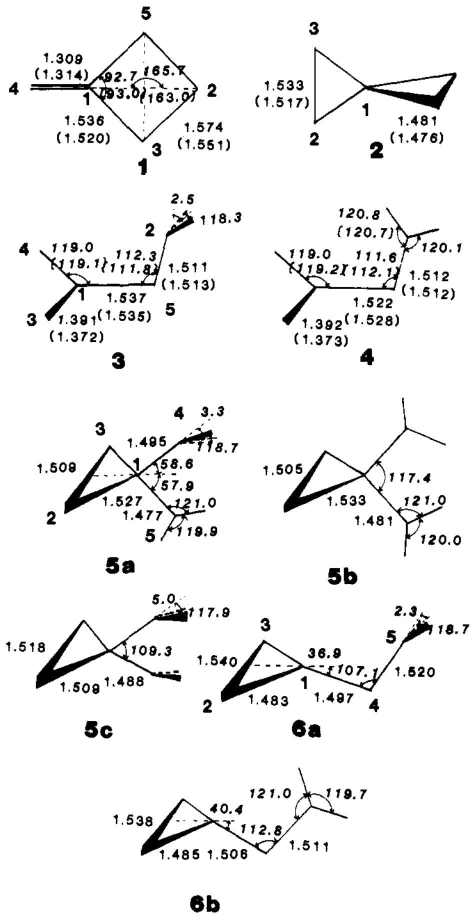


Figure 1. Optimized geometries (in Å and deg) at the UHF/3-21G level. Parameters in parentheses for **1** and **2** are from HF/6-31G* optimization. Parameters in parentheses for **3** and **4** are from ROHF/3-21G optimization.

Table I. Calculated Mulliken Atomic Spin Densities for the Singlet UHF Wave Functions[a]

species	3	4	5a	5b	5c	6a
C_1	1.08	0.96	0.10	0.00	0.00	1.42
C_2	1.50	1.51	−0.14	0.00	0.00	−0.14
C_3	−1.18	−1.18	−0.14	0.00	0.00	−0.14
C_4	−1.18	−1.18	1.47	1.46	1.36	0.05
C_5	−0.28	−0.29	−1.40	−1.46	−1.36	−1.40

[a] At the UHF/3-21G//UHF/3-21G level.

---

(13) Skancke, P. N.; Yamashita, K.; Morokuma, K. *J. Am. Chem. Soc.* **1987**, *109*, 4157.

(14) Binkley, J. A.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Pople, J. A. GAUSSIAN82, Carnegie-Mellon Chemistry Publishing Unit, Pittsburgh, 1984.

(15) For example: Yu, J. G.; Fu, X. Y.; Liu, R. Z.; Yamashita, K.; Koga, N.; Morokuma, K. *Chem. Phys. Lett.* **1986**, *125*, 438.

(16) GAUSSIAN 86; Frisch, M. J., Binkley, J. S., Schlegel, H. B., Raghavachari, K., Melius, C. F., Martin, R. L., Stewart, J. J. P., Bobrowicz, F. W., Rohlfing, C. M., Kahn, L. R., Defrees, D. J., Seeger, R., Whiteside, R. A., Fox, O. J., Fleuder, E. M., Pople, J. A., Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1984.

Table II. Energies (kcal/mol) Relative to the Reactant Methylenecyclobutane (**1**) at Different Levels of Calculation at the HF/3-21G Optimized Geometries

	1	**2**	**3**	**4**	**5a**	**5b**	**5c**	**6a**	**6b**	**7**
HF/3-21G	−192.863 99[a]	26.9	20.7	19.9	49.8	48.5	48.7	60.6	61.3	38.0
HF/6-31G*	−193.941 55	15.3	22.6	21.7	46.0			53.9		
HF/6-31G*//HF/6-31G*[b]	−193.942 67	15.6								
CASSCF/3-21G	−192.929 47		43.7	42.1						55.9
MP2/6-31G*	−194.579 27	9.7	61.0	59.9	69.7			79.3		
MP3/6-31G*	−194.620 98	12.1	55.5	54.4	67.1			75.7		
MP4(SDQ)/6-31G*	−194.630 45	13.9	54.1	53.0	67.4			75.9		

[a] Total energy in hartree. [b] This row only at the HF/6-31G* optimized geometry.

a shortening of the allylic C–C bond by ~0.02 Å in going to the ROHF approximation.

Analytically calculated vibrational frequencies in the UHF approximation using the 3-21G basis at the C_s-constrained optimized geometries gave one imaginary frequency for each of the species, 32i cm^{-1} and 112i cm^{-1} for **3** and **4**, respectively. These frequencies are both associated with a vibrational mode of a″ symmetry. In order to analyze the rather complex associated modes in a consistent way, the equilibrium geometries (of C_s symmetry) were perturbed along the corresponding modes and subsequently used as starting points for geometry optimizations without symmetry restriction. The optimization of **4** revealed a very flat surface around the C_s symmetry and led to a shallow minimum **4a** for a dihedral angle (3–1–5–2) of 77.9° confirming that **4** is not a TS for the ring-closure reaction. The UHF energy for **4a** is less than 0.1 kcal/mol below the energy of **4**, indicating a virtually constant energy in a broad area around the C_s symmetry. The symmetry-breaking optimization of **3** also led to **4a** which implies that the retention species is a transition state for the conversion of **4a** into its enantiomer. The energy difference between **3** and **4a** is predicted to be 0.8 kcal/mol at this level of calculation. This indicates that the migrating CH_2 group has virtually free rotation around C_5–C_2. One should note that the UHF and UMP energies of **3**, **4**, and **4a** relative to **1** are overestimated due to spin contamination (vide infra).

The search for the TS for the ring-opening reaction in the [1,3]-sigmatropic rearrangement of **1** gave the fully optimized structure **7** given in Figure 2. The fact that this is a transition state has been established by one imaginary vibrational frequency of 387i cm^{-1} in the normal coordinate analysis based on the analytical second derivatives. The major contribution to the normal mode associated with this frequency comes from a rotation of the terminal allylic CH_2 group around the C(1)–C(3) bond as shown in Figure 2. In this rotation the H atom that is on the same side of the allylic moiety as the migrating CH_2 group has an outward motion. The reaction from **1** to the intermediate **4a** is very asynchronous and takes place in three stages. At the beginning the reaction coordinate is mainly the C–C bond stretching to break the bond. Then the rotation around the C(1)–C(5) bond occurs to separate odd electrons. And finally the allylic CH_2 group begins to move into planarity with the remaining part of the allylic moiety at the transition state. After the TS, the energy of the system drops sharply due to delocalization of the π-electrons and we end up with the local minimum of C_1 symmetry described above.

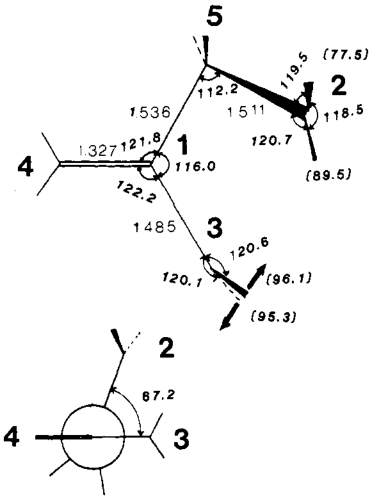
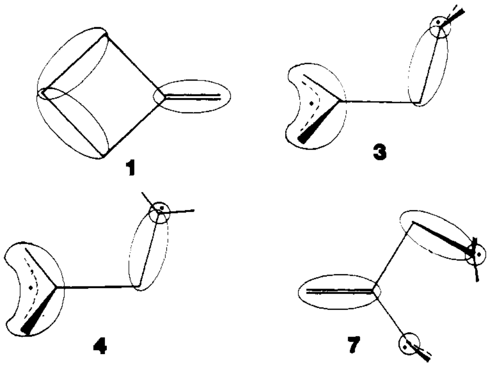


Figure 2. Optimized geometry (in Å and deg) of the transition state **7** at the UHF/3-21G level. Values in parentheses are dihedral angles H–C(2)–C(5)–C(1) and H–C(3)–C(1)–C(4). Arrows are the reaction coordinate vector at the transition state.

CASSCF Calculations

As referred to above the UHF approximation is reasonably accurate for prediction of geometries even if spin contamination of the singlet function is large. However, for an estimate of the energetics of the transient species, correlation energy has to be invoked. In these calculations beyond the UHF level we have assumed HF/3-21G optimized geometries.

In the CASSCF calculations, carried through with the program GAMESS,[17] the active space was limited to six electrons and six orbitals. The choice of orbitals for the degenerate rearrangement is the following: in **1** the two exo π orbitals, the two σ orbitals (σ and σ*) associated with the ring bond to be broken, and their counterparts generated under C_s symmetry; in **3** and **4** also having C_s symmetry the three π orbitals of the allylic moiety, the orbital accommodating the lone electron on the migrating group, and the two σ orbitals (σ and σ*) for the C–C bond between the migrating carbon and its neighbor; and in the TS **7** the two π orbitals in the double bond, the two terminal orbitals holding each one electron, and the σ orbitals related to the same C–C bond as in **3** and **4**. The local minimum having C_1 symmetry was found to be so close to **4** both in geometry and energy at the UHF level that calculations beyond this level were made only on **4**.



For **1** the CASSCF calculations confirmed the closed shell ground state, the configuration |...$(13a')^2(6a'')^2$| having the coefficient 0.98. The energy lowering relative to the HF calculation is given in Table II.

The open-shell nature of the species **3**, **4**, and **7** is confirmed by these CASSCF calculations. In the case of **3** two natural orbitals[18] (NO's), 7a″ and 13a′, are found to have unpaired electrons, with the occupation number of 1.000 each. Here 7a″ is the nonbonding π orbital of the allylic unit and 13a′ is exclusively

---

(17) Dupuis, M.; Spangler, D.; Wendoloski, J. J. *NRCC Software Catalog*, Vol. 1, Program GG01 (GAMESS), 1980.

(18) Löwdin, P.-O. *Phys. Rev.* **1955**, *97*, 1474.

Table III. Effect of Basis Set, Electron Correlation, and Spin Projection on the Energy of Transition State **7** Relative to **1** (kcal/mol) at the UHF/3-21G Optimized Geometries

	3-21G		6-31G			
	UHF	UMP2	UHF	UMP2	UMP3	UMP4
unprojected	38.0	65.7	34.9	63.4	60.6	59.7
projected	23.1	46.9	19.3	43.5	41.2	40.1

located on the migrating carbon. For **4** two NO's, 6a″ and 7a″, have the occupation number of 1.153 and 0.847, respectively, where 6a″ and 7a″ are in-phase and out-of-phase combinations of the nonbonding allylic π and the pure p function on the migrating carbon, respectively. One notices that the NO's of the CASSCF wave functions for **3** and **4** led to a localized description of the former and a delocalized description of the latter, which implies that there is an interaction between the allylic moiety and the migrating center in **4**. Such an interaction between the two singly occupied orbitals is prevented by symmetry in **3**. The transition state **7** having C_1 symmetry has the occupation number 1.064 and 0.937 for NO's 19 and 20, respectively, where 19 and 20 are the bonding and antibonding combinations of atomic orbitals located at the two radical centers.

The energy profile for the automerization obtained by the CASSCF calculations may be found in Table II. The predicted barrier height is 55.9 kcal/mol. Zero-point vibrational energies (ZPE) obtained from HF/3-21G//HF/3-21G calculations, 77.3 and 70.6 kcal/mol for **1** and **7**, respectively, give a ZPE corrected barrier height of 49.2 kcal/mol. This may be compared with the experimental activation energy of 49.5 ± 1.0 kcal/mol, where the agreement with the calculation may be fortuitous.

Møller–Plesset Calculations and Spin Projection

Although geometries predicted by the UHF approximation usually are rather accurate, it has been shown to be crucial to remove spin contaminations from the UMPn wave functions in order to obtain reliable estimates of energies for species having one or more broken bonds, and different schemes for projecting out spin contaminations have been published.[19-23] One should be careful in eliminating not only the states giving the major contamination but also a high-spin state which may lead to appreciable energy corrections even if its weight is small.

In our case the ^{1}UHF function of **7** has an $\langle S^2 \rangle$ value of 1.1181 at the UHF/3-21G level. After projection of the triplet contribution to the wave functions the $\langle S^2 \rangle$ values are 0.9231. In **7** there are three electrons from the allylic unit and one on the migrating center that are primarily involved in the reaction, and the high $\langle S^2 \rangle$ values after triplet projections show the presence of a significant quintet coupling of these electrons. The energy change due to this contamination may be estimated by a small extension of the approximate scheme developed by Yamaguchi et al.[23] shown in Appendix.

The energy values thus calculated are given in Table III. Conclusions drawn from these calculations are as follows. (1) The effect of basis set (3-21G vs 6-31G) is small (<3 kcal/mol) for **7**, as was the case for **3** and **4** (3-21G vs 6-31G*) in Table II. (2) The effect of order *n* of perturbation in MP*n* calculation is small (<4 kcal/mol). (3) The spin projection changes the relative energy of **7** as much as 15 (UHF) to 20 (UMP2) kcal/mol. (4) The highest level of the MP calculation, EYUMP4, seems to underestimate the barrier, compared with experiment and CASSCF result, by 10–15 kcal/mol.

Exploratory Calculations on Spiropentane Conversion

UHF calculations on **5** and **6** revealed their biradical characters as shown by the atomic spin densities given in Table I. The HF solutions for these species were mainly contaminated by triplets, as demonstrated by the $\langle S^2 \rangle$ values before and after annihilation. Typical values were 1.00 and 0.15, respectively. One notes that the molecular orbitals obtained for the singlet biradicals, **5b** and **5c**, at this level of calculation have only C_s symmetry despite their C_{2v} structural symmetry. The energy data displayed in Table II show that the biradicals generated by radial bond cleavage, **6**, have a substantially higher energy than those resulting from peripheral bond fission, **5**. The limited data obtained at higher levels of calculation, also presented in Table II, support this observation. Thus we may conclude that the conversion **2** → **1** most likely is initiated by a peripheral bond rupture in accordance with experimental information on the isopropenyl derivative of **2**.[11] Accordingly we did not pursue further studies of **6a** and **6b**. One should note the energies of **5** and **6** are underestimated due to contamination by the lower-energy triplet. Some of the parameters obtained by the complete geometry optimization of these species are, however, included in Figure 1.

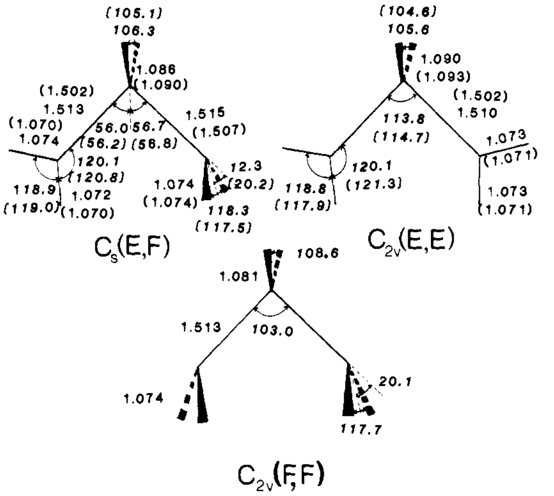


Figure 3. Optimized geometries (in Å and deg) of three different forms of trimethylene at the UHF/3-21G level. Parenthesized parameters for the (E,F) and (E,E) forms are MCSCF values from ref 28.

The biradicals **5a**–**5c** are expected to have some features similar to the trimethylene biradicals. The latter ones have been studied theoretically at many different levels and for different purposes.[24-29] However, for the sake of comparison with **5a**–**5c** we have optimized the three different forms of trimethylene by UHF/3-21G calculations, adopting C_s symmetry of the wave functions of the E,E and F,F forms. The optimized geometries are shown in Figure 3. The values obtained may be compared with values determined by a 5-configuration MCSCF calculation using a 4-31G basis for the (E,E) and (E,F) forms.[28]

This comparison shows that geometries may be predicted with rather high confidence in the UHF approximation. These geometries may accordingly serve as a reliable reference in the more important comparison between **5a**–**5c** and their trimethylene counterparts. The most significant difference between the two sets of geometries is the enlarged angle C(4)–C(1)–C(5) in the spiro compounds. This angle opening may be interpreted in terms of change in hybridization at the central carbon atom when going from trimethylene.[30] In order to increase overlap in the ring

---

(19) Gill, P. M. W.; Radom, L. *Chem. Phys. Lett.* **1986**, *132*, 16.

(20) Sosa, C.; Schlegel, H. B. *Int. J. Quant. Chem.* **1986**, *29*, 1001.

(21) Schlegel, H. B. *J. Chem. Phys.* **1986**, *84*, 4530.

(22) Knowles, P. J.; Handy, N. C. *J. Chem. Phys.* **1988**, *88*, 6991.

(23) Yamaguchi, K.; Takahara, Y.; Fueno, T.; Houk, K. N. *Theor. Chim. Acta* **1988**, *73*, 337.

(24) Sin, A. K. Q.; St. John, W. M., 3rd.; Hayes, E. F. *J. Am. Chem. Soc.* **1970**, *92*, 7249.

(25) Horsley, J. A.; Jean, Y.; Moser, C.; Salem, L.; Stevens, R. M.; Wright, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 279.

(26) Hay, P. J; Hunt, W. J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1972**, *94*, 634.

(27) Yamaguchi, K.; Nishio, A.; Yabushita, S.; Fueno, T. *Chem. Phys. Lett.* **1978**, *53*, 109.

(28) Yamaguchi, K.; Takahara, Y.; Fueno, T.; Houk, K. N. *Theor. Chim. Acta* **1988**, *73*, 337.

(29) Schoeller, W. W. *Z. Naturforsch.* **1979**, *34A*, 858.

(30) Eckert-Maksic, M.; Maksic, Z. B.; Skancke, A.; Skancke, P. N. *J. Phys. Chem.* **1987**, *91*, 2786.

bonding in **5a**–**5c** atom C(1) uses hybrids with a large p-content in these functions, and concomitantly orbitals with more s-character in the bonding to the terminal carbons. This may also explain the shorter bond distances between the central carbon and the radical terminals in **5a**–**5c** as compared to trimethylene.

Conclusions

On the basis of the results obtained by our calculations we arrive at the following conclusions:

(1) The thermal degenerate rearrangement in methylenecyclobutane is a two-step process going through a diradical intermediate of nearly C_s symmetry. The intermediate is stabilized by π-electron delocalization in the allylic moiety.

(2) The TS from methylenecyclobutane to the intermediate has C_1 symmetry with one of the two CH_2 groups in the allylic unit forming a π bond with the central carbon atom and the other being orthogonal to this CH_2–C plane. Its energy is found to be around 14 kcal/mol above the intermediate in the CASSCF calculation. This destabilization is mainly due to the breaking of the π-electron delocalization in the allylic unit.

(3) The singlet UHF wave functions for the intermediate and the TS were found to have extensive contaminations of the quintet state arising from coupling of the quartet component of the allylic fragment electrons with the lone electron on the migrating group.

(4) Exploratory UHF calculations on the conversion of spiropentane to methylenecyclobutane indicate that the reaction starts with a peripheral bond cleavage.

Acknowledgment. One of us (P.N.S.) thanks the Institute for Molecular Science for facilities placed at his disposal and for hospitality enjoyed during the period this work was carried out. He would also like to thank the Scandinavia-Japan Sasakawa Foundation for a generous grant that made it possible to carry through this project. We would like to thank Professor Yamaguchi for enlightening discussions on approximate spin projections. The numerical calculations were carried out at the Computer Center of IMS.

Appendix

In the extended Yamaguchi scheme the ^{1}UHF wave function is approximated by

$$^1\mathrm{UHF} = a\,^1\mathrm{PUHF} + b\,^3\mathrm{PUHF} + c\,^5\mathrm{UHF}$$

where a, b, and c are coefficients. Similarly the ^{3}UHF wave function is expressed as

$$^3\mathrm{UHF} = d\,^3\mathrm{PUHF} + e\,^5\mathrm{UHF}$$

where d and e are coefficients. By using the conditions for the expectation values of the $\mathbf{S}^2$ operator

$$\langle \mathbf{S}^2(^1\mathrm{UHF})\rangle = 2b^2 + 6c^2$$

$$\langle \mathbf{S}^2(^1\mathrm{UHF},\ \text{triplet projection})\rangle = 6c^2/(a^2 + c^2)$$

$$\langle \mathbf{S}^2(^3\mathrm{UHF})\rangle = 2d^2 + 6e^2$$

and the normalization conditions of ^{1}UHF and ^{3}UHF, one can calculate the absolute values of the coefficients. Then, the energy of the approximately projected singlet is given by

$$E(^1\mathrm{PUHF}) = \frac{1}{a^2}[E(^1\mathrm{UHF}) - b^2E(^3\mathrm{PUHF}) - c^2E(^5\mathrm{UHF})]$$

By this procedure we obtained for **7** the spin-state weights (a^2, b^2, c^2) of (0.693, 0.181, 0.126) and (0.714, 0.148, 0.138) and a lowering of the ^{1}UHF energy amounting to 14.9 and 15.6 kcal/mol for the 3-21G and 6-31G basis sets, respectively.

The coefficients a–e are not very sensitive to the correlation correction. Therefore, the UHF values for the coefficients are used at UMP levels as well.

Registry No. 1, 1120-56-5; **2**, 157-40-4.

Linear Semibridging Carbonyls. 2. Heterobimetallic Complexes Containing a Coordinatively Unsaturated Late Transition Metal Center

Andrew L. Sargent and Michael B. Hall*

Contribution from the Department of Chemistry, Texas A&M University,
College Station, Texas 77843. Received June 20, 1988

Abstract: The electronic structure and bonding of four heterobimetallic carbonyl complexes, (tmed)CuCo(CO)$_4$, $(PPh_3)_2CuMo(CO)_3(\eta^5\text{-}C_5H_5)$, $(PPh_3)_2MoRh(CO)_3(\eta^5\text{-}C_5H_5)$, and $(tmed)CuMo(CO)_3(\eta^5\text{-}C_5H_5)$, are analyzed by the parameter-free Fenske–Hall molecular orbital method. The distinguishing characteristics of these four complexes are that one of the metal centers is a coordinatively unsaturated late transition metal center and that one or more carbonyls linearly semibridge the metal–metal bond. Coordinatively unsaturated late transition metal centers have been thought to accept electron density from semibridging carbonyl ligands to satisfy the 18-electron rule. Our results, however, suggest that these centers *donate* electron density from a high energy occupied metal dπ orbital to the unoccupied π^* orbitals of the linear semibridging carbonyl ligands.

Two basic types of bonding representations for unsymmetrically bridging homobimetallic carbonyl complexes have appeared in the literature and only recently does there seem to be some agreement on which representation is more accurate. The heart of the discrepancy concerns the direction of electron density flow between the metals and the bridging ligand, i.e., whether the bridging carbonyl donates electron density to or accepts electron density from the secondary metal center.

The first representation described the asymmetrically bridging carbonyl ligand in $Mn_2(CO)_5(dpm)_2$ (dpm = (diphenylphosphino)methane) as a four-electron donor, with two electrons donated from a CO σ orbital to one Mn atom and two electrons donated from a CO π orbital to the other Mn atom.[1] The donation of electrons from the CO π orbital was thought to be similar to metal–olefin bonding in complexes such as Zeise's salt and was necessary to achieve an 18-electron count around each metal atom.

The next representation to appear in the literature described the role of the unsymmetrically bridging carbonyl ligands as electron acceptors rather than electron donors.[2] The bonding

---

(1) Colton, R.; Commons, C. J. *Aust. J. Chem.* **1975**, *28*, 1673. Commons, C. J.; Hoskins, B. F. *Aust. J. Chem.* **1975**, *28*, 1663. Colton, R.; Commons, C. J.; Hoskins, B. F. *J. Chem. Soc., Chem. Commun.* **1975**, 363.

0002-7863/89/1511-1563$01.50/0