Inorg. Chem. **1991**, *30*, 3547-3551

Contribution from the Department of Chemistry,
The University of Texas at Arlington, Arlington, Texas 76019-0065

A Computational Model for the Chair-to-Chair Rearrangement in Bis(cyclopentadienyl)pentasulfidotitanium(IV)

Michael S. Lawless and Dennis S. Marynick*

Received January 8, 1991

The potential energy surface for the chair-to-chair rearrangement of the six-membered TiS$_5$ ring in bis(cyclopentadienyl)pentasulfidotitanium(IV) has been calculated using the method of partial retention of diatomic differential overlap (PRDDO). The energetics were recalculated at the ab initio Hartree–Fock level by using a large basis set including d polarization functions on sulfur. The PRDDO and ab initio energies agree very well, although both overestimate the barrier by ~5.9 kcal/mol. The potential energy surface consists of a double well potential in which a twist boat and skew boat are local minima separated by a boat-shaped transition state. The energies relative to the chair structure are 11.7, 21.6, and 10.2 kcal/mol for the twist boat, boat, and skew boat, respectively. The activation barrier for the rearrangement is shown to be dominated by the large amount of strain energy associated with the sulfur angles in the ring of each transition-state structure.

Introduction

The conformation of six-membered rings is a subject which is dealt with in second year chemistry,[1] when the structure of cyclohexane is discussed. For C_6H_{12}, the most stable conformation is the chair structure. Ring inversion occurs with a rate constant of 10^4–10^5 s^{-1} at 300 K.[2] The process involves transforming the chair structure into a twist structure and then back to the chair conformer. This conversion requires an activation energy of ~11 kcal/mol and involves a half-twist transition state. It is not necessary to proceed through a boat structure, which is ~1–2 kcal/mol higher in energy than the twist conformation.

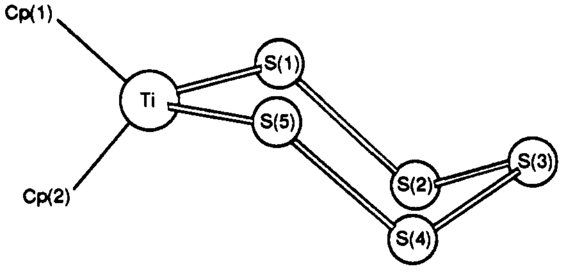
Replacement of carbon atoms with sulfur atoms in cyclohexane increases the ring inversion barrier.[3] Incorporation of transition-metal atoms into polysulfide rings has resulted in a wealth of cyclic compounds.[4] A number of inversion barriers in these systems have been measured. For example, $Cp^*_2S_3Ti$ (Cp^* = pentamethylcyclopentadienyl) has an activation barrier of 9.6 kcal/mol for the inversion of the four-membered TiS$_3$ ring.[5] Variable-temperature NMR studies indicate that the barrier to ring inversion in Cp_2S_5M (M = Ti, Zr, Hf) increases in the order Zr < Hf < Ti.[6] In 1978, Abel et al. reported that the barrier for the chair-to-chair rearrangement in Cp_2S_5Ti occurs with an activation energy of 16.5 kcal/mol.[7]

A number of theoretical studies on sulfur compounds have appeared over the last decade. Several molecular mechanics calculations on cyclic sulfur systems have been performed.[8] In 1990, Dixon and Wasserman used gradient optimizations to determine the geometries of S_4–S_8 molecules.[9] Very recently, Quelch, Schaefer, and Marsden performed ab initio calculations on S_4.[10] This study used state of the art theory to investigate practically every S_4 isomer. Although a handful of molecular orbital calculations on sulfur compounds exists, there have been no such studies on molecules that include a transition metal atom in the sulfur ring.

In this paper, we explore computationally the ring inversion process in Cp_2S_5Ti. We calculate the full potential energy surface for the chair-to-chair rearrangement of the six-membered TiS$_5$ ring using the linear synchronous transit (LST)/orthogonal optimization approach[11] and PRDDO methodology.[12] This approach provides an inexpensive means of probing the potential energy surface without a priori assumptions about the transition state or costly second derivative calculations. Four different ring conformers, the chair, the twist boat, the boat, and the skew boat, were fully optimized. These structures were linked together in a series of LST/orthogonal optimizations to produce a low-energy pathway for the chair-to-chair rearrangement. In order to determine the energetics of the rearrangement at a higher level of theory, ab initio Hartree–Fock calculations were performed on the minimum energy and transition-state structures obtained from the PRDDO geometry optimizations.

Computational Methods

All structures were optimized using the PRDDO molecular orbital approximations.[12] This is a nonempirical formalism that produces relatively accurate geometries for transition-metal complexes[13] with only a modest amount of computational effort. The starting structure for Cp_2S_5Ti was obtained from the X-ray crystal structure of Muller, Petersen, and Dahl[14] and idealized to C_s symmetry. The numbering scheme is shown as structure **1**. All geometrical parameters were optimized except for the C–H distances, which were fixed at 1.07 Å. Local C_{5v} symmetry was assumed in the Cp rings.[15] The four structures that correspond to the different orientations of the Cp rings (endo–endo, endo–exo, etc.)[16] were optimized. All PRDDO calculations were per-



1

---

(1) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 5th ed.; Allyn and Bacon: Boston, MA, 1987; pp 447–450.

(2) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry Part A: Structure and Mechanisms*; Plenum: New York, 1984; p 113.

(3) For example, see the ΔG values for various $C_{6-n}S_n$ rings compiled in: Abel, E. W.; Booth, M.; Orrell, K. G. *J. Organomet. Chem.* **1978**, *160*, 75.

(4) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742.

(5) Bird, P. H.; McCall, J. M.; Shaver, A.; Siriwardane, U. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 384.

(6) McCall, J. M.; Shaver, A. *J. Organomet. Chem.* **1980**, *193*, C37.

(7) Abel, E. W.; Booth, M.; Orrell, K. G. *J. Organomet. Chem.* **1978**, *160*, 75.

(8) See Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC, 1982; pp 235–242.

(9) Dixon, D. A.; Wasserman, E. *J. Phys. Chem.* **1990**, *94*, 5772.

(10) Quelch, G. E.; Schaefer, H. F.; Marsden, C. J. *J. Am. Chem. Soc.* **1990**, *112*, 8719.

(11) Halgren, T. A.; Lipscomb, W. N. *Chem. Phys. Lett.* **1977**, *49*, 225.

(12) Marynick, D. S.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 1341. Halgren, T. A.; Lipscomb, W. N. *J. Chem. Phys.* **1973**, *58*, 1569.

(13) Marynick, D. S.; Axe, F. U.; Kirkpatrick, C. M.; Throckmorton, L. *Chem. Phys. Lett.* **1983**, *99*, 406. Marynick, D. S.; Reid, R. D. *Chem. Phys. Lett.* **1986**, *124*, 17.

(14) Muller, E. G.; Petersen, J. L.; Dahl, L. F. *J. Organomet. Chem.* **1976**, *111*, 91.

(15) The hydrogen atoms were allowed to bend out of the plane of the Cp ring. The C_5 axis is the centroid of the Cp ring–Ti axis. Thus, all R(Ti–C) distances were constrained to be equal.

0020-1669/91/1330-3547$02.50/0

Table I. Geometric Parameters[a] for PRDDO Ground-State and X-ray Structures

	PRDDO	ref 23	ref 14
R(C–Ti) in Cp(1)	2.41	2.37[b]	2.38[b]
R(C–Ti) in Cp(2)	2.42	2.38[b]	2.36[b]
R(C–C) in Cp(1)	1.39	1.35[b]	
R(C–C) in Cp(2)	1.39	1.38[b]	
R(Ti–Cp(1))	2.10	2.07	2.07
R(Ti–Cp(2))	2.11	2.07	2.05
R(Ti–S(1))	2.33	2.45	2.44
R(S(1)–S(2))	2.08	2.06	2.08
R(S(2)–S(3))	2.07	2.06	2.04
R(S(3)–S(4))	2.07	2.07	2.04
R(S(4)–S(5))	2.08	2.06	2.04
R(S(5)–Ti)	2.33	2.42	2.40
Cp(1)–Ti–Cp(2)	126	134	133
Cp(1)–Ti–S(1)	104	101	102
Cp(1)–Ti–S(5)	104	100	100
Cp(2)–Ti–S(1)	111	111	110
Cp(2)–Ti–S(5)	111	111	111
Ti–S(1)–S(2)	108	107	109
S(1)–S(2)–S(3)	102	105	105
S(2)–S(3)–S(4)	103	107	107
S(3)–S(4)–S(5)	102	103	104
S(4)–S(5)–Ti	108	109	109
S(5)–Ti–S(1)	99	95	95

[a] All distances and angles in ångstroms and degrees respectively. [b] Average.

formed on a Solbourne Series 5/602 computer. A typical single-point energy calculation required about 280 s. This can be compared to 27 s on a CRAY Y-MP/864 computer.

Once the geometry of the ground-state chair conformer was obtained, we proceeded to examine other possible stable minimum energy structures on the global surface. An obvious starting place was the boat conformer. This conformer was produced by setting the S(3)–S(2,4)–S(1,5) angle in the chair conformer equal to the Ti–S(1,5)–S(2,4) angle.[17] All four Cp conformers were again optimized under the same constraints as the chair conformer. Two other stable structures were found by breaking the C_s symmetry constraint. The twist boat conformer was generated by starting with the lowest energy boat structure, rotating the S(5)–Ti–S(1)–S(2) dihedral angle by 25°, and reoptimizing the geometry. The skew boat was produced by starting from a planar TiS_5 ring and rotating the S(2)–S(3)–S(4)–S(5) and S(4)–S(3)–S(2)–S(1) dihedral angles in opposite directions and then optimizing the resulting structure. The constraints on the Cp rings for the twist and skew boats were the same as those in the chair and boat conformers.

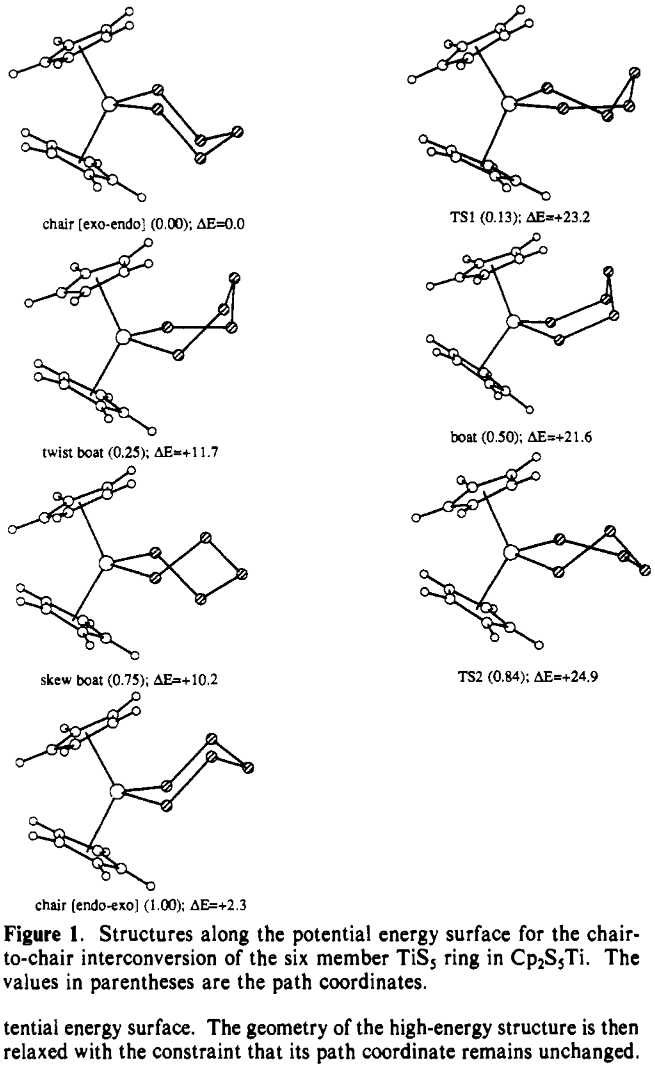
The potential energy surfaces were obtained by using the LST/orthogonal optimization method.[11] This procedure has worked very well in calculating many reaction pathways.[18] In this method, the path coordinate, P, is defined as

$$P = d_r/(d_r + d_p)$$

where d_r and d_p are summations of distances between identical atoms associated with an intermediate structure and the reactant and the product, respectively. They are defined as

$$d_r = [(1/N) \sum_{\omega=x,y,z} \sum_{a=1}^{N} [(\omega_a(c) - \omega_a(r))^2]]^{1/2}$$

with a similar definition for d_p. Here, N is the number of atoms, $\omega_a(c)$ is the x, y, or z coordinate of the current geometry, and $\omega_a(r)$ is the x, y, or z coordinate of the reactant when the reactant and product are at maximum coincidence. The reactant is usually assigned a path coordinate of 0.00 and the product a path coordinate of 1.00. Next, a continuous set of structures is generated between the product and reactant. A plot of energy versus path coordinate yields a first guess for the potential energy surface. The geometry of the high-energy structure is then relaxed with the constraint that its path coordinate remains unchanged. This is called an orthogonal optimization. This procedure is repeated until the surface is adequately characterized. The highest energy structure can be viewed as an *estimate* of the transition state because the LST/orthogonal optimization method defines a series of continuous structures, and therefore the maximum energy point on the surface is an upper bound to the true transition-state energy at the PRDDO level. A true transition state has one and only one negative eigenvalue of the Hessian matrix. In the system examined here, calculation of the requisite second derivatives would take a prohibitively large amount of computer time.


chair [exo-endo] (0.00); ΔE=0.0

TS1 (0.13); ΔE=+23.2

twist boat (0.25); ΔE=+11.7

boat (0.50); ΔE=+21.6

skew boat (0.75); ΔE=+10.2

TS2 (0.84); ΔE=+24.9

chair [endo-exo] (1.00); ΔE=+2.3

Figure 1. Structures along the potential energy surface for the chair-to-chair interconversion of the six member TiS_5 ring in Cp_2S_5Ti. The values in parentheses are the path coordinates.

In order to more rigorously estimate the energetics, ab initio calculations were performed on the minimum energy structures and the estimated transition-state geometries. The Cp ligands were described at the STO-3G[19] level. The sulfur basis set consisted of a 4-31G[20] basis set augmented with six Cartesian d functions with an orbital exponent of 0.65. The titanium basis set was triple ζ in the 3s/3d region and double ζ in the 3p and 4sp space.[21] This results in a total of 37 contracted basis functions on the titanium atom, which yields a grand total of 192 con-

---

(16) We define a Cp ring to be endo if the in-plane CH group points toward the sulfur ring. The notation endo–exo refers to Cp(1) being endo and Cp(2) being exo.

(17) The notation S(1,5) refers to the S(1)–S(5) midpoint.

(18) Axe, F. U.; Marynick, D. S. *Organometallics* **1987**, *6*, 572. Hansen, L. M.; Marynick, D. S. *J. Am. Chem. Soc.* **1988**, *110*, 2358. Jolly, C. A.; Marynick, D. S. *J. Am. Chem. Soc.* **1989**, *111*, 7968. Hansen, L. M.; Marynick, D. S. *Inorg. Chem.* **1990**, *29*, 2482. Marynick, D. S.; Axe, F. U.; Hansen, L. M.; Jolly, C. A. In *Topics in Physical Organometallic Chemistry*; Gielen, M., Ed.; Freund Publishing House Ltd.: London, 1989; Vol. 3, pp 43–84.

(19) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. Hehre, W. J.; Ditchfield, R.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1970**, *52*, 2769.

(20) Hehre, W. J.; Lathan, W. A. *J. Chem. Phys.* **1972**, *56*, 5255.

(21) This is basis set A for the ^3F atomic configuration of titanium in: Hansen, L. M.; Marynick, D. S. *J. Phys. Chem.* **1988**, *92*, 4588. These basis sets are designed to utilize the sixth Cartesian Gaussian d function to describe the 3s orbital on the metal. Each basis function is a Gaussian expansion of a Slater type orbital (STO). The 1s, 2s, and 2p orbitals are described by a three-Gaussian (3G) expansion of single-ζ STOs with exponents of 21.44020, 7.68816, and 9.03231, respectively. The 3p and 4sp orbitals are described by a two-term Gaussian expansion of a double-ζ STO. The exponents are 4.044 and 2.535 for the 3p shell and 2.429 and 1.477 for the 4sp shell. Here, the 4sp shell has the same orbital exponents as were used for the 4p orbital in: Hansen, L. M.; Marynick, D. S. *J. Am. Chem. Soc.* **1988**, *110*, 2358. The 3d orbital is a 2G expansion of a triple-ζ STO with orbital exponents 8.041, 3.770, and 1.752.

Table II. Geometric Parameters

path coordinate	chair 0.00	TS1 0.13	twist boat 0.25	boat 0.50	skew boat 0.75	TS2 0.84	chair 1.00
			Distances (Å)				
R(C–Ti) in Cp(1)	2.41	2.43	2.41	2.44	2.43	2.44	2.42
R(C–Ti) in Cp(2)	2.42	2.44	2.41	2.45	2.42	2.42	2.42
R(C–C) in Cp(1)	1.39	1.39	1.39	1.39	1.39	1.38	1.39
R(C–C) in Cp(2)	1.39	1.39	1.39	1.39	1.38	1.38	1.39
R(Ti–Cp(1))	2.10	2.13	2.10	2.13	2.13	2.14	2.12
R(Ti–Cp(2))	2.11	2.14	2.10	2.15	2.11	2.12	2.12
R(Ti–S(1))	2.33	2.34	2.39	2.30	2.34	2.33	2.32
R(S(1)–S(2))	2.08	2.07	2.08	2.08	2.07	2.07	2.07
R(S(2)–S(3))	2.07	2.07	2.07	2.07	2.10	2.10	2.07
R(S(3)–S(4))	2.07	2.07	2.10	2.07	2.06	2.06	2.07
R(S(4)–S(5))	2.08	2.08	2.06	2.08	2.07	2.08	2.07
R(S(5)–Ti)	2.33	2.34	2.28	2.30	2.35	2.31	2.32
			Angles (deg)				
Cp(1)–Ti–Cp(2)	126	126	127	124	127	126	126
Cp(1)–Ti–S(1)	104	103	108	112	104	106	110
Cp(1)–Ti–S(5)	104	106	113	112	110	110	110
Cp(2)–Ti–S(1)	111	109	106	103	110	110	104
Cp(2)–Ti–S(5)	111	108	103	103	105	103	104
Ti–S(1)–S(2)	108	108	109	118	105	127	110
S(1)–S(2)–S(3)	102	99	103	105	104	109	101
S(2)–S(3)–S(4)	103	100	102	104	108	105	102
S(3)–S(4)–S(5)	102	104	105	105	102	97	101
S(4)–S(5)–Ti	108	126	118	118	101	103	110
S(5)–Ti–S(1)	99	104	95	100	99	100	98
			Dihedral Angles (deg)				
Ti–S(1)–S(2)–S(3)	−73	−76	−59	−10	−82	−18	+73
S(1)–S(2)–S(3)–S(4)	+82	+101	+92	+76	+33	−32	−82
S(2)–S(3)–S(4)–S(5)	−82	−68	+38	−76	+50	+89	+82
S(3)–S(4)–S(5)–Ti	+73	+26	−41	+10	−89	−93	−73
S(4)–S(5)–Ti–S(1)	−61	−7	+66	+43	+36	+38	+58
S(5)–Ti–S(1)–S(2)	+61	+30	−11	−43	+41	+14	−58

tracted basis functions for Cp_2S_5Ti. These calculations were performed by using the program GAMESS[22] on a CONVEX C220 computer and an IBM 4381-3 computer at the University of Texas at Arlington. The calculations with C_s symmetry required ~13 h on the IBM computer and 2.5 hours on the CONVEX computer. A typical C_1 symmetry point group calculation required ~4 h on the C220 computer. Unless otherwise noted, all energies referred to in this paper are ab initio values, although the PRDDO and ab initio ΔEs agree remarkably well (see below).

In order to estimate the degree of angle strain about the sulfur atoms in the ring, an approximate S–S–S angle deformation potential was calculated for S_3H_2. The geometry of S_3H_2 was fully optimized at the PRDDO level. Next, the S–S–S angle was then varied from 90 to 144° without relaxing any other geometrical parameters. The relative energy, $E(\theta)$, was plotted against the S–S–S angle, θ, and the curve was fit to a second-order equation of the form

$$E(\theta) = c_1 + c_2\theta + c_3\theta^2$$

The S–S–S angle strain energy, ϵ, was defined as the sum of the five $E(\theta)$s for the angle about each sulfur atom in the ring.

Results and Discussion

The PRDDO calculations show that the global minimum energy structure of Cp_2S_5Ti contains a chair conformation of the six-membered ring, in agreement with experiment.[14,23] Its structure is shown in Figure 1. Table I contains geometric parameters for the PRDDO structure and the X-ray structures. The calculated structure is very similar to the X-ray crystal structures[14,23] except that our *R*(Ti–S) is ~0.1 Å shorter than the experimental values. The PRDDO S–Ti–S "bite" angle is 99°, which compares well to the experimental value of 95°.[14,23] All *R*(S–S) are ~2.07 Å with S–S–S angles of approximately 102°. These values are very similar to Dixon and Wasserman's values of 2.07 Å and 103° for S_6 calculated with ab initio theory and large basis sets.[9] In general, PRDDO does a good job of describing the geometry of the ground state.

Table III. Relative Energies of Various Cp Orientations at the PRDDO Level (kcal/mol)

	chair	boat
endo–endo	0.7	24.6
exo–endo	0.0	17.8
endo–exo	2.1[a]	25.2
exo–exo	5.4	21.3

[a] 2.3 kcal/mol at the ab initio level.

A previous NMR study showed that rotation of the Cp rings about an axis defined by the centroid of the ring and the titanium atom is facile.[7] Although we did not calculate the full path for these rotations, we optimized the geometries of all four conformers, which differ with respect to the orientation of the Cp rings. These energetics, at the PRDDO level of calculation, are contained in Table III. All of the conformers lie within ~5 kcal/mol of each other, consistent with the NMR results.

The bonding analysis of Cp_2ML_n molecules has been previously discussed.[24] We think of Cp_2S_5Ti as a 16-electron complex where the oxidation state of Ti is +4. Both Cp rings are η^5-bound and therefore contribute a total of 12 electrons. Each sulfur atom bound to titanium contributes two electrons to the total electron count. This yields a total of 16 electrons. The Ti–S bonds contain a small amount of double-bond character. This is illustrated by the degrees of bonding[25] of ~1.3 for the Ti–S bonds (see Table IV). Additionally, the localized molecular orbitals (LMOs)[26] of the ground-state molecule exhibit *two* LMOs for each Ti–S bonding interaction. The majority of the Ti–S bond is represented by an LMO that contains 1.37 electrons on S and 0.63 electron on Ti. Another LMO is formed when one of the sulfur lone pairs donates charge to an empty Ti orbital. This LMO is made up of 1.78 electrons on S and 0.21 electron on Ti.

---

(22) Dupius, M.; Spangler, D.; Wendoloski, J. J. GAMESS. General Atomic and Molecular Electronic Structure System. National Resources for Computations in Chemistry. The version of GAMESS used for these calculations is described in: Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE Bull.* **1990**, *10*, 52.

(23) Epstein, E. F.; Bernal, I.; Köpt, H. *J. Organomet. Chem.* **1971**, *26*, 229.

(24) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(25) Degrees of bonding are 1 for a single bond, 2 for a double bond, etc. Armstrong, D. R.; Perkins, P. G.; Stewart, J. P. *J. Chem. Soc., Dalton Trans.* **1973**, 838.

(26) Boys, S. F. In *Quantum Theory of Atoms, Molecules and the Solid State*; Löwdin, P. O., Ed.; Academic Press: New York, 1966; pp 253–262.

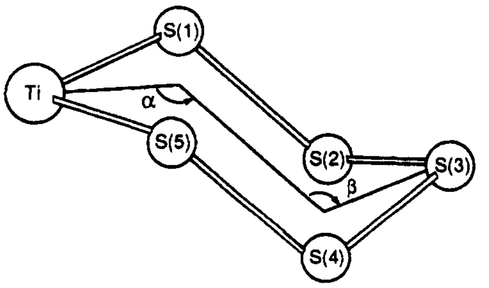
Table IV. Degrees of Bonding and Mulliken Charges

	chair	TS1	twist boat	boat	skew boat	TS2	chair
path coordinate	0.00	0.13	0.25	0.50	0.75	0.84	1.00
			Degrees of Bonding				
Ti–Cp(1)	1.78	1.74	1.77	1.70	1.75	1.70	1.74
Ti–Cp(2)	1.74	1.71	1.76	1.71	1.76	1.74	1.75
Ti–S(1)	1.32	1.29	1.18	1.35	1.28	1.30	1.33
S(1)–S(2)	0.95	0.95	0.95	0.94	0.96	0.94	0.95
S(2)–S(3)	0.99	0.99	0.99	0.98	0.95	0.96	0.99
S(3)–S(4)	0.99	0.99	0.96	0.98	0.98	1.00	0.99
S(4)–S(5)	0.95	0.93	0.95	0.94	0.95	0.95	0.95
S(5)–Ti	1.32	1.28	1.43	1.35	1.28	1.34	1.33
total TiS_5	6.50	6.43	6.46	6.53	6.50	6.43	6.46
			Mulliken Charges				
Cp(1)	–0.10	–0.11	–0.11	–0.13	–0.10	–0.12	–0.13
Cp(2)	–0.13	–0.12	–0.10	–0.10	–0.10	–0.11	–0.10
S(1)	–0.04	–0.05	–0.07	–0.05	–0.06	–0.08	–0.04
S(2)	–0.02	–0.01	–0.01	–0.01	–0.02	–0.01	–0.02
S(3)	–0.02	–0.01	–0.03	–0.01	–0.04	–0.02	–0.01
S(4)	–0.02	0.00	–0.03	–0.01	–0.01	0.00	–0.02
S(5)	–0.04	–0.09	–0.03	–0.05	–0.06	–0.04	–0.04
Ti	0.37	0.38	0.38	0.35	0.38	0.38	0.37
Ti(3d)	2.07	2.02	2.05	2.03	2.05	2.03	2.06
Ti(4sp)	1.72	1.75	1.73	1.77	1.73	1.74	1.73

The boat structure shown in Figure 1 is 21.6 kcal/mol higher in energy than the ground-state structure at the ab initio level of theory. The rotation of the Cp ligands has a larger effect on the relative energies than that seen in the ground state. These values, at the PRDDO level of theory, are shown in Table III. The lowest energy boat structure has an exo–endo arrangement. Rotating either Cp(1) or Cp(2) by 180° causes an increase of 6.8 or 3.5 kcal/mol, respectively, whereas rotating both Cp rings increases the energy by 7.4 kcal/mol. As discussed below, these increases in energy are due to angle strain at the sulfur atoms.

The twist and skew boat structures were also found to be local minimum energy structures. Their structures are illustrated in Figure 1. They lie 11.7 and 10.2 kcal/mol higher in energy, respectively, than the ground-state structure. In cyclohexane, the twist boat is generally considered to be more stable than the boat due to a lowering of the steric repulsion between the "flagpole" hydrogen atoms. In our twist boat, the energy is probably lowered due to a smaller strain angle about the sulfur atoms. This will be more clearly elucidated later.

The Potential Energy Surface. Our initial approach to the rearrangement was to simply convert the chair to the boat and then back again. This method will maintain C_s symmetry in all of the structures throughout the potential energy surface because the LST method preserves symmetry elements that are common to the reactant and product. At first thought, it seems as though this process would generate a symmetric potential energy surface, but it does not due to the presence of the $TiCp_2$ fragment. The first part of the potential energy surface varies the angle α (structure **2**) in order to obtain a boat conformer. The next half of the surface varies the angle β to regenerate the chair structure. This potential energy surface is shown as Figure 2. This pathway produces a very high energy "transition state" whose energy is 30.2 kcal/mol relative to the ground state. Note that this cut through the energy surface portrays the boat structure as a local minimum. Clearly, one cannot blindly input reactant and product into the LST algorithm and obtain the lowest energy pathway.



2

When the C_s symmetry constraint is removed, a more sensible pathway can be mapped out. This approach incorporates the twist and skew boat conformations. We linked the product and reactant together with four LST/orthogonal optimizations. The first part of the pathway transforms the chair structure into a twist boat. Next, the twist boat becomes a boat conformer that has C_s symmetry. The boat form then gives way to a skew boat. Finally, the skew boat reverts back to the chair. Note that the final product has a different arrangement of the cyclopentadienyl rings than that of the reactant. Thus, the overall ΔE of the reaction is 2.3 kcal/mol.

The potential energy profile for the full chair-to-chair rearrangement is shown in Figure 3 and the energetics listed in Table V. Note the remarkable agreement between PRDDO and ab initio energetics. The

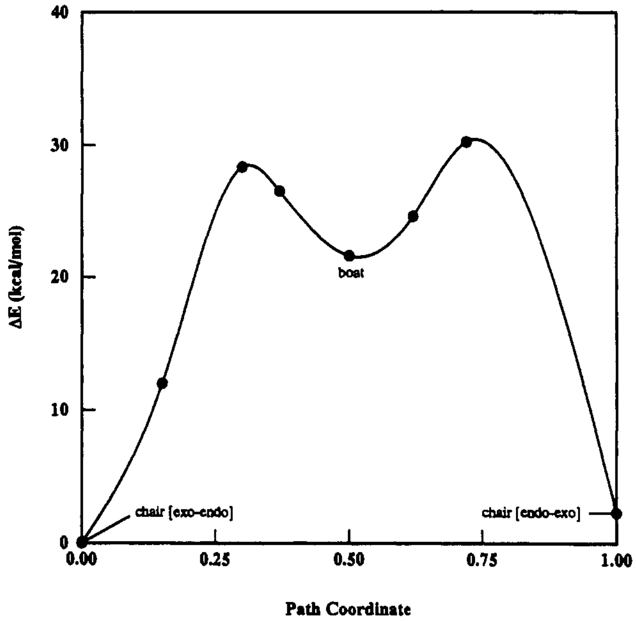


Figure 2. Potential energy surface for the chair-to-chair rearrangement which maintains C_s symmetry in each structure.

Table V[a]

structure	path coord	PRDDO ΔE	ab initio ΔE	ϵ_a	ϵ_d	ϵ_t
chair	0.00	0.0	0.0	5.5	0.2	5.7
TS1	0.13	22.1	23.2	18.9	6.6	25.5
twist boat	0.25	11.2	11.7	11.3	7.6	18.9
boat	0.50	17.7	21.6	16.5	15.4	31.9
skew boat	0.75	8.9	10.2	4.9	6.2	11.1
TS2	0.84	21.9	24.9	20.7	11.6	32.3
chair	1.00	2.1	2.3	6.8	0.3	7.1

[a] See text for definitions of ϵ_a, ϵ_d, and ϵ_t.

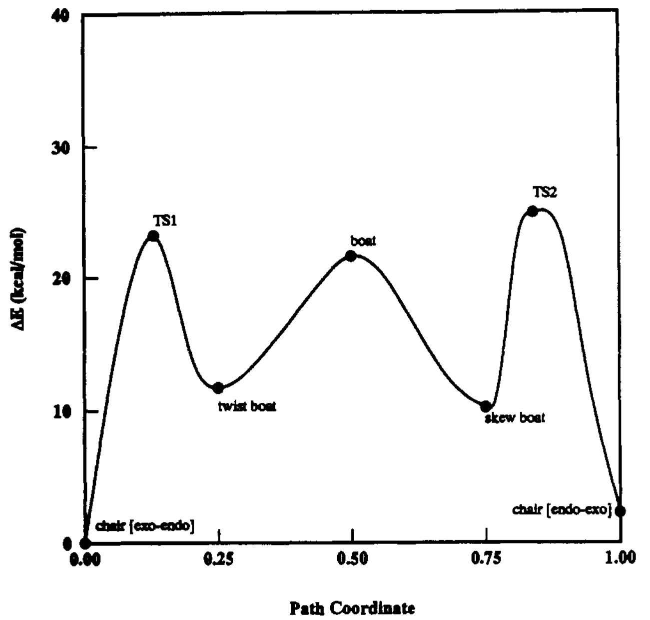


Figure 3. Low-energy potential energy surface for the full chair-to-chair rearrangement.

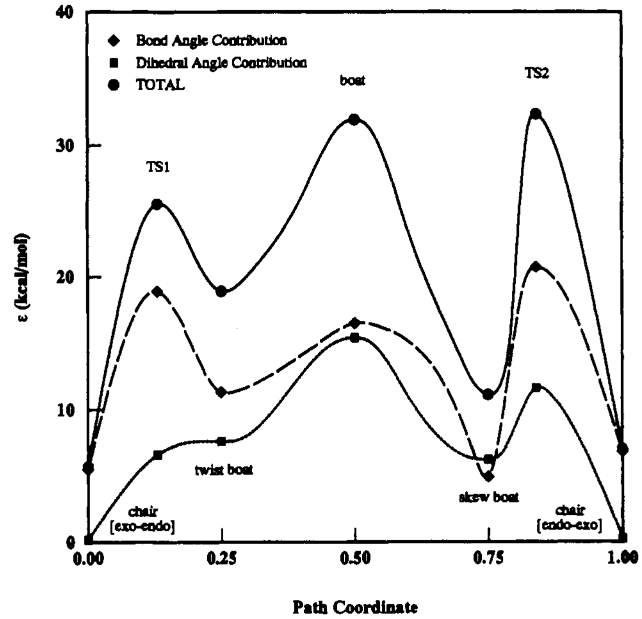


Figure 4. Plot of the sum of the five strain energies, ε, against path coordinate.

surface is a typical double-well potential. It contains three transition states. The first one, labeled TS1, occurs at a path coordinate of 0.13 and is 22.3 kcal/mol less stable than the ground state. The path coordinate is approximately halfway between the chair-shaped ground state and the twist boat. One can imagine this transformation as a simple rotation of S(5) about the Ti–S(4) axis. Ti, S(1), S(4), and S(5) are almost in a plane in this transition state as indicated by the S(4)–S(5)–Ti–S(1) dihedral angle of -7° (see Table II and Figure 1). The S(4)–S(5)–Ti angle is deformed to 126° compared to 108° in the ground state. The conversion from the twist boat to the boat occurs smoothly and without an activation barrier. Similarly, going from the boat to the skew boat does not involve a transition state. The boat structure is a transition state in this pathway whereas in the C_s symmetry potential energy surface it appeared to be a minimum. The final section of the surface transforms the skew boat into the chair structure. One may visualize this conversion as a rotation of S(2) about the S(1)–S(3) axis. This occurs with an activation barrier of 24.9 kcal/mol. The activated complex has a path coordinate of 0.84, which is slightly closer to that of the skew boat than that of the product. The transition state is labeled TS2 in Figures 1 and 3. Its geometry is characterized by an almost planar arrangement of S(5), Ti, S(1), and S(2). This is similar to the geometry of TS1. Here, the Ti–S(1)–S(2) angle is 127°, which is close to the Ti–S(5)–S(4) angle in TS1.

What is responsible for the activation energy of the chair-to-chair interconversion? Steric factors are inconsequential. In order to illustrate this, we calculated the nonbonded repulsion energy for each point along the potential energy surface from standard empirical potentials.[27] These calculations show that the steric component of the barriers are no greater than 2.0 kcal/mol. This leads us to the conclusion that electronic effects are the major factor in determining the energetics. These effects are not associated with the Ti–Cp, Ti–S, or S–S bonds whose bond interactions do not vary significantly throughout the reaction path. This is clearly seen in Table IV where the degrees of bonding are illuminated for the important structures along the potential energy surface.

On the other hand, the angles in the ring vary largely from structure to structure (for example, consider the Ti–S(1)–S(2) and S(4)–S(5)–Ti angles in Table II). The largest changes occur in the angles about the sulfur atoms directly bound to titanium. The larger the angles about each sulfur, the higher the relative energy. In order to further delineate the angle strain energy, we constructed a bending potential for the S–S–S angle in H_2S_3.[28] This is a very crude approximation because only the angles about the sulfur atoms were considered in the function. The S–Ti–S angle was not treated. The bending potential is relatively flat, i.e. between 90 and ~115° the ΔE is less than 5 kcal/mol. It begins to rise steeply at ~120 and at 130° the ΔE is ~20 kcal/mol. A second-order fit[29] of the curve produces the strain energy, $E(\theta)$, as a function of the S–S–S angle. This was used to calculate the overall strain energy, ϵ_a, associated with the five sulfur angles in the ring. The values for each molecule are shown in Table V and plotted in Figure 4. One can easily see the correlation between the S–S–S strain energy of the ring and the activation energies. While the empirically computed barriers are somewhat smaller than those calculated rigorously, Figure 4 clearly shows that the relative energies of the various conformations are intimately tied to the deformation angles about the sulfur atoms.

To further quantify the origins of the barriers, we employed a similar procedure for the S–S–S–S dihedral angles, modeled by H_2S_4. The dihedral angle strain, ϵ_d, is also plotted in Figure 4, as is $\epsilon_t = \epsilon_a + \epsilon_d$. While the *form* of the ab initio potential is better mimicked by ϵ_a, it is clear that both ϵ_a and ϵ_d contribute significantly to the energetics.

The identification of sulfur angle strain as an important contribution to the barriers suggests an obvious explanation for the fact that all of our calculated barriers are somewhat too high: Force constants calculated at the Hartree–Fock level are generally too large. Thus, we would expect that the addition of an appropriate electron correlation treatment would lower our calculated barriers.

Conclusions

We have fully optimized several conformations of Cp_2S_5Ti using the PRDDO methodology. Ab initio calculations using the PRDDO optimized geometries yielded energetics that are remarkably similar to those found with PRDDO. The chair structure is the ground state and lies 10.2 and 11.7 kcal/mol lower in energy than the twist and skew boats, respectively. A boat-shaped TiS_5 ring is 21.6 kcal/mol higher in energy than the ground state. The full potential energy surface is a double-well potential. The overall activation energy is 24.9 kcal/mol. This energy is due almost entirely to angle variations about the sulfur atoms in the ring. This is clearly demonstrated by an empirical potential which correlates the strain energy, ϵ_t, with the activation energies of the transition-state species.

Acknowledgment. We thank the Robert A. Welch Foundation (Grant Y-743) and the Texas Advanced Technology Program for support of this work.

Registry No. TiS_5, 12116-82-4.

---

[27] These calculations were performed by using CHEM-X from Chemical Design Inc. The titanium atom was not included because these parameters are not available.

[28] The geometrical parameters that resulted from the PRDDO optimization are R(S–S) = 2.07 Å, R(S–H) = 1.36 Å, ∠S–S–S = 102.0°, ∠H–S–S = 99.5°, and ∠H–S–S–S = 75.0°.

[29] The function is described by $E(\theta) = c_1 + c_2\theta + c_3\theta^2$, with $c_1 = 240.9174$, $c_2 = 4.7209$, and $c_3 = 0.0232$.