Quantum Chemical Calculations of Topology of Molecular Systems. I. The Degenerate Rearrangement in Cyclopentadiene and Cyclopentadienylsilane

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Abstract: A potential curve close to the reaction coordinate for the [1,5] rearrangement in cyclopentadiene and in cyclopentadienylsilane is calculated. A fast-convergence optimization procedure is elaborated for the computation of a geometry of the points on the curve. Scanning the calculated points and processing these with the corresponding orbitals method allow us to distinguish three regions on the reaction coordinate: (A) minima, where energy is a quadratic function; (B) descents, where the energy change is practically linear; (C) passes, where energy is almost constant. At the A and B regions the total energy is to the greatest extent affected by the bending angles of the methylene hydrogens with respect to the ring plane. The "permissibilities" of the transition from the ground state to the regions A and B do not undergo any significant change. At the region C the "permissibilities," the ring π orbitals, the C–C bonds, and the migrating H–C distance change strongly. The calculated activation energy is 10.2 kcal/mol with CNDO/2 and 18.4 kcal/mol with MINDO/2 methods; the experimental value is 24 kcal/mol. There are significant differences between the potential surface energy patterns calculated *via* these two methods (*e.g.*, the CNDO/2 overestimates the pass length); however, the optimized geometries are quantitatively identical. For a cyclopentadienylsilane molecule, the calculated energy of activation is 6 kcal/mol, one-half the experimental energy. "Permissibility" of the rearrangement is 0.749 for C_5H_6 and 0.798 for $C_5H_5SiH_3$. The main spatial factor which governs the rearrangement course is the alteration of bending angle formed by the Si–C bond and the C_5H_5 ring plane, by reference to the methylene angle in C_5H_6. The calculation demonstrates that the channels of the [1,1] and [1,3] rearrangements, forbidden through symmetry and spatial factors cannot be related to any potential curve which would be close to the reaction coordinate.

Experimental investigations of a reaction mechanism allow one just to make indirect prediction of the geometry of a metastable intermediate or of the activated complex. Quantum chemical calculations may help to go beyond this and provide insights not yet accessible experimentally. In order to calculate a chemical reaction in some detail one should be able, in the first place, to calculate quantitatively the geometry of stable molecules. It has been shown already that with CNDO/2,[1] INDO,[2] NDDO,[3] MINDO/2,[4,5] STO-3G,[6] STO-4-31G,[7] and some other methods the geometry can be obtained practically accurate in several cases. Second, one must be able to predict the energy associated with different paths of a reaction with a qualitative accuracy, at any rate. Actually it is difficult to estimate the errors involved in quantitative prediction of potential surface, even when rigorous *ab initio* quantum chemical methods are used. Then, a qualitative prediction of the reaction path is usually the most reliable result of a detailed calculation for a complicated molecular system. Further, as far as the computation of geometry for a number of points of the potential surface is time consuming, a fast-convergence optimization procedure should be elaborated. Finally, an interpretation of the calculated data and the data processing with standard procedures allow one to select the criteria for the reaction mechanism.

The quantum mechanical calculation is possible only for an isolated molecular system, for which the mechanism of the energy exchange with the environment cannot be included into the consideration. This approximation holds for intramolecular rearrangements. Those rearrangements were an objective of the detailed quantum chemical calculation recently made.[8–11]

In this work we have investigated the reaction paths for an intramolecular rearrangement in cyclopentadiene and cyclopentadienylsilane.

Quantum-Chemical Technique Selected

A quantum-chemical method to calculate the reaction coordinate should satisfy at least the following conditions: (A) the calculated ground state geometry should be close to the experimental one; (B) a pattern of the energies associated with different reaction channels should agree qualitatively with the chemical properties; (C) the computation time should be short enough to permit a large, interesting from the point of view of experimental chemistry, molecule to be calculated on the available computer, with the optimization of the geometry variables being included.

Modern *ab initio* methods usually violate condition C. All three conditions could be satisfied by the semi-

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empirical methods EHT,[12] CNDO/2,[1,13] INDO,[14] NDDO,[15] and MINDO.[16,17]

EHT Technique. The off-diagonal matrix elements are calculated through the formula

$$H_{ij} = (f(S)S)_{ij}g(H_i,H_j) \quad (1)$$

which is an extension of the Wolfsberg–Helmholtz equation.[18]

Particular versions of eq 1 can hardly satisfy condition A when an EHT version without iteration is employed. We have considered 11 different $f(S)$ functions, *e.g.*, $f(S) = k$, $f(S) = 2 - |S|$ (*cf.* the paper[19] by Cusacks), and four $g(H_i,H_j)$ functions, and found no version which would at least qualitatively result in a correct geometry for simple molecules. If condition A is satisfied by applying an iterative variation of H_i and H_j, then the respective EHT technique will gain no advantage of semiempirical MO–SCF methods with respect to condition C.

Semiempirical MO–SCF Techniques. The methods CNDO/2, INDO, and NDDO lead, to all practical purposes and intents, to the same departure (on the average, 4%) of the calculated geometrical characteristics from the experimental ones. CNDO is the most widespread technique since it fits with condition C best of all. As calculations of barriers to internal rotation have shown, CNDO/2 may satisfy condition B as well; at any rate, this is so for noncharged molecular systems containing H, C, N, O, and Si atoms.

Recently, Dewar and his coworkers have developed some versions of the MINDO method[16,17,20] to satisfy not only condition A but also (*cf.* the numerous calculations in ref 21) condition B. Condition C is satisfied by both CNDO/2 and MINDO/2 equally well. However, the MINDO has not yet been extended to embrace elements of the third period of the periodic system. Our main task was to compare driving forces operating in cyclopentadiene and cyclopentadienylsilane rearrangements; therefore, we have limited ourselves to adjusting the calculation to condition B qualitatively and employed the CNDO/2 technique, with the MINDO/2 method being used for check-up purposes in some cases.

Optimization Procedure

A point on the reaction coordinate requires, in principle, $3N - 6$ geometrical parameters to be calculated for an N-atomic molecule. Such a calculation defies even the performance of a modern large computer; therefore convergence inherent in the optimization procedure should be as high as possible. Reportedly,[3,22] the computation time is kn^m, where n is the number of parameters to be optimized, m is usually greater than two. We have worked out a procedure characterized by $m = 1$ and k usually equal to or lying below six.

Consider n parameters (M_1^0, M_2^0, M_3^0, . . . , M_n^0) and n steps (d_1, d_2, . . . , d_n) of variation of M. Calculate total energies E_1, E_2, and E_3 for M_i^0, $M_i^0 + d_i$, and $M_i^0 - d_i$, respectively, with all the other M being fixed. Interpolate the resulting three energies by a parabola and calculate $M_1^{(1)}$ corresponding to its minimum. If $|M_i^{(1)} - M_i^0| > 6d_i$, then shift $M_i^{(1)}$ by $6d_i$ toward the minimum or else substitute $M_i^{(1)}$ for M_i^0. Now, calculate new values of E_1, E_2, and E_3 for $M_i^{(1)}$ if $6d_i > |M_i^{(1)} - M_i^0| > 3d_i$ or for M_k^0 ($k \neq i$) if $|M_i^{(1)} - M_i^0| < 3d_i$. After all $M_i^{(1)}$ are calculated, analyze the differences $|M^{(1)} - M^0|$. If for an M_j^k the difference is below Δ_j (a preset accuracy), then do not optimize this parameter any longer. Reiterate the procedure applied to M^0 for all the remaining parameters $M^{(1)}$ and obtain $M^{(2)}$ and so on until all the parameters have been optimized. As a rule, the number of M^0 is several times that of $M^{(2)}$.

The quantities Δ_i are expressed through $\Delta_i = d_i/k$ where k is 5, 10, or 20, depending on the accuracy desired. The magnitudes of d_i are equal to 0.01–0.03 Å (distances) and 1–3° (angles). This optimization technique takes $^1/_8$ to $^1/_{15}$ the time required by the Brown and Lo program[22] (see, however, ref 23).

The number of parameters to be optimized may be reduced with the aid of symmetry considerations. The parameters M^0 for a structure under study may be the geometry parameters obtained for a similar structure with the same quantum chemical method; *e.g.*, CNDO/2 usually gives a C–H distance of 1.10–1.12 Å, so $M^{(1)}$ (or, in the worst case, $M^{(2)}$) is already accurate to Δ. If the starting geometry (the set of parameters M^0) is qualitatively incorrect, the program will automatically start treating another structure by means of rapid scanning with a step of $6d$ along a few parameters. The calculation accuracy depends on the second derivative of the function $E(M_i)$. In principle, an accuracy of 10^{-9} Å or 10^{-9} degree may be achieved quite rapidly. Practically, the CNDO/2 iteration accuracy is 10^{-5} eV with respect to the first occupied level, so the bond lengths are accurate to 10^{-3} Å and the angles to 0.1°. Local extremes ("beats") which sometimes arise in the region of the energy minimum associated with a parameter deteriorate the calculation accuracy and raise the computation time.

Calculations

The calculations were carried out using a TOREAMOR program written by one of us (G. A. S.) and Gloriozov. The program includes the various versions of EHT, CNDO, INDO, and MINDO methods and a processing of the calculated data with standard procedures. The calculation of one point on the reaction coordinate of cyclopentadiene took approximately 1.5 hr on a BESM-6 computer (it is approximately as fast as an IBM-360/65).

Rearrangement Model Selected

The rearrangement in cyclopentadiene is one of a

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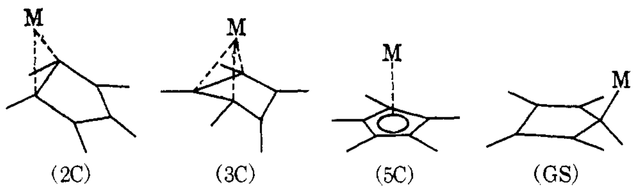

Figure 1. Schematic representation of types of transition states possible in the migration of an organometallic group (M, which may also be hydrogen or a CH_3 group) in cyclopentadiene derivatives. GS denotes the ground state.

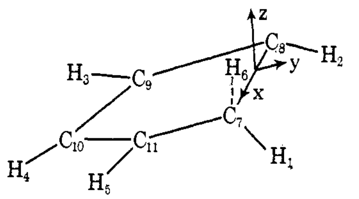

Figure 2. The numbering of atoms and the coordinate system chosen for the proton H_6 migration in cyclopentadiene.

vast number of degenerate intramolecular rearrangements discovered and studied during the last 10 years.[24] For organometallic σ-cyclopentadienyl compounds, in particular, nmr techniques helped to demonstrate that the rearrangement occurs *via* the 1,2 shift predominantly,[24,25] that is, it is a [1,5]-sigmatropic rearrangement in terms of the Woodward–Hoffmann notation.[26] The prototropic rearrangement mechanism in cyclopentadiene and deuterated cyclopentadienes was studied with ir[27] and nmr[28] methods in detail.

A priori, three basic mechanisms are possible for the rearrangement of σ-cyclopentadienyl compounds,[11] referred to as the transition states 2C, 3C, and 5C in Figure 1.

Migration *via* 2C

The coordinate system chosen is shown, and the atoms are numbered, in Figure 2. The X and Y axes lie on the $C_{11}C_7C_8$ plane.

The Z axis is perpendicular to the plane. The following 26 variables have been optimized: (1) ten bond lengths R_i (all the bonds except C_9–C_{10}); (2) nine angles φ_i formed by the atom–atom bonds and the Y axis (all angles of the type, except for the angles associated with C_7 and H_6); (3) five angles θ_i by which the CH_i bonds ($i \leq 5$) deviate away from the plane formed with the carbons nearest to the H_i hydrogens; the angle was assumed positive when the bond deviated toward the atom H_6 (the angle θ_6 for H_6 is the angle between the Y axis and the perpendicular dropped from the point H_6 onto the line C_7–C_8); (4) dihedral angles: ψ_1 formed by the planes $C_7C_8C_{10}$ and $C_8C_9C_{11}$, ψ_2 formed by $C_9C_{10}C_{11}$ and $C_8C_9C_{11}$ (the angles ψ_1 and ψ_2 were assumed positive when the planes $C_8C_9C_{11}$ or $C_9C_{10}C_{11}$ deviated toward the atom H_6).

All these variables were optimized for 16 fixed points lying on the X axis. The bond lengths are accurate to 10^{-3} Å and the angles to 0.1°.

According to their influence upon the energy the geometry parameters may be divided into three types: (i) strongly influential (distances R(CC) and angles φ(CCC) between C–C bonds), (ii) moderately influential (distance R(CH) and dihedral angles ψ), (iii) weakly influential (angles φ_H and θ_H). An increment of 0.02 Å (distances) or 0.02 radian (angles) requires, on the average, the following energies (eV): (i) 0.04 for R(CC) and φ(CCC), (ii) 0.01 for R(CH), 0.005 for ψ_1 and ψ_2, (iii) 0.0008 for θ_H, and 0.0005 for φ_H. The calculation has demonstrated that the geometric variables of the first five hydrogens depend on X weakly. Consequently, the energy change is mainly due to the change in the carbon skeleton and to the shift of H_6.

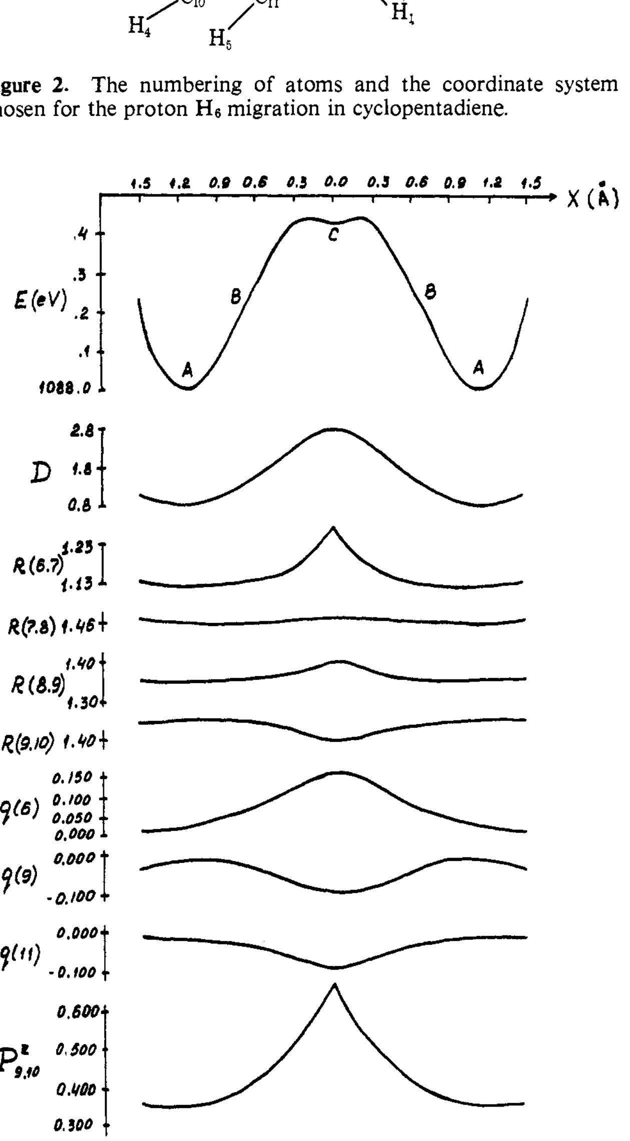

Figure 3. The pattern of total energy (E), dipole moments (D), bond lengths (R), net atomic charges (q), and π-bond orders ($P_{ik}{}^z$) for the calculated points of the reaction coordinate (1,2 shift in cyclopentadiene), with the CNDO/2 method.

Note that some of the geometrical parameters have sometimes two local minima each, the minima being close in their energies. This is so for θ_H (at $\theta_H > 0$ or $\theta_H < 0$) or, *e.g.*, for X = 0.60 Å for which there is a minimum at R(7,11) = 1.4554 Å and another one (whose energy is by 0.01 eV higher) at R(7,11) = 1.4674 Å. These minima interchange their positions at X = 0.75 Å; therefore, this point somewhat deviates from the regularities observed for the variation in the parameters associated with the other points on the X axis.

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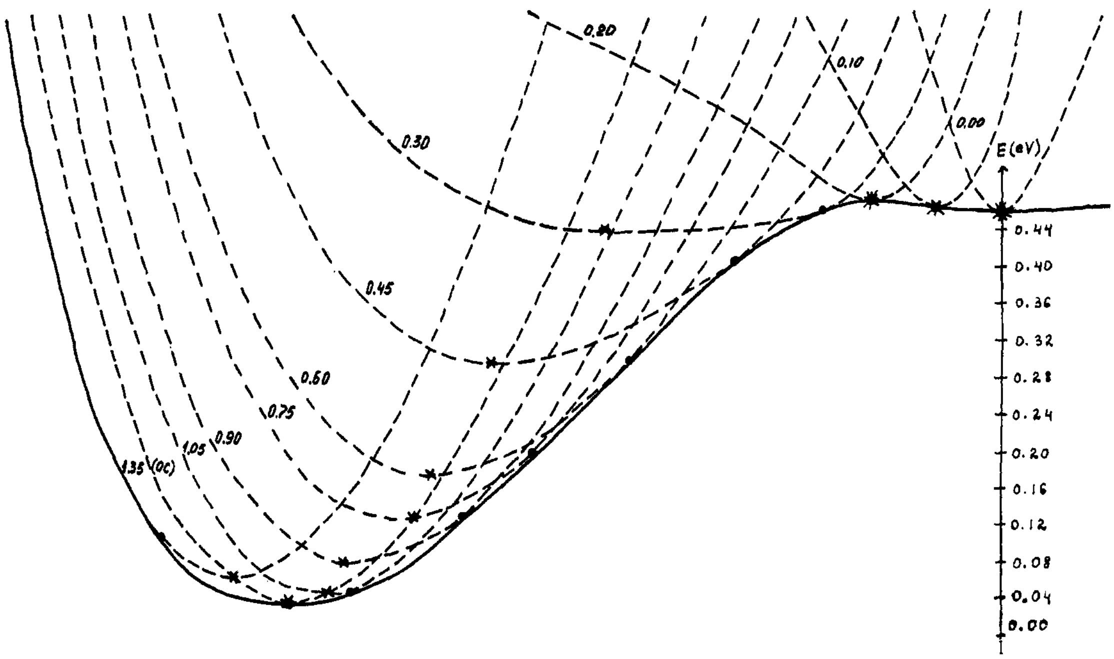

Figure 4. Results (dotted lines) obtained with scanning the parameter, X, for fixed points (filled circles) of the reaction coordinate X for C_5H_6. Asterisks denote minima of the functions $U_i(X)$.

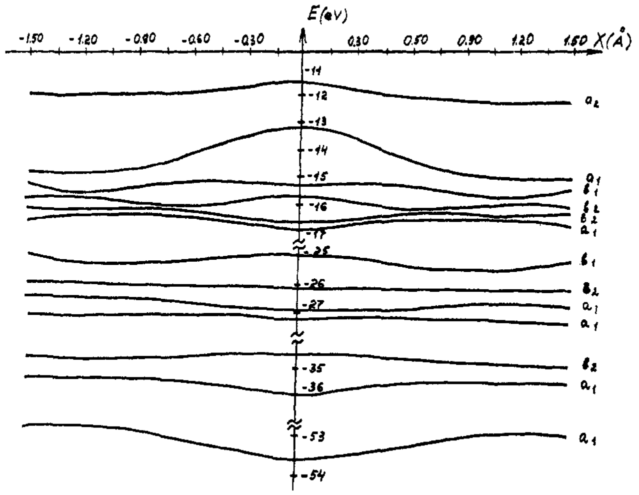

Figure 5. The correlation diagram calculated for the hydrogen 1,2 shift in cyclopentadiene, with respect to the C_{2v} irreducible representations (a_1, a_2, b_1, b_2); a_2 is a π orbital.

For the ground state (X = 1.1476 Å), the minimum at R(7,11) = 1.47 Å turns to lie below the minimum at R(7,11) = 1.467 Å; therefore, this state slightly deviates from the C_{2v} symmetry. We cannot say whether the presence of two minima is real or is due to an uncertainty inherent in the CNDO/2 method.

The reaction coordinate corresponding to the H_6 1,2 shift is shown in Figure 3. The state 2C is described by a shallow (0.2 kcal/mol in depth) minimum. The transition state lies at X = 0.174 Å. That minimum is, probably, an artifact inherent in the CNDO/2 method. Actually, the method overestimates the energy gain associated with the three-center bonds.[29-31] Recently, some points on the total energy curve have been calculated for cyclopentadiene, Figure 3. The results obtained by the authors[32] fit well with those obtained in this work; however, our preset accuracy was better (10^{-5} eV in the first occupied level energy), so our central minimum is one-half as deep. Another interesting result obtained by the authors[32] is that the central minimum is at all absent from the potential energy curve calculated through the INDO method. Consequently, the energies resulting from a CNDO/2 approach are, apparently, far from quantitative. But these errors of the method do not change our qualitative conclusions (see below) on the physical properties of the computed reaction coordinate. Figure 3 shows the variation in some geometrical parameters, net atomic charges, and π bond orders.

The scanning with respect to X has been made for C_5H_6, with the geometry variables which correspond to the calculated point on the reaction coordinate being fixed. Figure 4 shows the scanning results (dotted lines) and part of the reaction coordinate (solid line) at $X < 0$.

Energy levels as a function of X are shown in Figure 5. On the right, the energy levels are assigned to the C_{2v} irreducible representations on the basis of the GS MO coefficients.

The pattern obtained for $C_5H_5SiH_3$[33] is qualitatively the same as that for C_5H_6. In Table I, the parameters that govern the rearrangement course are collated.

The energy variation along the Y' axis is shown in Figure 6. The origin of Y' is chosen to lie on the carbon C_{10}; the system of coordinates results from a parallel shift of the system in Figure 2 along the Y axis.

The state 2C lies at the Y' of about 2.30 Å. The point Y' = 2.81 Å corresponds to an antarafacial transition ($2C_a$). This transition cannot, however, re-

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Table I. Variation of Some Geometrical Parameters for a Number of Points on the Reaction Coordinate for Rearrangement in Cyclopentadiene and Cyclopentadienylsilane

	C_5H_6				$C_5H_5SiH_3$			
X	θ^a	θ_6	$-\theta_1$	$-\theta_2$	θ^a	θ_{Si}	$-\theta_1$	$-\theta_2$
0.00	52.6	75.8	7.0	7.1	67.6	77.5	12.5	12.5
0.15	57.8	74.7	12.9	4.2	69.2	75.4	16.3	10.7
0.30	63.2	73.4	18.9	2.6	70.0	73.3	20.0	8.9
0.45	68.2	73.2	23.4	1.6	71.4	72.5	22.7	8.9
0.60	70.8	72.0	29.3	1.3				
0.75	70.7	70.7	33.9	0.9				
0.90	66.4	67.9	39.8	1.2				
GS	59.7	59.7	51.5	0.7	70.7	70.7	31.5	2.3

[a] The angle formed by the H_6–C or Si–C bond and cyclopentadienyl ring.

sult from continuous variation of geometry parameters with reference to 2C, since for the atoms H_1 and H_2 the angles θ_1 and θ_2 vary from -7 to $-10°$ whereas they have opposite signs in the state $2C_a$. Accordingly, the points $Y' = 2.70$ and 2.81 are joined by a dotted line.

Moving from $2C_s$ (s denotes suprafacial) leftward strongly raises the angle ψ_1 (its value is shown near the points), with the atom C_{10} meeting H_6; the angle θ_1 varies from -7.1 to $-14.1°$; θ_3 from -1.4 to $-9.3°$; θ_4 from zero to $-7.7°$ ($Y' = 1.10$) and then to $-1.0°$ ($Y' = 0.10$); $R(C_7–H_6)$ varies from 1.220 to 1.349 Å; $R(C_9–H_{10})$ from 1.392 to 1.422 Å; the remaining geometry variables are practically not affected. In going from 2C to the point $Y' = 0.10$ Å, the charge on H_6 falls from 0.17 down to -0.07, the dipole moment rises from 2.80 up to 4.50 D. These data suggest that the state 5C, of the C_{5v} symmetry ($Y' = 1.206$ Å), is inaccessible if the molecule starts from 2C.

For $C_5H_5SiH_3$, the pattern is qualitatively the same, although the parameters vary in a less pronounced fashion. Moving leftward from $2C_s$ up to $Y' = 0.90$ Å raises the angle ψ_1 to 20.9° and the ΔE value by 1.22 eV.

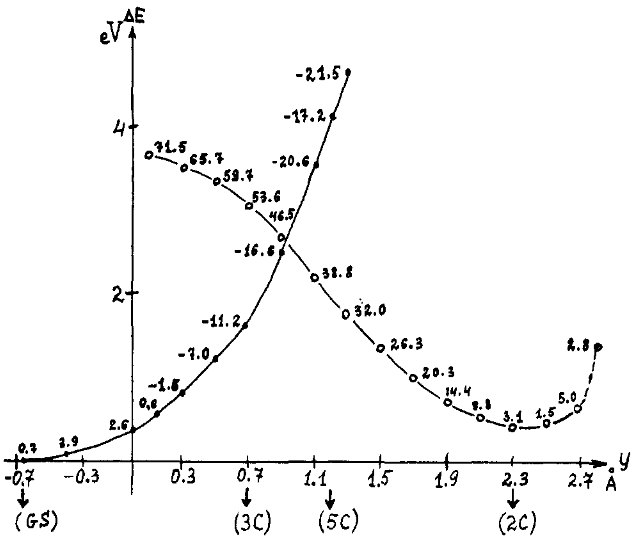

Figure 6. ΔE *vs.* Y' for cyclopentadiene *via* CNDO/2. Left-hand curve, the motion starts from GS. Right-hand curve, same from 2C. The figures near the points are the dihedral angle ψ_1 values.

the orbital types are affected by the rearrangement. Table II lists the values of $Q_{AB} = (\Pi_i d_i)^{1/2}$ for some points on the reaction coordinate X for C_5H_6.

Table III lists the d_i values that lie below 0.99. Let xy denote the set of coefficients $C_{i\mu}$ of the orbital $\psi_i = \Sigma_\mu C_{i\mu}\chi_\mu$, the coefficients which correspond to the χ_μ = $2p_x$, $2p_y$ carbon orbitals, and let π denote the set of $2p_z$. The molecular orbitals in Table III will correspond to the following interaction types: no. 8, $(H_6|xy)$ for GS and 2C; no. 11, $(H_1H_6|\pi)$ for GS, $(H_i|xy)$ for 2C; no. 12, $(H_i|xy)$ for GS, $(H_6|\pi)$ for 2C; no. 13, $(\pi|\pi)$ for GS and 2C; $i \leq 5$ throughout.

Migration *via* 5C

The [1,3]-rearrangement channel, allowed antarafacially, and the [1,1]-rearrangement channel, allowed suprafacially, are both impossible owing to spatial considerations.

Table II. Q_{AB} for Geometry Configurations Corresponding to Various Points on the Reaction Coordinate X for C_6H_5

	X							
X	1.05	0.90	0.75	0.60	0.45	0.30	0.15	0.00
1.14 (GS)	0.996	0.983	0.965	0.944	0.915	0.877	0.821	0.749
1.05		0.996	0.984	0.968	0.942	0.908	0.853	0.781
0.90			0.996	0.987	0.967	0.938	0.887	0.817
0.75				0.996	0.984	0.961	0.916	0.849
0.60					0.995	0.979	0.943	0.884
0.45						0.994	0.970	0.921
0.30							0.990	0.957
0.15								0.987

Reaction Coordinate Points Processed with the Corresponding Orbitals Method

In terms of the corresponding orbitals method,[34,35] a criterion for the "permissibility" of the transition between the geometrical configurations A and B of a molecular system is the matrix $D_{ik} = (\psi_i^A|\psi_k^B)$ where ψ_i^A is the *i*th occupied orbital in configuration A. On diagonalizing D^+D we obtain a set of roots, d_i, and deviations of the roots from unity will indicate which of

Figure 6 demonstrates that the state 5C of the C_{5v} symmetry ($Y' = 1.206$ Å) is inaccessible if the molecule starts from GS ($Y' = -0.67$ Å), while for the 3C state there is no minimum. In their motion from GS, the atoms C_{10} and H_6 move in the opposite directions; the hydrogen H_4 follows the direction of H_6. By collating this to the H_6 motion starting from GS, we obtain that the [1,1] shift along the route: GS → 3C → 5C → $2C_s$ → $2C_a$ and further (at the back side of the ring) $2C_s$ → 5C → 3C → GS is impossible, since the curves in

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(34) H. F. King, R. E. Stanton, H. Kim, R. E. Wyatt, and R. G. Parr, *J. Chem. Phys.*, 47, 1936 (1967).

(35) C. Trindle, *J. Amer. Chem. Soc.*, 92, 3251 (1970).

Table III. Roots of Matrix D^+D for C_5H_6

	Orbital no.							
	8	11	13	8	11	13	12	13
	X							
X	1.14 (GS)			1.05			0.90	
1.05	0.996	0.998	0.999					
0.90	0.982	0.993	0.998	0.979	0.999	0.999		
0.75	0.958	0.984	0.996	0.957	0.984	0.998	0.995	1.000
0.60	0.930	0.973	0.995	0.921	0.971	0.998	0.981	1.000
0.45	0.887	0.957	0.995	0.870	0.955	0.997	0.954	0.999
0.30	0.831	0.939	0.994	0.847	0.948	0.997	0.911	0.971
0.15	0.752	0.910	0.994	0.994	0.766	0.918	0.842	0.947
0.00	0.661	0.870	0.991	1.000	0.703	0.889	0.753	0.909

	Orbital no.									
	12	13	12	13	12	13	12	13	12	13
	X									
X	0.75		0.60		0.45		0.30		0.15	
0.60	0.995	1.000								
0.45	0.978	0.992	0.993	0.998						
0.30	0.994	0.982	0.970	0.991	0.992	0.997				
0.15	0.883	0.961	0.921	0.974	0.986	0.958	0.998	0.995		
0.00	0.800	0.926	0.942	0.846	0.960	0.898	0.995	0.987	0.999	0.998

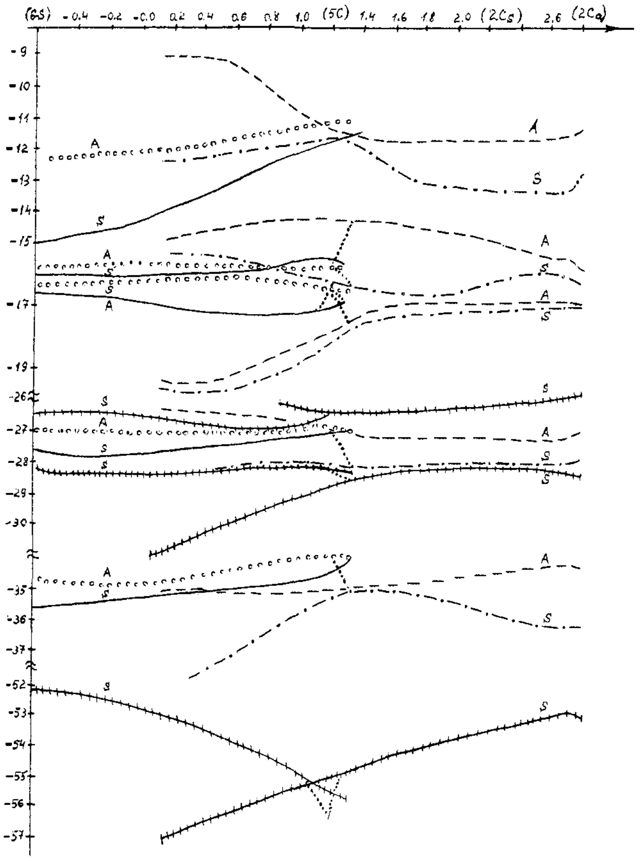

Figure 7. Correlation diagram for energy levels for the route GS → 3C → 5C → $2C_s$ → $2C_a$: (+) nondegenerate levels for 5C, (○) and (—) degenerate levels for 5C when the motion starts from GS, (- - -) and (-·-) degenerate levels for 5C when the motion starts from 2C, (· · ·) correlation with the state 5C (the C_{5v} symmetry).

Figure 6 do not intercept because they lie on different sections of the potential surface (the different angles ψ_1). The same conclusion follows from Figure 7.

The corresponding orbitals approach shows that in the transition under discussion the most affected is orbital no. 11. It is in the form of $(H_1H_6|\pi)$ for GS, $(H_i|xy)$ for 2C, while H_6 takes no part in it in the case of 3C and 5C. For $C_5H_5SiH_3$, the last occupied orbital is affected; it has the form of $(p_z(Si)|\pi)$ for GS while for 5C it coincides with the last occupied π orbital and forms a degenerate π orbital. The values of Q(GS,5C) are 0.565 and 0.659 for C_5H_6 and $C_5H_5SiH_3$, respectively.

Discussion

The calculation demonstrates that the state 5C is inaccessible, since the atoms M and C of the M–C bond (M is H, SiH_3) move along the opposite directions when they start from GS. Thus, there is no reaction coordinate that could have corresponded to the [1,3] or [1,1] shifts of the group M. In the final analysis, the motion from GS to 5C leads to dissociation of the molecule resulting in the ions M^+ and $(C_5H_5)^-$.

The state 5C is not accessible either when the motion starts from 2C; this motion leads, practically, to the dissociation resulting in the radicals M· and (C_5H_5)·.

For the symmetry-forbidden antarafacial [1,5] shift, for which the group M and the four carbons lie on the same plane (the state $2C_a$), there is no reaction coordinate either.

For the symmetry-allowed suprafacial [1,5] shift, we have obtained a potential curve (Figures 3 and 4) close to the reaction coordinate. The energies of activation obtained by CNDO/2 for the degenerate rearrangements in C_5H_6 and $C_5H_5SiH_3$ are 10.2 and 6 kcal/mol, respectively. They are approximately twice lower than the experimental values (24 and 13 kcal/mol, respectively).[25,36] The energy of activation obtained through MINDO/2 (ref 17) is 18.4 kcal/mol. Although the results provided by the two methods differ in terms of the potential surface energy pattern, the optimized geometries coincide quantitatively.[11,31,32] The calculated geometry fits to the experimental one[37–39] not only qualitatively but also quantitatively well. The highest

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(36) S. McLean and P. Haynes, *Tetrahedron*, **21**, 2329 (1963).

(37) G. Liebling and R. E. Marsh, *Acta Crystallogr.*, **19**, 202 (1965).

(38) L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, **43**, 2765 (1965).

(39) J. E. Bentham, D. W. H. Rankin, *J. Organometal. Chem.*, **30**, C54 (1971).

departure (2.5%) is observed for $R(7,8)$. The calculation shows that when GS is replaced with 2C the angles θ_1, θ_2, and θ_6 are affected to the greatest extent, the carbon skeleton parameters are less affected, whereas the parameters of the atoms (H_3, H_4, and H_5) farthest from the migrating H_6 remain almost unaffected. The $R(7,8)$ bond length associated with the carbons between which the hydrogen H_6 migrates does not undergo any significant change either.

The following three regions in Figure 3 are worth special discussion: (A) minima, where energy is a quadratic function of X, $1.35 > X > 0.90$; (B) descents, where the energy change is practically linear, $0.90 > X > 0.35$; (C) passes, where energy is almost constant, $0.30 > X > -0.30$.

Region A (Ground State). The most sensitive variables are the angles θ_1, θ_6, and ψ_1 (they change from -51.5, 59.7, and 0.7° to -33, 71, and 5.4° respectively) and the orbitals no. 8 and 11 associated with the interactions $(H_6|xy)$ and $(H_1H_6|\pi)$.

Region B (Intermediate). The interaction $(H_1H_6|\pi)$ (orbital no. 12) starts rising. Consequently, the angle φ_8 (or the valence angle φ (11,7,8)) increases markedly (by 3°). Positive charge on H_6 augments strongly (from 0.063 to 0.137) while negative charges on C_9 and C_{11} decrease. The electric moment and the H_6–C_7 distance increase noticeably.

Region C (Transition State). The ring π orbital (no. 13) changes strongly. Therefore, all the C–C bond lengths (except for $R(7,8)$) and, in parallel, the π bond orders are affected. The dihedral angle ψ_1 falls from 3.7 down to 0°; the angle ψ_2 increases from 0.2 up to 1.8°. The C_7–H_6 distance becomes 0.1 Å longer. The electric moment and the charges on H_6, C_9, and C_{11} rise. The quantities Q_{AB} are affected to the greatest extent in the region under discussion; therefore this region may be the least accessible.

In going from GS to 2C, the charge on H_6 jumps from 0.028 up to 0.165. The molecular dipole moment rises from 0.84 D in GS to 2.80 D in 2C. The experimental value[40] is 0.53 D. For $C_5H_5SiH_3$, the reaction coordinate behavior is qualitatively the same (the depth of the shallow minimum at the pass is in this case within the calculation accuracy). A difference relates to the d_i values, of which the following undergo the most significant alteration: $d_{16} = 0.823$, $d_{15} = 0.886$, $d_{13} = 0.915$, and $d_{12} = 0.958$. They correspond to the following interactions: $(\pi|\pi)$; $(p_z(Si)|\pi(C_5H_5))$; $(p_xp_y(Si)|p_xp_y(C_5H_5))$; and $(H_1H_2|p_xp_y(C_5H_5))$, $(p_xp_yp_z(Si)p_xp_y(C_5H_5))$. Q(GS,2C) is 0.793. This difference is due to the fact that silicon has p orbitals and may relate to the variation in the cyclopentadienyl skeleton (see tables in ref 11 and 33), the angles θ, θ_1, and θ_2 (Table I).

Figure 4 allows one to make the following conclusions. (1) The reaction coordinate is an envelope of a set of functions $U_1, U_2, \ldots, U_n$ of one variable. The set of minima of the functions U_i has its upper and lower limits. (2) The curves U_i are unsymmetrical, except for $X = 0$. The unsymmetry prompts that there is a trend for the transition into 2C at region C; the trend for GS holds at region A. The curves are the most sensitive in the transient B region.

The data in Figure 4 can be interpreted only after additional calculations have been done.[41]

Conclusion

There is no reaction coordinate for the $[1,3]_a$-, $[1,1]_s$-, and $[1,5]_a$-sigmatropic-rearrangement mechanisms forbidden by symmetry and spatial considerations in cyclopentadiene or cyclopentadienylsilane. The configuration of the C_{5v} local-site symmetry is inaccessible, and the motion thereto leads, practically, to the dissociation resulting in ions or radicals.

A potential curve close to the reaction coordinate has been calculated for the symmetry-allowed $[1,5]_s$-rearrangement channel. Whether or not the rearrangement will be facile depends on (i) the angle formed by the M–C bond (M is H, SiH_3) and the cyclopentadienyl ring plane, (ii) the angles by which the C–H bonds nearest to the M–C bond deviate away from the ring plane, and (iii) leveling of C–C bonds in the ring.

Acknowledgment. The authors are grateful to I. P. Gloriozov for his valuable assistance in the programming.

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(41) G. A. Shchembelov, results in preparation for publication.