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CNDO/2 and INDO Calculations of a Reaction Pathway for the Sigmatropic [1, 5] H-Shift in Cyclopentadiene

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CNDO/2 and INDO calculations have been carried out in order to construct a suitable model for the activated complex during the reaction. In this reaction model the migrating hydrogen atom moves along an edge of the cyclopentadiene ring. An analysis of this situation suggests a partial electron transfer from the migrating hydrogen to the nascent cyclopentadienyl system. This charge transfer is discussed in terms of aromaticity. The calculated activation enthalpies are 10 kcal/mole (CNDO/2) and 17 kcal/mole (INDO), whereas the experimental value is ca. 24 kcal/mole [1].

Key words: Thermal sigmatropic hydrogen shifts – Transition state geometry – Aromaticity of odd-membered cycloradicals

Introduction

Thermal [1, 5] sigmatropic rearrangements have been reported in many linear and cyclic conjugated polyenes [2, 3, 4, 5]. The kinetic activation parameters of [1, 5] H-shifts show large mutual differences, $\Delta H^{\neq}$ varying between ca. 20 and 40 kcal/mole.

Starting an attempt to correlate these energy differences with transition state geometries, we performed CNDO/2 and INDO calculations according to Pople [6, 7].

In a similar way modified INDO calculations have been described earlier for the Cope rearrangement [8] and the butadiene$\leftrightarrows$cyclobutene isomerization [9]. Very recently the activation energy for the suprafacial and antarafacial [1, 5] H-shift in *cis*-piperylene has been calculated using the MINDO/CI method [10].

Results

In the transition state of the [1, 5] sigmatropic H-shift in cyclopentadiene we assumed a three-center bond between the migrating hydrogen atom and two carbon atoms. This presupposition was justified by the results of Shchembelov and Ustynyuk who considered also the four- and six-center bonds [11]. The ground state geometry was constructed using microwave spectroscopic data [12]. Concerning the bond lengths and angles which were varied in our minimization procedure, we used the values obtained by Shchembelov and Ustynyuk [11], see Fig. 1.

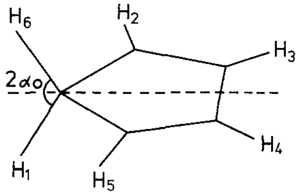


Fig. 1

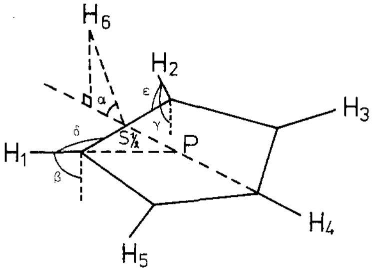


Fig. 2

Assuming a suprafacial sigmatropic shift of H_6 from C_1 to C_2, the symmetric transition state will be as depicted in Fig. 2. In this study the reaction coordinate is defined by the angle (S_RPC_1).

R	$(S_RPC_1)°$	
1/8	10	S_R, P and H_6 are situated in a plane perpendicular to the cyclopentadiene ring, while S_R moves along C_1–C_2.
1/4	20	
3/8	30	
1/2	40	

Energy minimization was carried out using the SIMPLEX method [13], with respect to eight geometrical parameters:

- angle α
- distance S_R–H_6
- angles β and γ (corresponding with out-of-plane movements of H_1 and H_2)
- angles δ and ε (in the cyclopentadiene plane)
- distance C_1–C_2 (two parameters).

Other dimensions have not been optimized by CNDO/2 or INDO methods. They were derived from the ground state dimensions by applying simple geometric relations. See Table 1.

Table 1

	R = 0	R = 1/8	R = 1/4	R = 3/8	R = 1/2	R = 1
C_3–C_4 (Å)	1.460	1.450	1.441	1.411	1.402	1.344
C_4–C_5 (Å)	1.344	1.366	1.370	1.383	1.399	1.460
$C_3C_4C_5$ (°)	109.3	109.1	108.9	108.4	108.6	109.3

Table 2. CNDO/2 results

R	C_1–C_2	S_R–H_6 (Å)	α (°)	β (°)	γ(°)	δ (°)	ε (°)	$C_1C_2C_3$ (°)	ΔE (kcal/mole)	ϱH_6
0	1.470	1.090	53.0	−53.0	0.0	127.3	124.4	108.3	0.0	0.97
1/8	1.465	1.138	63.3	−36.2	−1.9	127.7	122.7	109.8	6.0	0.95
1/4	1.460	1.119	71.0	−25.9	−2.2	129.4	123.5	109.6	10.0	0.90
3/8	1.460	1.075	76.1	−13.4	−3.2	127.6	123.3	108.4	10.4	0.85
1/2	1.470	1.050	76.6	− 6.3	−6.9	126.7	125.5	107.6	10.0	0.83

Table 3. INDO results

R	C_1–C_2 (Å)	S_R–H_6 (Å)	α (°)	β (°)	γ (°)	δ (°)	ε (°)	$C_1C_2C_3$ (°)	ΔE (kcal/mole)	ϱH_6
0	1.470	1.090	53.0	−53.0	0.0	127.3	124.4	108.3	0.0	1.00
1/8	1.470	1.146	62.9	−36.8	1.8	127.6	122.7	109.7	6.7	0.98
1/4	1.463	1.130	69.6	−26.6	−1.4	128.6	123.6	109.5	12.9	0.93
3/8	1.468	1.079	74.4	−13.8	−2.7	126.4	124.5	108.2	16.5	0.88
1/2	1.471	1.058	76.0	− 8.8	−5.8	125.9	125.3	107.0	17.2	0.86

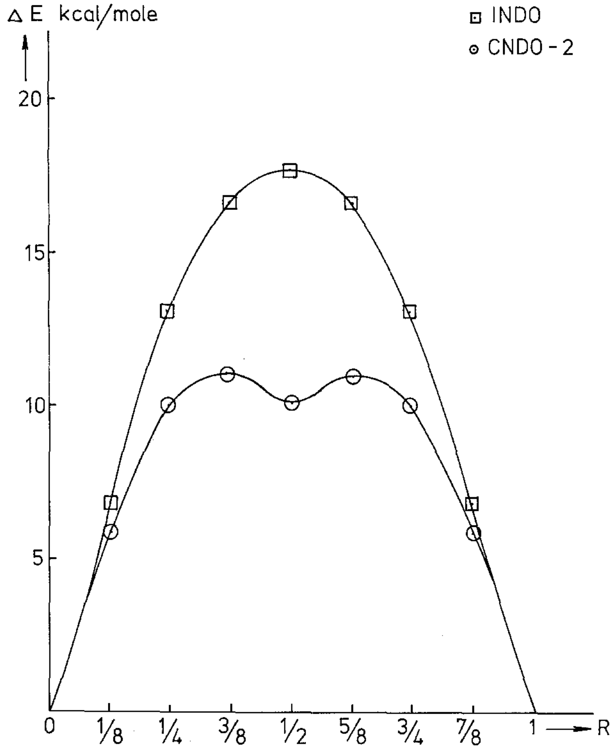


Fig. 3

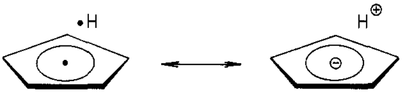
In fact, variation of these dimensions is bound to have some influence on the total energy. However, a very similar influence is to be expected in the total energy of the ground state molecule, thus the energy difference is not affected.

The resulting energies, geometries and electron densities on the migrating hydrogen atom are shown in Tables 2 and 3 and Fig. 3.

Discussion

The results of the CNDO/2 and INDO calculations for the reaction pathway indicate that the electron density on the migrating hydrogen varies between 1.0 and 0.8. This is immediately reminiscent of one of Woodward and Hoffmann's early remarks: "In the $[1,j]$ sigmatropic migration of hydrogen within an all-*cis*-polyene framework, $R_2C^1{=}CH{-}(CH{=}CH)_k{-}C^jHR_2$, one may envisage the transition state as made up by the combination of the orbital of a hydrogen atom with those of a radical containing $2k+3\pi$-electrons".

Generally, at each point of the reaction coordinate a charge transfer process takes place which can be described as a "hybrid" of two configurations. The intermediate position ($R=1/2$) can be indicated as follows:



In this situation all carbon atoms are sp^2-hybridized, thus creating optimal conditions for charge delocalization. In the CNDO/2 approximation this situation is calculated to be an intermediate. This intermediate is probably inherent to the CNDO/2 method, it does not appear in the INDO-calculations. The weights for the "no-bond" configuration and the "dative" configuration are approximately in the ratio 6 : 1. The relatively small contribution of the latter "aromatic" configuration is due to the high ionization potential of hydrogen and its small penetration magnitude. If one uses aromaticity as a criterion for predicting the course of the reaction, the question whether radicals containing $2n+3$ conjugated carbon atoms and $2n+3\pi$-electrons are aromatic, should be solved first. Dewar suggests that Hückel $4n+3$-radicals are probably aromatic although there might be some doubt about the cyclopropenyl radical [14][1].

Simple PPP calculations indeed predict aromaticity for the cyclopropenyl and cyclopentadienyl radicals, compared with the open structure radicals. The aromaticity of the cycloheptatrienyl radical has been concluded after resonance energy determining experiments [15].

We might conclude that in our picture a suprafacial hydrogen shift is only thermally allowed when both the "dative" and the "no-bond" configurations are aromatic.

The reason why "$4n+2$" aromaticity may be used as a criterion for an allowed sigmatropic process in cyclic systems, seems to be that cycloradicals containing $2n+3$ carbon atoms and $2n+3\pi$-electrons are aromatic.

The reaction pathway borne out by our calculations may be visualized as follows: between $R=0$ and $R=1/2$ the atom H_1 shifts gradually towards the plane of the cyclopentadiene ring, while H_2 will stay in or close to that plane ($C_2\,sp^2$-hybridized). This leads to a symmetrical state with both H_1 and H_2 close to (within 0.1 Å) the plane of the ring when $R=1/2$ (C_1 and $C_2\,sp^2$-hybridized). The angle α increases gradually from 53 to 77°.

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[1] In this respect it may be of interest to note that (+)-1-bromo-2-methylbutane reacts with Br˙ and DBr under formation of (+)-1-bromo-2-methyl-2-D-butane with retention of configuration [16].

This discussion is substantiated by preliminary calculations on the 1,3-cyclohexadiene system. We find analogous parameters with ringbending as an extra feature. The electron density on the migrating hydrogen ranges between 0.8 and 0.9 in the transition state. Mechanistic implications of the shifts in the cyclohexadiene ring are apparently very similar to those described for the cyclopentadiene system. A detailed description and kinetic parameters of the 1,3-cyclohexadiene system will be published in due course.

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