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AB INITIO TRANSITION STRUCTURES FOR 1,5-SIGMATROPIC HYDROGEN SHIFTS OF 1,3-PENTADIENE AND CYCLOPENTADIENE

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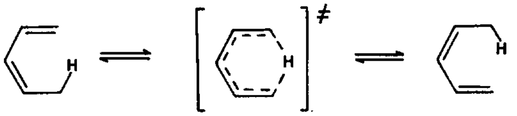
Summary: 3-21G transition structures for 1,5-sigmatropic hydrogen shifts of 1,3-pentadiene and cyclopentadiene have been located. The C--H--C angles in the transition structures are 130° and 68°, respectively. The difference in calculated activation energies for the two reactions agrees with the experimental difference.

The thermal 1,5-sigmatropic hydrogen shifts of conjugated dienes, discovered in 1961,[1] are allowed suprafacial processes involving six-membered transition states, as formulated below.[2,3]



Recently, Kwart proposed that the 1,5 hydrogen shift must occur in a linear, or nearly-linear fashion, based on the temperature dependent primary isotope effect of the reaction.[4] This is contrary to the usual non-linear formulation. During the course of our investigations, Hess and Schaad reported that the 3-21G transition structure for the isomerization of 1,3-pentadiene shows that H-transfer occurs in a significantly non-linear fashion.[5] We wish to report our identical results, and to compare the calculated transition structures for the thermal isomerizations of 1,3-pentadiene and cyclopentadiene.

Transition structures were obtained using the split-valence 3-21G basis set[6] and gradient optimizations.[7] The computed transition structures are depicted in three different representations in Figures 1 and 2. The 3-21G vibrational frequencies were determined in order to confirm the authenticity of the transition structures,[8] and to evaluate the entropies of activation, $\Delta S^{\ddagger}$, and zero point energies of reactants and transition structures.

1,3-Pentadiene Isomerization

The transition structure for the 1,3-pentadiene isomerization, shown in Figure 1, is identical to that of Hess and Schaad.[5] It is distinctly chair-like,[5] since the central carbon(C_3) moves 0.18Å out of the $C_1C_2C_4C_5$ plane. All the C-C bonds lengths (1.39-1.40Å) are nearly the same as those of benzene, in accord with the description of this as an aromatic transition structure. The C_1-C_5 distance is 2.62Å, implying no significant C_1C_5 interaction. The migrating hydrogen lies 60° out of the $C_1C_2C_4C_5$ plane and forms a 'transfer angle', CHC, of 130.° This is contrary to Kwart's model, but is consistent with the original model of Roth.[2] The partially formed (and broken) C--H bond length is 1.45Å, which is 33% stretched compared to a standard C-H bond length. For comparison, the C--H bond length in the 3-21G transition structure for the reaction of methyl radical with methane is 1.36Å.

Figure 1c is a Newman projection about the C_1-C_2 and C_4-C_5 bonds. C_1 and C_5 are significantly pyramidalized to maintain bonding with the migrating H. C_3 distorts away from planarity in order to maximize overlap of the p orbitals at C_2 and C_4 with the rotated hybrid orbitals at C_1 and C_5. The pseudo-equatorial hydrogens on C_1 and C_5 are almost eclipsed (<HCCH=7°) with the hydrogens bonded to C_2 and C_4, respectively. The pseudo-axial hydrogens are 2.08Å apart and have torsion angles of 62° with respect to the CC bonds of C_3. *It is apparent that the stereoselectivity of the isomerization of* cis-1,3-hexadiene to cis,trans-2,4-hexadiene[9] can be rationalized by the preferential formation of the equatorial methyl transition state, as has been previously proposed.[10]

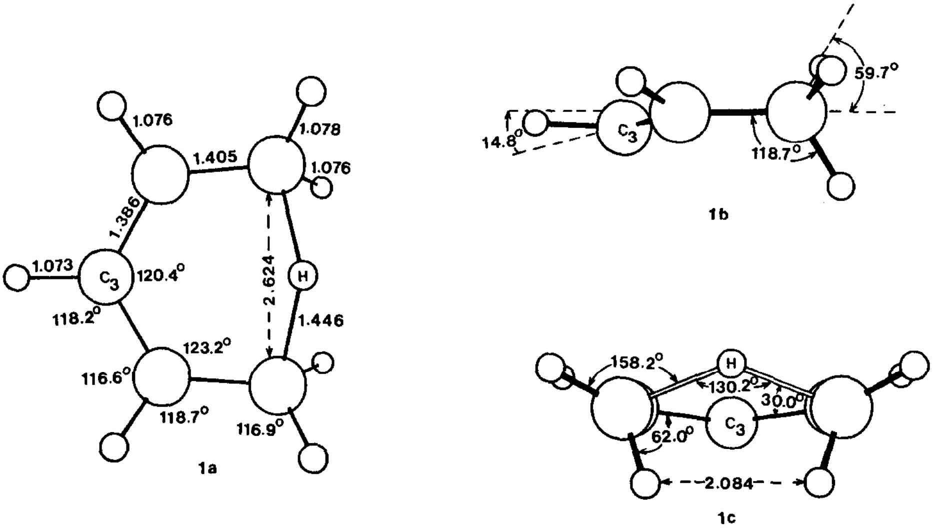


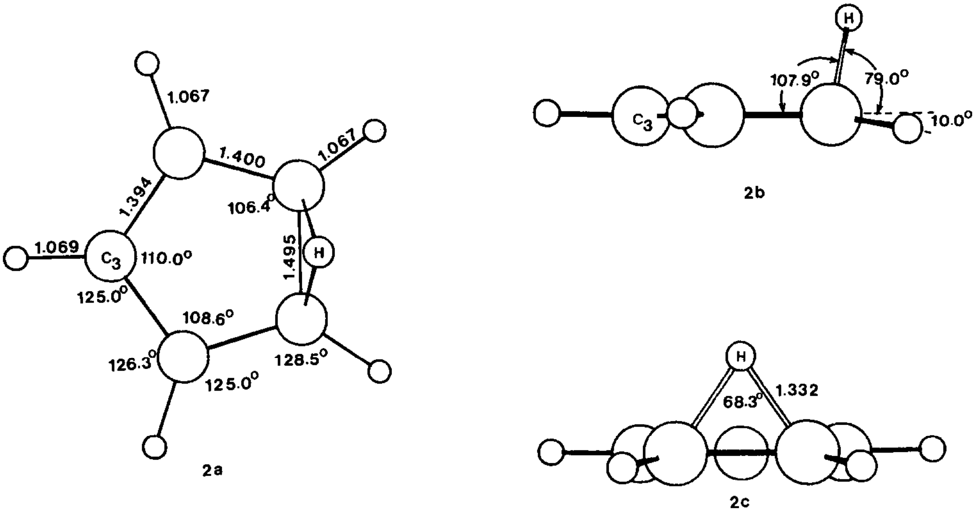
Figure 1. Three views of the 3-21G transition structure for the 1,5 hydrogen shift of 1,3-pentadiene.

The 3-21G calculated activation energy after zero-point energy corrections is 52.8 kcal/mol, 16-20 kcal/mol higher than the experimental range of 31-37 kcal/mol for 1,3-pentadiene and substituted derivatives.[2,10,11] Inclusion of correlation energy corrections would significantly lower the activation energy. For example, Radom and coworkers found that the 4-31G activation energies of both modes of 1,3 hydrogen migration in propene are lowered by 13-22 kcal/mol upon inclusion of polarization functions and correlation energy corrections.[12] The computed activation entropy, $\Delta S^{\ddagger}$, is -7.3 eu. For comparison, the activation entropy for the thermal isomerization of 1,1-dideutero-1,3-pentadiene to 5,5-dideutero-1,3-pentadiene is -4.9 eu.[2] The authenticity of the computed transition structure was confirmed by the single large 3-21G imaginary frequency(1936*i*).

Cyclopentadiene Isomerization

Three representations of the transition structure for the 1,5 hydrogen shift of cyclopentadiene are shown in Figure 2. All five carbons and the hydrogens attached to C_2-C_4 stay virtually in plane. The CC bond lengths, except that between C$_1$-C$_5$, are aromatic bond lengths. The C$_1$-C$_5$ bond is only shortened by 0.02Å relative to the 3-21G CC single bond in cyclopentadiene. Indeed, the carbon skeleton framework is unlike the cyclopentadienyl anion, in which all CC bond lengths are identical. Instead, the five carbons and migrating hydrogen form an aromatic 6-electron monocycle, with a relatively minor perturbation from the C$_1$-C$_5$ overlap. Examination of the Mulliken charges revealed that the migrating hydrogen is only slightly proton-like (0.1 more positive charge than for H$_5$ of cyclopentadiene or the migrating H in Figure 1), consistent with the model suggested by McLean.[14]

The nonmigrating hydrogens at C$_1$ and C$_5$ are 10° out of plane, a very small distortion compared to that in 1,3-pentadiene. The migrating hydrogen is 79° out of plane, 19° more than in 1,3-pentadiene. The 'transfer angle', CHC, of 68° is much smaller than for the acyclic counterpart, due to the closeness of the carbons involved in the transfer. The partially formed (and broken) C--H bond length is 0.12Å shorter than that in the 1,3-pentadiene transition structure.



2a

2b

2c

Figure 2. Three views of the 3-21G transition structure for the 1,5 hydrogen shift of cyclopentadiene.

The zero-point energy corrected activation energy of 39.7 kcal/mol for cyclopentadiene is 18 kcal/mol higher than the experimental quantity measured by Roth for pentadeuterocyclopentadiene[13] and by McLean for substituted cyclopentadienes.[14] The calculated activation energy for cyclopentadiene isomerization however is 13 kcal/mol lower than that of 1,3-pentadiene, in close agreement with the experimental difference. The calculated activation entropy, $\Delta S^{\ddagger}$, is +0.20 eu. The experimental entropy of activation for the isomerization of 1,2,3,4,5-pentadeuterocyclopentadiene to 1,2,3,5,5-pentadeuterocyclopentadiene is -3.3 eu.

The 3-21G imaginary frequency for cyclopentadiene(1552i) is smaller than in 1,3-pentadiene. More O'Ferrall found a direct relationship between the transfer angle,<CHC, and the magnitude of the imaginary frequency.[15] Indeed, the transfer angle(68°) and imaginary frequency(1552i) for cyclopentadiene are smaller than the transfer angle(130°) and imaginary frequency(1936i) for 1,3-pentadiene isomerization.

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