

The Mechanism of the Photochemical Hydrogen Migration in 1,3,5-Cycloheptatriene: A Theoretical Study

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Abstract: Based on CASSCF calculations for the reaction profile of the photochemical [1,7]-sigmatropic hydrogen shift in 1,3,5-cycloheptatriene (CHT), the detailed mechanism of the excited-state reaction is discussed. The results are in agreement with the observed ultrafast rates for passage from the initially-excited $1A''$ state by way of the dark $2A'$ state to the ground-state ($1A'$) potential-energy surface. The kinetics and the selectivity of the reaction are characterized by a small energy barrier on the dark $2A'$ state that separates the excited-state minimum

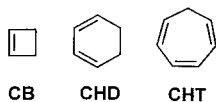
from a conical intersection at pericyclic geometries. This intersection is responsible for efficient, excited-state deactivation. At the CASSCF level the barrier height is calculated to be $7.3 \text{ kcal mol}^{-1}$. If dynamic correlation effects are taken into account with the CASPT2 method, the barrier is reduced to $3.8 \text{ kcal mol}^{-1}$. The existence of an excited-state barrier

as the decisive mechanistic feature of the hydrogen migration was verified by considering 1-substituted CHT. The barriers calculated for sigmatropic shifts away from and toward the substituent differ considerably. In agreement with experimental observation, the smaller barrier is found for migration away from an acceptor and toward a donor substituent. The differences in barrier height are in excellent agreement with the experimentally observed product distribution.

Keywords: ab initio calculations • 1,3,5-cycloheptatriene • photochemical selectivity • reaction mechanisms • sigmatropic shift

Introduction

It has been known for some time that ground-state forbidden pericyclic reactions proceed photochemically by way of a totally symmetric dark state.^[1, 2] Therefore, they must proceed in two stages, with the first stage being the transition from the spectroscopic $1A''$ state (in C_s symmetry) to the $2A'$ state. This transition has been shown to be very fast.^[3] The measured lifetimes of the spectroscopic states for the ring-opening reactions of cyclobutene (CB)^[4] and cyclohexadiene (CHD)^[5] are less than 30 fs, and for the suprafacial sigmatropic [1,7]-H shift in cyclohexatriene (CHT) values between 35 and 70 fs have been reported.^[6] In the second stage the ground-state potential-energy surface (PES) of the product is reached. Earlier investigations claimed that the time required for this stage is 6 ps for CHD^[5b] and 26 ps for the [1,7]-H shift in



CHT.^[7] However, recent measurements suggest much shorter times, less than 100 fs for the ground-state repopulation of CHD^[5c, 8] and CHT.^[8, 9]

The short, excited-state lifetimes are known to be due to conical intersections between the excited state and the ground-state PES;^[10] these have recently been found to be quite common in nonadiabatic singlet photoreactions.^[10, 11] Passage through such a conical intersection is very fast and occurs within one vibrational period.^[12] Longer excited-state lifetimes, for example, longer than 100 fs, indicate some retardation of the motion on the excited-state PES toward the conical intersection. In CHD, for instance, a sloped conical intersection^[13] was located about 1 kcal mol^{-1} above the excited state of the ring-opened product.^[14] This is consistent with the reported product appearance time.^[8] More recent calculations yield an excited-state minimum-energy path toward an asymmetric stationary point, from which the system can evolve along a path with virtually no energy barrier toward the conical intersection.^[15]

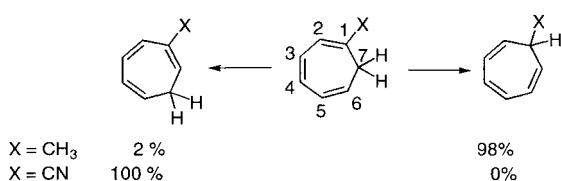
The appearance time for the [1,7]-H shift reaction in CHT suggests that also in this case a conical intersection occurs that might be somewhat less easily accessible than the one in CHD. For a concerted reaction, such a conical intersection is to be expected in the region of the pericyclic geometries with the migrating hydrogen between the two carbons involved. For unsubstituted CHT, reactant and product are the same and

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the paths of the forward and reverse reactions must be equivalent. Therefore, when the molecule leaves the excited-state PES for fast relaxation to the ground-state PES, the hydrogen atom will have completed half its journey. On the basis of the small mass of the migrating hydrogen, the hydrogen-shift reaction in CHT would be expected to be considerably faster than the ring-opening reaction of CHD. The fact that this is not the case must be a result of some excited-state energy barrier or energetically up-hill path toward the conical intersection.

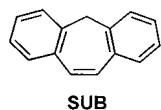
Two distinct models have been proposed to explain the regioselectivity of the [1,7]-H shift in substituted CHT. Paulick et al.^[16] proposed a model according to which excitation of CHT leads to a near-planar intermediate from which the sigmatropic shift takes place as dictated by orbital symmetry conservation. This is in agreement with detailed resonance Raman studies of the [1,7]-sigmatropic shift as well as the low fluorescence quantum yield of CHT. These studies showed^[6] that the hydrogen-shift reaction proceeds sequentially with planarization of the ring occurring on the $1A''$ surface before rapid internal conversion to a lower-energy surface upon which the sigmatropic shift occurs. Another mechanism has been proposed by Tezuka et al.^[17] which accounts for the regioselectivity of the sigmatropic shift in substituted CHT on the basis of sudden polarization^[18] that results from twisting one of the terminal ethylenic bonds. However, it should be mentioned that Paulick^[16] as well as Tezuka et al.^[17] considered only the spectroscopic state and did not take into account the possibility that the hydrogen shift might occur in the dark state.

In this paper we report the results of quantum-chemical calculations for the [1,7]-hydrogen shift in CHT, 1-cyanocycloheptatriene (CN–CHT), and 1-methylcycloheptatriene (Me–CHT) in order to discuss the effect of electron-acceptor and -donor substituents on the regioselectivity. It has been shown that in 1-cyanocycloheptatriene, the hydrogen atom moves exclusively to the unsubstituted terminal carbon of the heptatriene moiety, while in 1-methylcycloheptatriene only 2% of the product exhibits this regiochemistry and 98% corresponds to a hydrogen shift toward the substituted carbon (Scheme 1).^[19]



Scheme 1. Representation of the effect of substituents on the [1,7]-hydrogen shift in cycloheptatriene

In addition, the discussion of the [1,7]-H shift in CHT finally confirms the hypothesis that the different photochemical behavior of CHT and its derivatives on the one hand and dibenzocycloheptatriene (suberene, SUB) on the other is due to the involvement of different electronic excited states in the photoreactions of these



molecules.^[20] SUB exhibits photodeprotonation, the photochemical reactivity expected for the $1A''$ excited state.^[21] However, for CHT this reaction is not observed, owing to a rapid depopulation from the initially-prepared $1A''$ excited state into the $2A'$ state, the characteristic reaction of which is a very efficient [1,7]-sigmatropic hydrogen shift. In a previous paper^[22] we showed that the photodecarboxylation of cycloheptatrienyl carboxylic anion, which yields the same intermediate cycloheptatrienyl anion as the photodeprotonation reaction,^[23] is indeed the reaction of the $1A''$ state. In the present paper we will show that the characteristic reaction of the $2A'$ state is the [1,7]-sigmatropic hydrogen shift and discuss the fast deactivation of the $1A''$ state, which is the reason why its reactivity is not observed.

Computational Methods

Quantum-chemical calculations on the mechanism of photoreactions are rather demanding, since excited states can be described only by taking into account a sufficient amount of configuration interaction (CI). Therefore as in previous work on excited-state reactivity^[22] we used the semiempirical MNDOC-CI method (modified neglect of diatomic overlap parametrized for taking into account correlation effects explicitly) to explore excited-state geometries and potential-energy surfaces before using CASSCF methods to obtain the final results.

The MNDOC-CI method^[24] is based on spin-adapted CFSs (configuration state functions) and includes single and double excitations with respect to one or several reference configurations within a limited active space. For the determination of the potential-energy surfaces, the active space was chosen to comprise the three highest-occupied and the three lowest-unoccupied MOs of the π system. The single and double excitations with respect to the five reference configurations Φ_0 , Φ_{H-L} , Φ_{H-L+1} , Φ_{H-1-L} , and $\Phi_{H-L,H-L}$ that dominate the three lowest singlet states (where H and L denote the highest occupied and the lowest unoccupied MO, respectively) yielded a total of 126 configurations.

For the CASSCF calculations^[25] the two-step quasi-Newton method included in the GAUSSIAN 94 package was used.^[26] The active space included the eight MOs that were primarily composed of carbon p_x AOs and the s orbital of the migrating hydrogen; with eight electrons in these eight orbitals (8-in-8) a total of 1764 configurations resulted. Transition states were located starting from the MNDOC-CI geometries with a 3-21G basis set. The error associated with this choice was estimated by reoptimizing some stationary points with the 6-31G** basis set. The difference in the 6-31G** energies for these geometries was less than 0.5 kcal mol⁻¹. Conical intersections were optimized starting from the MNDOC-CI geometry for the S_1/S_0 conical intersection, while the S_2/S_1 conical intersection was located starting from the planar ground-state MNDOC-CI minimum geometry. In both cases the best convergence was obtained by including only the π MOs in a reduced 6-in-6 active space with the 6-31G* basis set. Increasing the active space to 8-in-8 did not significantly change the geometries and energies. Vibrational analyses were performed to verify all minima and transition structures both for the MNDOC-CI and the CASSCF results. Excitation energies at the ab initio CASPT2 level of theory^[27, 28] were obtained with the MOLCAS 4.0 program^[29] and the ANO basis set (C: 3s2p1d, H: 2s1p). For CHT initially the same active space was used as in the CASSCF calculation. However, calculations for the $1A'$, $2A'$, and $1A''$ states of CHT with six electrons in six orbitals yielded excitation energies that differed from those obtained with the larger active space by only 0.1–0.2 eV; the same range has been observed in other cases.^[30] The CASSCF wavefunction that was used as the reference function for the perturbational treatment was obtained by averaging over the singlet states of interest and adequate symmetry, and finally reoptimizing the state under consideration. Following the same procedure, CASPT2 calculations were performed for all the characteristic points of the reaction coordinate, especially to establish the validity of the conical intersections. However, for the conical intersection calculations, a

single-state CASSCF reference function optimized individually for each of the two degenerate states was used.

Owing to the larger size of the substituted systems Me-CHT and CN-CHT, the CASPT2/D method, as implemented in the MOLPRO96.4 program system^[31] was employed with the 6-31G* basis set. As for CHT, a 6-in-6 active space was chosen, with 16 and 18 core orbitals. This yielded in all cases 16 orbitals to be included in the perturbational treatment.

Results

As a first step in the discussion of the hydrogen shift reaction in CHT, potential-energy surfaces of the two lowest singlet states were calculated with the semiempirical MNDOC-CI approach. The results are shown in Figure 1, in which the energy is plotted against the distance R between the migrating hydrogen H_m and the center of the C_1-C_7 bond, and the angle θ which describes the rotation about an axis through C_4 and the center of the C_1-C_7 bond (i.e., in the molecular plane and perpendicular to the C_1-C_7 bond). Subject to the condition that all atoms except H_m , H_1 , and H_7 are coplanar, the other internal coordinates were optimized for the lowest excited state S_1 and for the ground state S_0 . The results are displayed on the left ($\theta = 30^\circ - 90^\circ$) and the right ($\theta = 90^\circ - 150^\circ$) hand side of Figure 1, respectively. Consequently, the diagram does not exhibit a plane of symmetry with respect to the transition state for the ground-state reaction at $\theta = 90^\circ$. In this figure, vertical excitation occurs at the planar ground-state structure in the right half of the diagram. However, the photochemical hydrogen-shift reaction starts on the S_1 surface at the relaxed excited-state minimum $4'$, then crosses a potential energy barrier at the transition state $5'$ and reaches the pericyclic geometry $6'$ where the two states S_1 and S_0 are degenerate. This region thus corresponds to a conical intersection, from which either the reactant or the product may be reached. Energies of the characteristic points along this reaction path calculated at fully optimized geometries are collected in the first column of Table 1. Our calculations showed that for these optimized structures,^[32] the $1A''$ excited

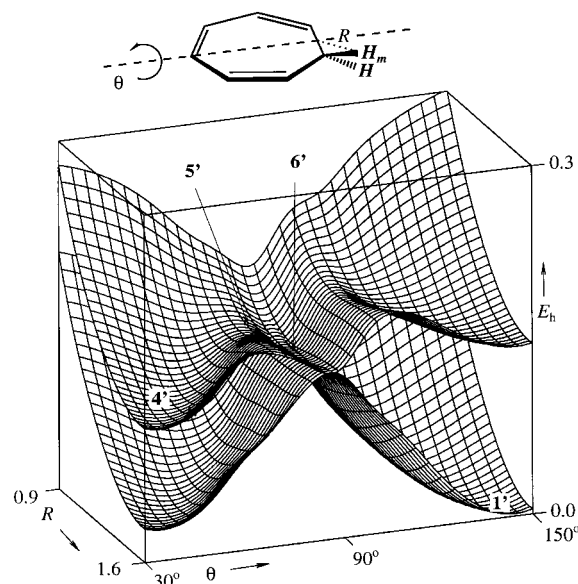


Figure 1. MNDOC-CI potential-energy surfaces for the [1,7]-H shift reaction of CHT. The definition of the coordinates R and θ of the migrating hydrogen H_m are shown on the top. Geometries were optimized for the ground state (right half of the diagram) and for the first-excited, singlet state (left half of the diagram).

state lies in the Franck–Condon region $0.4 \text{ kcal mol}^{-1}$ below the $2A'$ state, but owing to interstate crossing, the minimum $4'$ ($2A'$) on the totally symmetric potential-energy surface is reached instead of the higher $2'$ ($1A''$) minimum (however, see below). The transition state $5'$ between the $2A'$ minimum and the pericyclic geometry $6'$ is calculated to be $23.3 \text{ kcal mol}^{-1}$ higher in energy.

The existence of an excited-state barrier on the $2A'$ surface would be in agreement with the observation that in solution ground-state CHT appears only 26 ps after photolysis.^[7] However, very recent gas-phase experiments indicate an appearance time of less than 100 fs.^[9] Thus, the calculated

Table 1. Reaction coordinate of the [1,7]-H shift of cycloheptatriene. Absolute CASSCF and CASPT2 energies [a.u.] of S_0 , S_1 and S_2 at the geometries **1–6**, MNDOC-CI and relative energies (in brackets) [kcal mol^{-1}].

Geometry	MNDOC-CI		CASSCF		CASPT2	
	3-21G	6-31G*	6-31G	ANO	ANO	ANO
Ground state S_0						
1 (S_0 -min)	65.9 (0.0)	–268.28214 (0.0)	–269.76265 (0.0)	–269.78256 (0.0)	–269.80525 (0.0)	–270.66516 (0.0)
2 (S_2 -min)	71.3 (5.5)		–269.68872 (46.4)		–269.73388 (45.1)	–270.60521 (37.6)
3 (S_2/S_1 -CI)			–269.73344 (18.4)		–269.70401 (18.7)	–270.63992 (15.8)
4 (S_1 -min)	81.3 (15.5)		–269.70973 (33.2)		–269.74692 (36.6)	–270.62391 (25.9)
5 (S_1 -TS)	124.2 (58.4)		–269.67414 (55.5)		–269.71342 (57.6)	–270.59605 (43.3)
6 (S_1/S_0 -CI)	146.0 (80.7)	–268.11312 (106.0)	–269.61503 (95.4)	–269.63818 (90.5)	–269.65511 (94.2)	–270.54555 (75.1)
Excited state S_1						
1 (S_0 -min)	156.8 (21.8)	–268.05879 (38.7)	–269.54214 (39.9)	–269.55706 (50.3)	–269.58757 (38.6)	–270.48260 (36.5)
2 (S_2 -min)	141.8 (6.8)		–269.57313 (17.2)	–269.60671 (19.2)	–269.61668 (12.9)	–270.50081 (25.1)
3 (S_2/S_1 -CI)			–269.56291 (26.8)		–269.60753 (26.1)	–270.52042 (12.8)
4 (S_1 -min)	135.0 (0.0)	–268.11972 (0.0)	–269.60570 (0.0)	–269.63725 (0.0)	–269.64917 (0.0)	–270.54078 (0.0)
5 (S_1 -TS)	158.3 (23.3)	–268.10371 (10.0)	–269.58404 (13.6)	–269.62562 (7.3)	–269.62967 (12.7)	–270.53470 (3.8)
6 (S_1/S_0 -CI)	146.0 (11.0)	–268.11312 (4.1)	–269.61503 (3.0)	–269.63818 (–0.6)	–269.65364 (12.8)	–270.54664 (–3.7)
Excited state S_2						
1 (S_0 -min)	157.2 (8.0)	–268.01979 (31.3)	–269.50231 (31.4)	–269.53692 (33.9)	–269.54930 (30.9)	–270.47302 (27.8)
2 (S_2 -min)	149.2 (0.0)	–268.06964 (0.0)	–269.55233 (0.0)	–269.59028 (0.0)	–269.59854 (0.0)	–270.51735 (0.0)
3 (S_2/S_1 -CI)			–269.56291 (–6.6)		–269.60760 (–5.7)	–270.52489 (–4.7)
4 (S_1 -min)	155.2 (6.0)					

value of the barrier height is definitely much too high. In agreement with experiment^[6] planarization of the CHT ring begins immediately after excitation. Even whilst the equilibrium ground-state conformation is boatlike, the minimum **4'**, the transition state **5'**, and the pericyclic structure **6'** are all calculated to be planar. The transition structure no longer exhibits C_s symmetry, as the migrating hydrogen has moved slightly towards C_7 with distances of 1.23 Å for $r(C_1-H)$ (as compared with 1.12 Å for the ground-state equilibrium structure) and 1.56 Å for $r(C_7-H)$. As a consequence of the incipient hydrogen-shift reaction, the unsaturated carbons become polarized and exhibit alternating charges, with the accepting carbon being positively charged. Thus, an electron-donating or electron-withdrawing substituent on the carbon adjacent to the methylene group will stabilize or destabilize, respectively, the transition state for migration of H_m to the substituted carbon, in agreement with the experimentally observed regioselectivity. Finally at the pericyclic geometry, both the C_1-H and C_7-H lengths are equal to 1.41 Å. Since the excited state S_1 and the ground state S_0 are degenerate at this geometry, a fast transition occurs to the ground-state potential-energy surface, which slopes down steeply toward the product or back to the reactant.

Although for the [1,7]-sigmatropic shift reaction of CHT the semiempirical calculations yield a reaction mechanism that is in good qualitative agreement with all the experimental observations, the quantitative results, and in particular the value of 23 kcal mol⁻¹ for the excited-state barrier, require redetermination on the basis of more reliable ab initio methods. We therefore performed CASSCF as well as CASPT2 calculations for the characteristic points of this reaction, starting from the MNDOC-CI results. The CASSCF-optimized structures shown in Figure 2 are in most cases in perfect agreement with the MNDOC-CI-optimized structures, the only exception being the S_2 minimum (see below). The calculated energies are collected in Table 1.

Although the MNDOC-CI- and CASSCF-optimized ground-state geometries agree very well, the order of the excited states at this geometry, that is, in the Franck–Condon region, is interchanged. At the CASSCF level the $2A'$ state is 0.56 eV (13 kcal mol⁻¹) below the $1A''$ state. The calculated excitation energies (Table 2) are much higher than the experimental values. It is well-known that dynamic correlation

Table 2. Excitation energies [eV] of cycloheptatriene.

	MNDOC-CI	CASSCF		CASPT2	Exptl
		6-31G	ANO ^[a]	ANO ^[a]	
$2^1A'$	3.97	6.14	5.92	4.96	(4.56) ^[b]
$1^1A''$	3.95	6.69	6.97	5.23	4.85 ^[c]

[a] ANO basis set C: 3s2p1d, H: 2s1p, cf. ref. [29]. [b] Estimated from MCD spectrum.^[33] [c] Ref. [34].

is required to obtain realistic values for the excitation energies. We therefore performed CASPT2 calculations at the CASSCF-optimized ground-state geometry with the ANO basis set^[29] and obtained an excitation energy for the spectroscopically allowed $1A''$ state in fair agreement with the experimental value^[34–36] (cf. Table 2). The $2A'$ state is still 0.27 eV (6.2 kcal mol⁻¹) below $1A''$. We thus conclude that dynamic correlation affects both excited states such that their

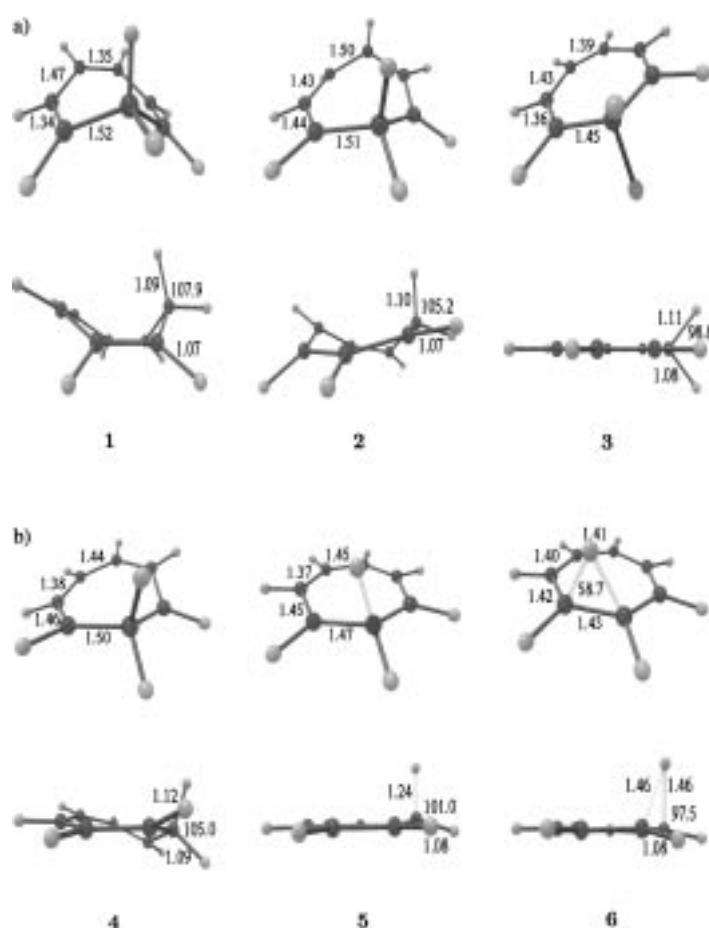


Figure 2. a) CASSCF-optimized geometries at characteristic points along the [1,7]-H shift reaction coordinate of CHT for the initial steps in the second-excited singlet state S_2 ($1A''$): **1** Franck–Condon geometry, **2** S_2 minimum, **3** S_2/S_1 conical intersection. The upper part shows the “top view” and the lower part the “side view”. b) “Top view” (upper part) and “side view” (lower part) of the CASSCF-optimized structures at characteristic points along the [1,7]-H shift reaction coordinate of cycloheptatriene (CHT) in the first-excited singlet state S_1 ($2A'$): **4** S_1 minimum, **5** S_1 transition state, **6** S_1/S_0 conical intersection.

ordering is unchanged and that their relative energies are well described by the CASSCF results.

If fast internal conversion from the initially-excited $1A''$ state into the lower $2A'$ state is possible, the general mechanism of the [1,7]-H shift in CHT derived from the semiempirical results shown in Figure 1 remains unchanged. Starting from the minimum at geometry **4** on the lower excited-state surface (cf. Table 1), the conical intersection at the pericyclic geometry **6**—0.6 kcal mol⁻¹ lower in energy—is reached through an excited-state barrier. Both the semiempirical and ab initio methods give very similar results for the geometry as well as the charge distribution in the transition structure **5** (Figure 3), and the CASSCF value of 7.3 kcal mol⁻¹ for the barrier although still fairly high is much more reasonable than the semiempirical result. CASPT2 calculations with the ANO basis set reduce this value to 3.8 kcal mol⁻¹, as shown in Table 1 (last column).

Thus it remains to be shown how the S_1 minimum at the geometry **4** is reached from the excited $1A''$ state. Following the gradient in the Franck–Condon region, a shallow S_2 minimum at geometry **2** is reached. This relaxation to the S_2

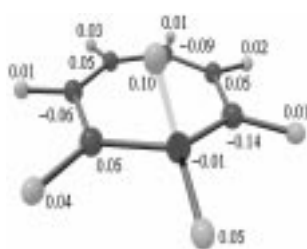


Figure 3. Charge distribution in the excited-state transition state **5** (S_1 -TS) for the [1,7]-H shift reaction in CHT.

state corresponds to a C–C stretch mode, and is similar to the initial S_1 excited-state relaxation of all-*trans*-hexatriene and related systems.^[15] The geometric structure of the S_2 minimum **2** (see Figure 2a) corresponds to two allylic π systems in the ring, the planes of which intersect at an angle of 52° . The two lowest vibrations at this geometry are deformation modes, the combination of which leads to a planarization of the ring. Following planarization, an S_2/S_1 conical intersection at **3** is reached. This conical intersection is approximately 6 kcal mol^{-1} lower in energy than the S_2 minimum at **2**, and $26.8 \text{ kcal mol}^{-1}$ higher than the S_1 minimum at **4**. The corresponding CASPT2 values are $4.7 \text{ kcal mol}^{-1}$ and $12.8 \text{ kcal mol}^{-1}$, respectively (see Figure 4 and Table 1). This explains the fast internal conversion from the initially-excited $1A''$ state to the S_1 minimum at **4**.

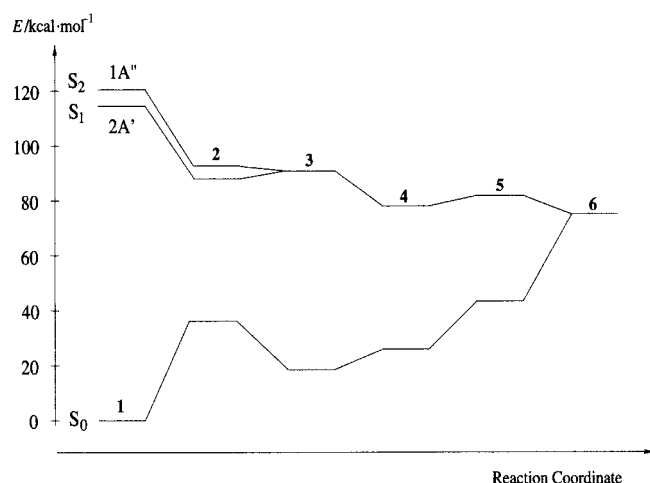


Figure 4. Total excited-state reaction path for the [1,7]-H shift reaction of CHT. CASPT2 energies E in kcal mol^{-1} are plotted relative to the energy of the ground-state minimum **1**.

The total excited-state reaction path for the [1,7]-hydrogen shift is schematically summarized in Figure 4, where CASPT2 energies are given. The decisive features of the mechanism described by this reaction path are the fast internal conversion from the spectroscopic $1A''$ state by way of an S_2/S_1 conical intersection and the existence of an excited-state barrier, which determines the kinetics as well as the selectivity of the reaction.

An important verification of this proposed mechanism comes from a comparison of the nonequivalent barriers in 1-substituted CHT. As examples of electron-accepting and -donating substituents we chose the methyl and cyano groups, respectively. Excited-state minima of 1-cyanocycloheptatriene (CN–CHT; **7**) and of 1-methylcycloheptatriene

(Me–CHT; **9**), and transition structures **8a–8b** (CN–CHT) and **10a–10b** (Me–CHT) were optimized; the results are collected in Table 3. The barriers calculated for sigmatropic shifts away from the substituent and toward the substituent

Table 3. Energies E [a.u.] of the excited-state minima **4**, **7** and **9** and the transition states **5**, **8a**, **8b**, **10a**, and **10b** for the H-shift reaction in cycloheptatriene (CHT), 1-cyanocycloheptatriene (CN–CHT) and 1-methylcycloheptatriene (Me–CHT). Barrier heights E are given in kcal mol^{-1} .

	CASSCF		CASPT2D		CASPT2	
	E	ΔE	E	ΔE	E	ΔE
CHT						
4 (S_1 -min)	-269.63752	0.0	-269.93536	0.0	-270.54075	0.0
5 (S_1 -TS)	-269.62562	7.5	-269.92497	4.0	-270.53470	3.8
CN–CHT						
7 (S_1 -min)	-361.38655	0.0	-361.80373	0.0		
8a (S_1 -TS ₁)	-361.35548	19.5	-361.78172	13.8		
8b (S_1 -TS ₆)	-361.37982	4.2	-361.79934	2.8		
Me–CHT						
9 (S_1 -min)	-308.68168	0.0	-309.04565	0.0		
10a (S_1 -TS ₁)	-308.66784	8.7	-309.03752	5.1		
10b (S_1 -TS ₆)	-308.66141	12.7	-309.03109	9.1		

differ considerably. The CASSCF values with a 6-31G* basis set are $4.2 \text{ kcal mol}^{-1}$ and $19.5 \text{ kcal mol}^{-1}$, respectively, for the cyano-substituted and $12.7 \text{ kcal mol}^{-1}$ and $8.7 \text{ kcal mol}^{-1}$ for the methyl-substituted CHT. CASPT2D calculations reduce these values to $2.8 \text{ kcal mol}^{-1}$, $13.8 \text{ kcal mol}^{-1}$, $9.1 \text{ kcal mol}^{-1}$, and $5.1 \text{ kcal mol}^{-1}$, respectively (see Figure 5). In agreement

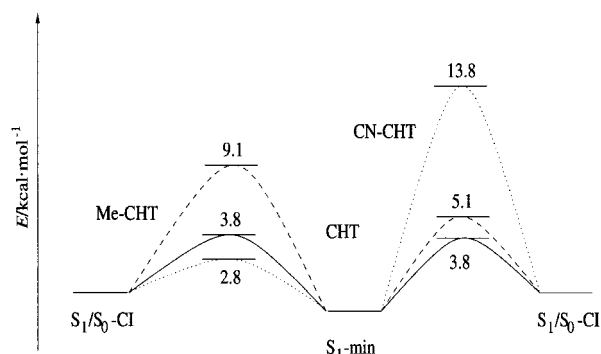


Figure 5. Schematic plot of the barrier heights E in kcal mol^{-1} for the hydrogen shift toward (right side) and away from (left side) the substituent in Me–CHT (broken line) and CN–CHT (dotted line). For CHT (solid lines) the two barriers are equivalent.

with experimental observations the smaller barrier is found for migration away from the acceptor and toward the donor substituent. Moreover, the differences in barrier height, which amount to $15.3 \text{ kcal mol}^{-1}$ (or $11.0 \text{ kcal mol}^{-1}$ on the CASPT2 level) for CN and $4.0 \text{ kcal mol}^{-1}$ for CH_3 are in excellent agreement with the experimentally observed product distributions. According to the Arrhenius equation these correspond to a distribution of 100:0 in the case of CN and 0.2:99.8 in the case of CH_3 for products of a sigmatropic shift away from and toward the substituent; these values compare well with the experimental values of 100:0 and 2:98.^[37] This very good agreement confirms the importance of the excited-state barrier and also confirms the mechanism for the [1,7]-sigmatropic shift derived from the calculated potential-energy surfaces shown in Figure 1.

Discussion

The important features of the mechanism for the [1,7]-hydrogen shift reaction of CHT are the fast internal conversion of the initially prepared excited $1A''$ state to the lower energy surface of the dark $2A'$ state, the existence of an excited-state energy barrier on the $2A'$ surface, and the occurrence of a conical intersection region located halfway along the reaction coordinate and at a lower energy than the $2A'$ minimum.

In a very recent experimental investigation by Fuß et al.^[9] three consecutive phases of the excited-state reaction could be distinguished. The first 10 fs and subsequent 60 fs were assigned to the times required to travel through two regions of the initially-excited $1A''$ state, and the final period of 70 fs to the sojourn on the lower S_1 surface and departure to the ground state. This assignment is strongly supported by our results. Although we could not identify the minimum-energy path from the Franck–Condon region to the S_2/S_1 conical intersection, two regions can be clearly distinguished for the reaction on the $1A''$ surface. The first corresponds to a very steep descent from the Franck–Condon region to the S_2 minimum, which is approximately 30 kcal mol^{-1} lower in energy ($33.9 \text{ kcal mol}^{-1}$ at the CASSCF and $27.8 \text{ kcal mol}^{-1}$ at the CASPT2 level). Only comparatively small geometry changes are involved that correspond to a C–C stretch mode combined with planarization of the ring and some rotational motion about the $C_3=C_4$ double bond (see Figure 2a). The second region extends from the S_2 minimum to the S_2/S_1 conical intersection and is rather flat with a barrier smaller than 1 kcal mol^{-1} . The total energy decrease is $6.6 \text{ kcal mol}^{-1}$ at the CASSCF and $4.7 \text{ kcal mol}^{-1}$ at the CASPT2 level. At the S_2/S_1 conical intersection the ring is planar, and the two C–H bonds of the CH_2 group that is perpendicular to the ring are still equivalent. This seems to contradict the conclusions of Fuß et al.^[9] who interpreted the isotope effect in region 2 by assuming a displacement along the hydrogen-shift coordinate. However, from the optimized geometries shown in Figure 2a we conclude that the isotope effect may be due to a symmetrical C–H stretch motion, which changes the C–H bond lengths from 1.08 \AA at the S_2 minimum to 1.11 \AA at the S_2/S_1 conical intersection.

The gradient difference vector \mathbf{x}_1 and the nonadiabatic coupling vector \mathbf{x}_2 at the S_2/S_1 conical intersection **3**, which span the branching space, are shown in Figure 6. They correspond to an antisymmetric deformation of the ring system and a symmetric C–C bond stretch motion, respec-

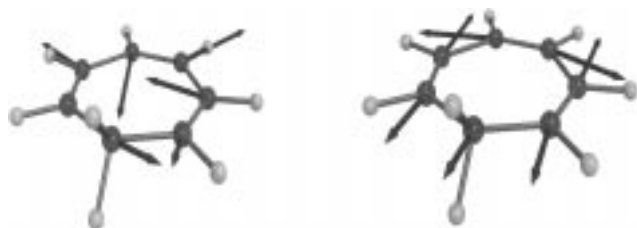


Figure 6. Gradient difference vector \mathbf{x}_1 (left) and nonadiabatic coupling vector \mathbf{x}_2 (right) at the S_2/S_1 conical intersection **3** for the [1,7]-H shift reaction of CHT.

tively. A comparison of the geometry at **3** (Figure 2a) with that of the S_1 minimum **4** (Figure 2b) reveals that these are just the geometry changes (bond alternation and deformation of the planar ring) that open a reaction path to the S_1 minimum **4**. From the geometry at the S_2/S_1 conical intersection it follows that the [1,7]-hydrogen shift motion takes place only on the lower S_1 ($2A'$) potential-energy surface. Since for practically all nonadiabatic, singlet photoreactions studied during the last ten years or so a conical intersection has been identified as the point of return to the ground-state surface, it is not surprising that such a characteristic was also located for the reaction under consideration. However, it is known that passage through a conical intersection in general occurs within one vibrational cycle.^[12] This implies that the longer appearance time of the product as compared with CHD must be due to the existence of an excited-state energy barrier on the $2A'$ surface. In view of the literature value of 26 ps for the ground-state recovery of photoexcited CHT,^[6] the barrier should be appreciable. However, the recent experimental value of less than 100 fs,^[9] suggests a barrier similar to or somewhat larger than that in CHD, as for the same barrier height the small mass of the migrating hydrogen in CHT would imply a higher speed and therefore a shorter appearance time than for CHD. In comparison with CHD, for which a barrier height of the order of 1 kcal mol^{-1} has been calculated,^[14] the CASPT2 value of $3.8 \text{ kcal mol}^{-1}$ appears to support our interpretation of the recent measurements^[9] and is in good agreement with the photophysics observed for CHD^[5] and CHT.^[7, 9]

In order to establish the origin of this excited-state barrier, we first consider the geometry changes in going from the S_1 minimum at **4** to the transition state at **5**. Apart from a more or less complete planarization of the ring, which has also been inferred from resonance Raman measurements,^[6] the C–H_m bond is elongated from 1.12 \AA to 1.24 \AA , and the C–C bond length between the CH_2 group and the carbon not involved in the hydrogen shift decreases from 1.50 \AA to 1.42 \AA . These geometry changes are connected with appreciable charge reorganization, leading to major changes in the wave function that are due to an increasing contribution from the Φ_{H-L} configuration (cf. Table 4). Initially, this configuration dom-

Table 4. Dominating configurations (CI coefficients in brackets) of the wavefunction of the electronic ground-state S_0 and the first two excited singlet states S_1 and S_2 at geometries along the reaction profile.

Geometry	Ground State S_0	Excited State S_1	Excited State S_2
1 (S_0 -min)	Φ_0 (+0.94)	Φ_0 (–0.55)	Φ_{H-L} (± 0.57)
	$\Phi_{H-L,H-L}$ (–0.13)	$\Phi_{H-L,H-L}$ (+0.37)	
		Φ_{H-1-L} (± 0.26)	
		Φ_{H-L+1} (± 0.24)	
2 (S_2 -min)	Φ_0 (–0.42)	Φ_0 (–0.47)	Φ_0 (+0.13)
	$\Phi_{H-L,H-L}$ (+0.43)	Φ_{H-L} (± 0.16)	Φ_{H-L} (± 0.55)
3 (S_2/S_1 -CI)	Φ_0 (+0.13)	Φ_{H-L} (± 0.68)	Φ_0 (+0.76)
	$\Phi_{H-L, H-L}$ (–0.93)		
4 (S_1 -min)	Φ_0 (–0.86)	Φ_0 (–0.25)	
	$\Phi_{H-L,H-L}$ (+0.33)	$\Phi_{H-L,H-L}$ (–0.54)	
		Φ_{H-L} (± 0.18)	
		Φ_0 (–0.03)	
5 (S_1 -TS)	Φ_0 (–0.86)	Φ_0 (–0.03)	
	$\Phi_{H-L,H-L}$ (+0.35)	Φ_{H-L} (± 0.52)	
		$\Phi_{H-L,H-L}$ (–0.42)	
6 (S_1/S_0 -CI)	Φ_0 (+0.93)	Φ_{H-L} (± 0.92)	

inates the S_2 state of A'' symmetry and mixing becomes possible only when the symmetry is reduced. At the pericyclic geometry **6**, S_1 is dominated by Φ_{H-L} and S_0 by Φ_0 . This verifies the existence of an avoided crossing as the origin of the energy barrier.

The situation can be clarified further by considering the MOs involved. In Figure 7 the natural frontier orbitals obtained from the CASSCF wavefunction of the S_1 state are shown together with their occupation numbers. At the excited-state transition structure **5**, these orbitals are similar to the HOMO and LUMO of hexatriene, while at the pericyclic geometry **6** they resemble the pair of nonbonding cyclooctatetraene π MOs. Three features are important:

- 1) The occupation numbers indicate that at the spectroscopic minimum as well as at the pericyclic geometry, the wavefunction has a strong biradical character, while near the transition state the LUMO is nearly doubly occupied, indicating a closed-shell structure.
- 2) In **5** a nodal plane passes through C_7 and the center of the C_3-C_4 bond, and in **6** through C_4 and the center of the C_1-C_4 bond. This change in the direction of the nodal plane clearly demonstrates the difference between the sigmatropic shift reaction and pericyclic reactions, for which the principle of orbital symmetry conservation applies and is the principle reason for an avoided crossing that yields the excited-state barrier.
- 3) The development of the frontier orbitals along the reaction coordinate is best understood by considering the reverse reaction from **6** to **5**. In order to minimize the bonding or antibonding interaction during the hydrogen shift, the MO becomes polarized. This together with the closed-shell structure at **5** explains the development of alternating charges.

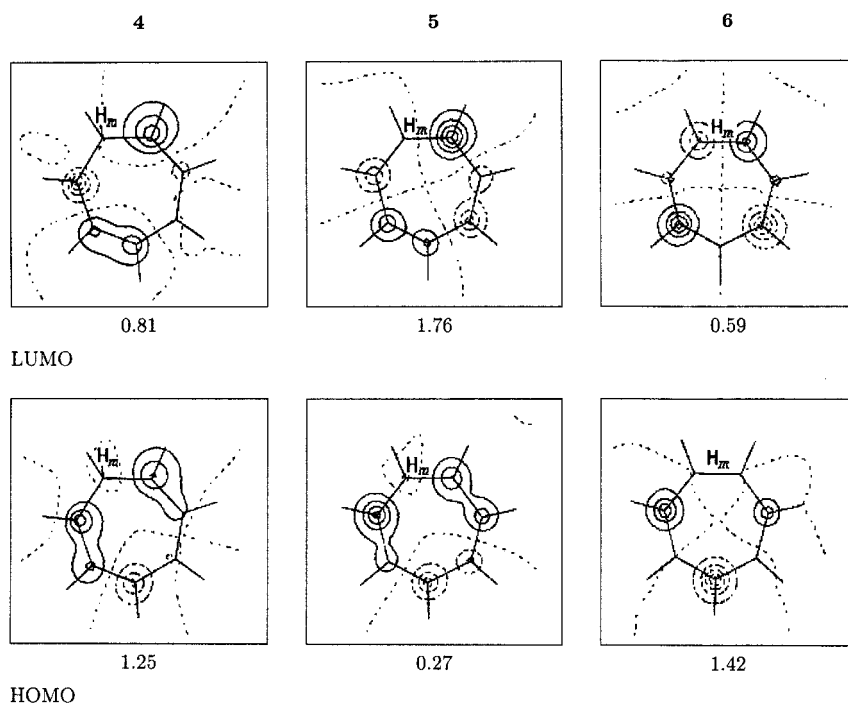


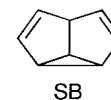
Figure 7. Contour diagram of the natural frontier orbitals and their occupation numbers at the S_1 minimum **4**, the S_1 transition state **5**, and the S_1/S_0 conical intersection **6** plotted in a plane 0.38 au above the molecular plane. Dotted lines refer to nodal planes.

Figure 8 depicts the vectors x_1 and x_2 for the S_1/S_0 conical intersection **6**. As it is in general not justified to attribute any significance to these vectors individually, since only the plane



Figure 8. Orthogonalized gradient difference and nonadiabatic coupling vectors x_1 (left) and x_2 (right) at the S_1/S_0 conical intersection **6** for the [1,7]-H shift reaction of CHT.

spanned by these vectors has a meaning,^[38] we present the orthogonalized vectors that exhibit the motions involved more clearly: x_1 corresponds to a symmetrical C–C bond stretch and x_2 describes the motion of the migrating hydrogen H_m . The resemblance of the frontier orbitals at the S_1/S_0 conical intersection to the cyclooctatetraene π MOs suggests a similarity of these vectors to those expected at the conical intersection for the photorearrangement of cyclooctatetraene to semibullvalene (SB). The analogy becomes particularly apparent from a comparison of x_1 with the structural formula of SB.



From our results it is quite clear that the [1,7]-H shift reaction in CHT proceeds in the $2A'$ state, that is to say, that the sigmatropic shift is the characteristic reaction of this

totally symmetric state, which is the lowest excited state nearly all the way along the reaction coordinate. Excitation of the spectroscopic $1A''$ state is followed by fast conversion to the reactive dark state through the S_2/S_1 conical intersection at geometry **3**. This is exactly the general behavior that was proposed for pericyclic reactions nearly 30 years ago. However, sigmatropic shift reactions differ from electrocyclic or cycloaddition reactions in that no Woodward–Hoffmann orbital correlation diagram based on orbital symmetry conservation or on nodal plane conservation can be constructed. While for electrocyclic or cycloaddition reactions the totally symmetric dark state descends steeply from the high-energy doubly excited state

and drops below the HOMO–LUMO excited state, these two states are more or less degenerate for the sigmatropic shift reaction. Even for the ground-state equilibrium geometry, the $2A'$ state is energetically quite close to the $1A''$ state.

Stabilization of the HOMO→LUMO excited state by fusion of two benzene rings to the CHT system ensures that the $1A''$ state will be the lowest excited state at all geometries of interest and will therefore be the reactive state.^[20] The characteristic reaction of this state is photodeprotonation to form the cycloheptatrienyl anion,^[21] as has been shown explicitly for the analogous photodecarboxylation reaction.^[22] This confirms our earlier suggestion that the different photochemical behavior of CHT and its derivatives on the one hand and SUB on the other is simply due to the fact that excited states of a different nature are involved in the photoreactions of these molecules.^[20]

As to the mechanism of the sigmatropic [1,7]-H shift reaction in CHT, our results are in very good agreement with the resonance Raman measurements,^[6] according to which only a fraction of the atomic movement necessary to achieve planar geometry occurs on the $1A''$ surface, while the majority of the rearrangement takes place on the $2A'$ surface. In contrast with the concerted rearrangement proposed by Woodward and Hoffmann^[39] it has been suggested by Paulick et al.^[16] that the photochemical sigmatropic shift proceeds sequentially through a biradical intermediate. Although the biradical nature of the $2A'$ excited-state minimum at **4** and the barrier separating this minimum from the pericyclic geometry **6** seem to support this suggestion, the biradical structure at **4** differs considerably from the proposed structure, which consists of a pentadienyl radical segment and a three-center bond at the saturated end of the ring. Furthermore, this minimum is very flat and the barriers separating it from the S_2/S_1 conical intersection are much too low to correspond to a real intermediate. As the reactive geometry, at which the transition from the excited state to the ground state occurs, is symmetric with the migrating hydrogen just halfway between the initial and the final position, this reaction should rather be classified as concerted.

Ter Borg et al.^[19] explained the selectivities for the sigmatropic shift in 1-substituted CHT by assuming that charge localization occurs during the rearrangement. This assumption is substantiated by our results for the transition structure, and it is this charge distribution which explains the substituent effect on the excited-state barrier that is responsible for selectivity. However, a tropylium-type intermediate stabilized by aromatic character as postulated by Ried et al.^[6a] cannot be reconciled with our results. Also the sudden polarization model proposed by Tezuka et al.^[17] is not compatible with the transition structure determined in the present work.

The height of the excited-state barrier is decisive for the course of the reaction, that is, for the regioselectivity of the [1,7]-sigmatropic shift and of the periselectivity of the electrocyclicization. The calculated charges indicate the most favorable transition states and may therefore be used as a basis for a simple, predictive model. Although electrocyclicization was not considered in this work, it may be concluded from the present data together with the experimental results of Ter Borg et al.^[19] that the excited-state energy barrier for the

[1,7]-sigmatropic shift increases with increasing donor strength of the substituent. This favors electrocyclicization to form bicyclo[3.2.0]heptadienes. This suggests that electrocyclicization may occur through a different conical intersection separated from the S_1 minimum by a different excited-state barrier. The barrier should be higher or lower than that on the sigmatropic-shift reaction path if the CHT ring is substituted in the 1-position by acceptor or donor substituents, respectively.

Conclusions

Semiempirical as well as ab initio CASSCF calculations demonstrate that the mechanism of the photochemical [1,7]-hydrogen shift in CHT can be characterized as follows: Excitation into the $1A'' \pi, \pi^*$ excited state is followed by a fast transition through a conical intersection into a dark state, which at the ground-state geometry corresponds to the $2A'$ state. Hydrogen motion starts only in this state and is characterized by a small barrier due to an avoided crossing; this separates the excited-state minimum from a conical intersection at the pericyclic geometry through which ultrafast return to the ground state occurs. Substituents in the 1-position affect the excited-state barrier such that hydrogen migration away from an acceptor substituent and toward a donor substituent is favored. More concisely the selectivity of the sigmatropic [1,7]-shift in CHT originates in a substituent-dependent excited-state barrier.

Therefore, neither sudden polarization effects nor biradical intermediates are necessary to explain the regioselectivity. However, as the barrier is due to an avoided crossing and the concomitant change in the wavefunction, a charge distribution similar to the model of Ter Borg et al.^[19] results. This enables the substituent effects on the excited-state barrier to be rationalized.

Acknowledgement

We thank W. Fuß for communicating his results prior to publication and for stimulating discussions. Financial support by DFG through the Graduiertenkolleg Hochreaktive Mehrfachbindungssysteme and by Fonds der Chemischen Industrie is gratefully acknowledged.

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Received: December 23, 1998 [F1505]