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Excited-State Energy and Geometry Changes during the [1,7]H-Shift Reaction of Cycloheptatriene

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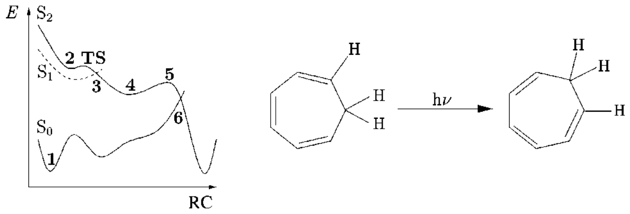
ABSTRACT



The minimum-energy path of the photochemical [1,7]H-shift reaction of 1,3,5-cycloheptatriene from the Franck–Condon region in the spectroscopic S_2 state to the S_2/S_1 conical intersection has been determined. These data together with previous results[1] were used to create a video, which visualizes the complete course of the excited-state reaction by displaying all energy and geometry changes that occur along the reaction coordinate.

On the basis of CASSCF calculations for the reaction profile, we recently discussed the detailed mechanism of the photochemical [1,7]-sigmatropic hydrogen shift in 1,3,5-cycloheptatriene (CHT),[1] the decisive feature of which is a barrier in the first excited singlet state S_1, being responsible for the photoselectivity observed in 1-substituted CHT.[2] It was suggested that the first two of the three phases which could be distinguished in the excited-state dynamics[3] correspond to the region of steep descent from the Franck−Condon (FC) geometry to the S_2 minimum and to a flat region extending from the S_2 minimum to the S_2/S_1 conical intersection. To verify this assignment, we calculated the detailed relaxation pathway from the FC geometry in the initially populated S_2 state to the S_2/S_1 conical intersection.

The results enabled us to put together an animated cartoon[4] available as Supporting Information, which visualizes all energy and geometry changes during the [1,7]H-shift reaction of CHT. A snapshot with the molecule sitting in the S_2 minimum is shown in Figure 1.

To obtain minimum-energy paths starting from nonstationary points, Robb et al.[5] suggested determining the initial relaxation direction (IRD) by locating the minima on hyperspheres centered around an appropriate starting geometry. The associated intrinsic reaction coordinate[6] (IRC) is computed subsequently by using the IRD vector to define the initial direction to follow. Using the Gaussian 95 development version,[7] we performed CASSCF calculations

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[1] Steuhl, H.-M.; Bornemann, C.; Klessinger, M. *Chem. Eur. J.* **1999**, *5*, 2404.

[2] Ter Borg, A. P.; Razenberg, E.; Kloosterziel, H. *J. Chem. Soc., Chem. Commun.* **1967**, 1210.

[3] Trushin, S. A.; Diemer, S.; Fuss, W.; Kompa, K. L.; Schmidt, W. E. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1431.

[4] The video contains geometries and energies of more than 100 high-level ab initio CASSCF calculations.

[5] Garavelli, M.; Celani, P.; Bernardi, F.; Robb, M. A.; Olivucci, M. *J. Am. Chem. Soc.* **1997**, *119*, 11487.

[6] (a) Gonzales, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154. (b) Gonzales, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

[7] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Strain, M. C.; Burant, J. C.; Stratmann, R. E.; Dapprich, S.; Kudin, K. N.; Millam, J. M.; Livelsberger, A.; Petersson, G. A.; Montgomery, J. A.; Zakrzewski, V. G.; Raghavachari, K.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Barone, V.; Stefanov, B. B.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Stewart, J. P.; Gonzalez, C.; Head-Gordon, M.; Gill, P. M. W.; Johnson, B. G.; Pople, J. A. Gaussian 95, Development Version (Revision F.1), Gaussian, Inc., Pittsburgh, PA, 1996.

10.1021/ol990997e CCC: $18.00

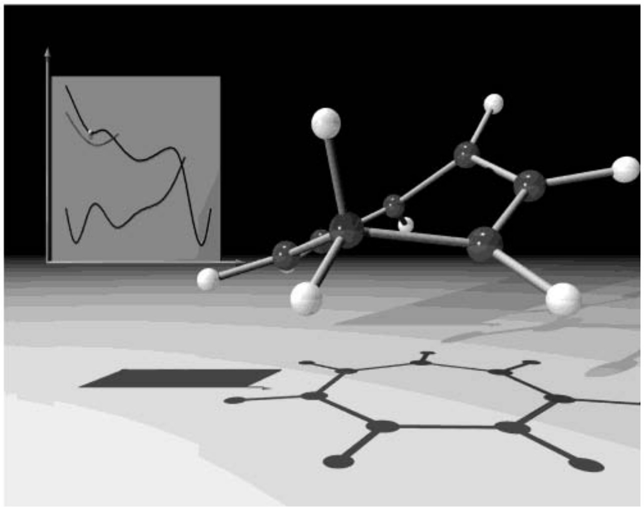

Figure 1. Snapshot of the video, which visualizes the energy and geometry changes during the [1,7]H-shift reaction of CHT. The white ball in the diagram on the left indicates that the molecule is sitting in the S_2 minimum; the structure of the molecule at this point of the reaction coordinate is shown on the right.

for the S_2 state of CHT to determine the minima **1′** and **1″** on hyperspheres with radii 0.025 and 0.05 au centered at the FC geometry. The active space comprised the three highest occupied and the three lowest unoccupied π orbitals of CHT, and the 6-31G basis set was employed. The minima and transition states **1**, **2**, **2′**, and **3** were calculated in the same way; to estimate the effect of a larger basis, we performed additional reoptimizations at these latter structures, using Gaussian 98[8] with the 6-31+G* basis set. Results are collected in Table 1.

Only one minimum exists on each hypersphere; the geometry **1′** of the minimum on the 0.025 au hypersphere is shown in Figure 2; compared to the FC geometry **1**, the single bonds are slightly shortened and the double bonds slightly lengthened, indicating that the initial relaxation proceeds substantially along a totally symmetric CC stretch mode. Starting from **1′** the IRC was calculated at the same level of theory.[8] As shown in Figure 2, it leads directly to the S_2 minimum **2**.

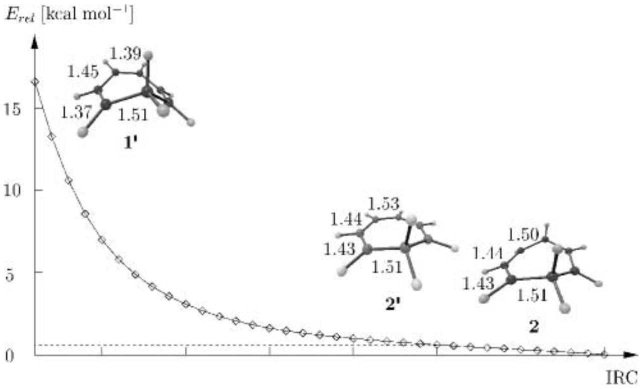

Figure 2. IRC (CASSCF/6-31G) starting at the hyperspherical minimum **1′** and leading to the unsymmetric S_2 minimum **2**; under C_s symmetry structure **2′** is reached.

If C_s symmetry is imposed, however, structure **2′**, 0.56 kcal mol^{-1} higher in energy than the unsymmetric S_2 minimum structure **2**, is reached. **2′** is a transition state in the full coordinate space, connecting the two equivalent S_2 minima of C_1 symmetry. Only comparatively small geometry changes are involved along the corresponding normal coordinate with an imaginary frequency of 188i cm^{-1}, leading to further planarization of the ring. In addition, a rotational motion around the $C_3{=}C_4$ double bond leads to the unsymmetric minimum **2**, the characteristic feature of this structure being two allylic π systems, the planes of which intersect at an angle of 52°. The IRC describes a very steep descent from the FC region to the S_2 minimum approximately 30 kcal mol^{-1} lower in energy. From these results it is quite clear that no direct pathway from the FC geometry to the S_2/S_1 conical intersection exists. Thus it remains to be shown how the conical intersection is reached. Due to the fact that the S_2/S_1 conical intersection **3** is approximately 13 kcal mol^{-1} lower in energy than the S_2 minimum **2**, a transition state **(TS)** must be located on the path connecting both geometries, which could be determined only assuming a linear pathway.

Table 1: Absolute Energies E in au and Relative Energies E_{rel} in kcal mol^{-1} for the S_2 State of CHT at the FC Geometry **1**, the Hyperspherical Minima **1′** (r = 0.025 Au) and **1″** (r = 0.05 Au), the S_2 Minimum **2**, the Transition State **2′**, the S_2/S_1 Conical Intersection **3** and the Transition State **TS**

	6-31G		6-31+G*	
	E	E_{rel}	E	E_{rel}
1	−269.41055	0.0	−269.50573	0.0
1′	−269.43009	−12.3	−269.52614	−12.8[a]
1″	−269.44248	−20.0	−269.54160	−22.5[a]
2	−269.45869	−30.2	−269.55899	−33.4
2′	−269.45779	−29.6	−269.55718	−32.3
3	−269.47732	−41.9	−269.56983	−40.2
TS	−269.45688	−29.1	−269.56116	−34.8

[a] CASSCF/6-31+G*//CASSCF/6-31G.

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(8) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, Revision A.6, Gaussian, Inc., Pittsburgh, PA, 1998.

Figure 3 shows that **TS** is only 1.1 kcal mol^{-1} higher in energy than **2**, thus indicating a very flat potential in the minimum region of the S_2 surface. Furthermore it exhibits alternating bond lengths similar to those in structure **3**. In contrast to the symmetric CC stretch mode leading from **1** to **2**, an antisymmetric deformation mode is necessary to reach the planar S_2/S_1 conical intersection **3** as can be seen from a comparison of the corresponding geometries.

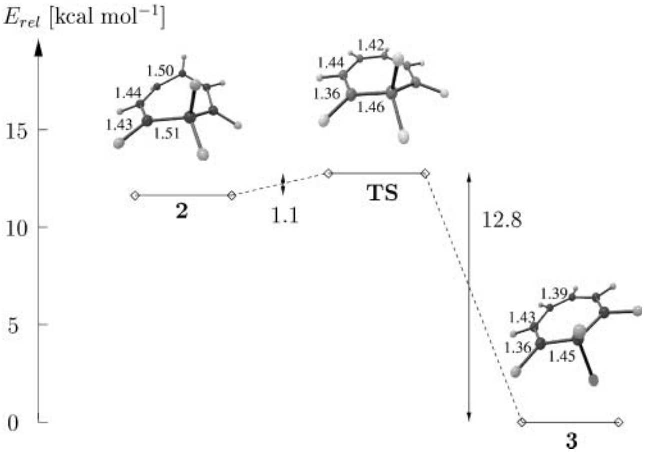

Figure 3. Energy diagram (CASSCF/6-31G) for the reaction path from the S_2 minimum **2** to the S_2/S_1 conical intersection **3**.

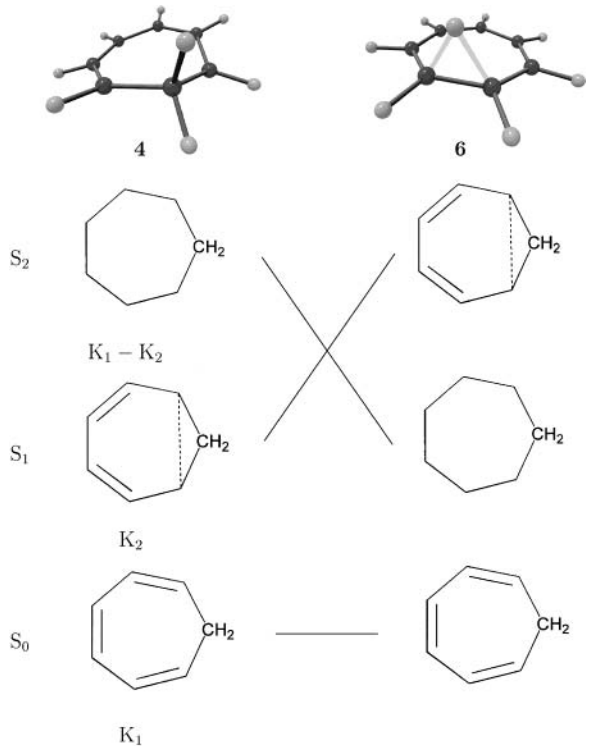

Figure 4. VB structures of the electronic ground-state S_0 and the first two excited singlet states S_1 and S_2 at the S_1 minimum **4** and the S_1/S_0 conical intersection **6**.

Finally, some additional evidence for the origin of the barrier **5** in the dark S_1 state between the S_1 minimum **4** and the pericyclic geometry **6** (S_1/S_0 conical intersection) could be obtained by an analysis[9] of the CASSCF wave function in terms of VB structures; the results are shown in Figure 4. While at the FC geometry **1** the electronic ground-state S_0 and the first excited singlet state S_1 are described by the Kekulé structures K_1 and K_2, the second excited singlet state S_2 is represented by the minus combination $K_1 - K_2$. Thus, the excited states of CHT can be described as benzene-like rather than as polyene states. Furthermore these structures dominate the wave functions of S_0, S_1, and S_2 along the [1,7]H-shift reaction coordinate from the FC geometry **1** to the S_1 minimum **4**. At the pericyclic geometry **6**, however, K_2 and $K_1 - K_2$ are interchanged, with the latter now dominating S_1. This result reveals quite clearly that the excited-state barrier **5**, which is responsible for the photochemical selectivity[2] observed in 1-substituted CHT, stems from an avoided crossing of the wave functions of S_1 and S_2 primarily described by K_2 and $K_1 - K_2$, respectively.

The [1,7]-sigmatropic H-shift reaction of CHT proceeds in two distinct steps in the initially populated second excited-state S_2, the first of which corresponds to a barrierless motion along a symmetric CC stretch mode to reach a shallow minimum, about 30 kcal mol^{-1} lower in energy, while the second step corresponds to a motion over a small barrier along an antisymmetric deformation mode. In view of the high translational energy gained during the relaxation, deactivation of the S_2 state to the dark S_1 state, where the photochemical hydrogen shift takes place, occurs, in agreement with recent experimental results,[3,10] on an ultrafast time scale as shown explicitly in the video (Supporting Information).

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Supporting Information Available: A video visualizing the energy and geometry changes of the [1,7]H-shift reaction of CHT in MPEG 1 format. This material is available free of charge via the Internet at http://pubs.acs.org and http://www.uni-muenster.de/ Chemie/OC/research/kle/cht.html.

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