Thermal Rearrangements of Norcaradiene

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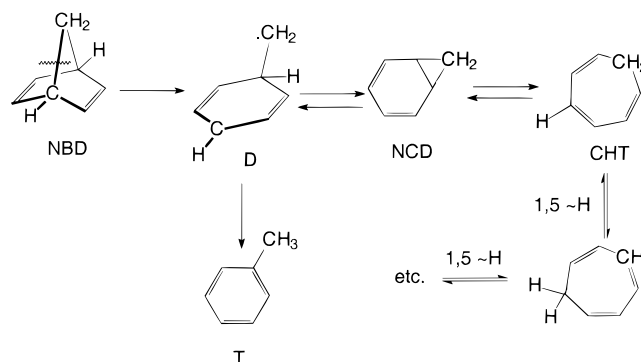
Abstract: Multireference ab initio methods and density functional theory with a 6-31G* basis set have been applied to study the interconversions of norbornadiene, 1,3,5-cycloheptatriene, norcaradiene, and toluene. These include the [1,5]hydrogen shift in cycloheptatriene, the [1,5]carbon shift (walk rearrangement) in norcaradiene, the ring flip of cycloheptatriene, and the formation of norcaradiene from cycloheptatriene. Our best theoretical calculations for the walk rearrangement predict that the Woodward−Hoffmann "forbidden" suprafacial-inversion transition state and the "allowed" suprafacial-retention pathway differ in energy by <1 kcal/mol. Further, both transition states are effectively biradical-like. The transition state for formation of toluene from norcaradiene proceeds via a hydrogen transfer transition state that is formed directly from the "allowed" transition state for the walk rearrangement but not from the "forbidden" transition state. Further, the transition state for the transannular hydrogen shift from the "allowed" transition state to 3-methylene-1,4-cyclohexadiene was calculated to be too high in energy to participate in the formation of toluene.

Introduction

Bicyclo[4.1.0]hepta-2,4-diene (norcaradiene, NCD) and the unusually rich chemistry of rearrangements involved with it have been extensively studied for more than three decades. In 1957, Woods[1] observed the thermal isomerization of bicyclo[2.2.1]-heptadiene (norbornadiene, NBD) to 1,3,5-cycloheptatriene (CHT). This reaction most likely proceeds via diradical D in Scheme 1 to NCD which then undergoes ring opening of the central bond. The reverse path provides a mechanism by which CHT can give toluene upon pyrolysis. That is, CHT can isomerize to NCD and then undergo bond cleavage to diradical *D* which undergoes a hydrogen shift to toluene (T). A few years after Woods' observation, experimental investigations turned toward the question of the nature of the cycloheptatriene-norcaradiene equilibrium and the related question of possible homoaromaticity. Is the bicyclic form merely a valence bond resonance structure for the monocyclic form or is it a stable intermediate structure involved in the process of the thermal isomerization of cycloheptatriene?

Vibrational spectra,[2] electron diffraction,[3] microwave spectroscopy,[4] and X-ray crystallography data[5] established a nonplanar structure for cycloheptatriene. A kinetic study of the thermal isomerization process of CHT to toluene[6] suggested that the bicyclic tautomer, NCD, is a likely intermediate, where the bicyclic−monocyclic equilibrium is shifted very much toward the monocyclic form. NCD was prepared in 1981 and the kinetics of its isomerization to CHT was followed by ultraviolet spectroscopy which provided an activation energy of 6.5 kcal/mol.[7] A rough estimate of 4 kcal/mol for the free energy

Scheme 1

difference between CHT and NCD suggested that the free energy of activation for ring closure of CHT to NCD is 11 ± 2 kcal/mol.[7]

Cycloheptatriene is nonplanar and undergoes facile interconversion between two equivalent boat conformations. At low temperature (below −140 °C), the methylene protons give separate signals in the NMR spectrum. As the temperature is raised, the signals broaden and coalesce into one sharp peak. This observation provides an activation energy of 6.3 kcal/mol for the interconversion process.[8] A high-temperature NMR study on hydrogen isotopomers of cycloheptatriene led to the discovery that at 100−140 °C, the molecule undergoes a process of [1,5]hydrogen shift with an activation energy of about 31 kcal/mol[9] (Scheme 1).

The original mechanism of isomerization of NBD proposed by Woods (Scheme 1) provides the possibility of NCD reversibly opening to the diradical. This proposal then provides a pathway for a [1,5]carbon rearrangement in NCD, commonly referred to as the "walk" rearrangement, which was discovered
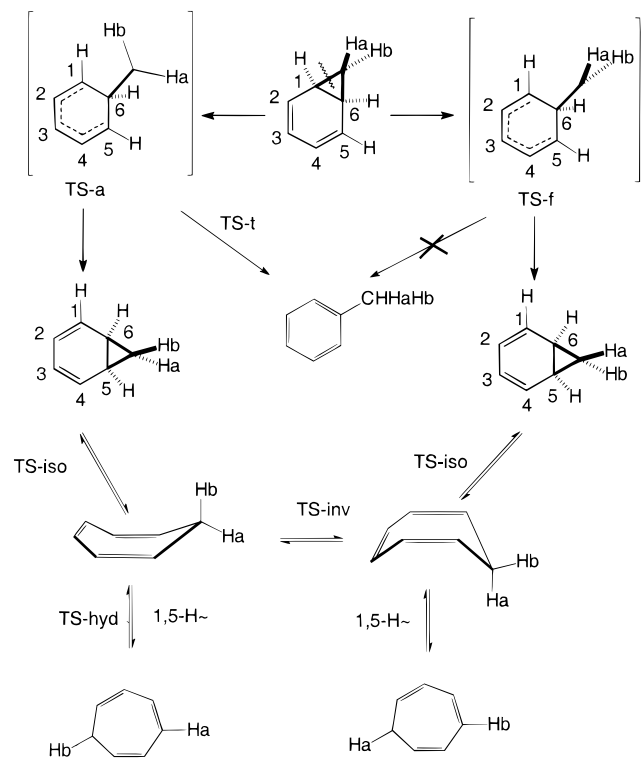
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Scheme 2

by Berson and Willcott in 1965.[10] This rearrangement is one of a large series of similar processes in which a carbon circumambulates a cyclic polyene or polyenylium ion. Formally, these processes can be characterized by the Woodward–Hoffmann (WH) designations as [*i,j*]-sigmatropic rearrangements[11] where *i* and *j* are the numbers of atoms over which the bond migrates from its original position. The stereochemical behavior of the migrating group differs depending on the number of total electrons involved in the process. In systems with no charges on atoms, the migrating group should retain its configuration in processes involving $j + i = 4n + 2$ electrons and it should invert in those involving $4n$ electrons, provided that the polyene system is used suprafacially as it must be in the NCD walk rearrangement (Scheme 2). The norcaradiene "walk" was assumed by Woodward and Hoffmann[12] to proceed with retention of configuration. Berson[13] discussed other possibilities including hydrogen migration and his experimental attempts to determine the actual pathway. Other [1,5]sigmatropic shifts of carbon have been observed with orbital-symmetry-forbidden transition states.[14] In 1974, by studying an optically active substituted CHT, Klärner[15] showed that the walk rearrangement occurs with inversion. Thus the "forbidden" path is favored.

The fascination with Woodward–Hoffmann rules based on orbital symmetry considerations provided the impetus to theoretical investigations of the symmetries of transition states. Prediction of possible TS symmetries in nondegenerate concerted reactions was investigated by Pechukas.[16] More recently,

Schaad and Hu[17] extended Pechukas' work to degenerate concerted reactions, i.e., one-step reactions in which reactant and product differ only by the interchange of identical atoms. The "walk" rearrangement belongs to this group of degenerate reactions (sometimes referred to as topomerization reactions).

Theoretical indications that the dynamics of thermal "walks" could be modified by hyperconjugation appeared in the discussion of the [1,3]-sigmatropic shift by Berson and Salem.[18] The relative stability of "allowed" and "forbidden" transition states involved in the "walk" process was a considerable challenge. In 1975, Schoeller,[19] using semiempirical MINDO/2[21] calculations including configuration interaction for proper bond dissociation, showed that inversion at the migrating carbon is favored by 1.4 kcal/mol over the retention process in agreement with the observations of Klärner and co-workers[13] for the [1,5]-sigmatropic shift. Unfortunately, the method used by Schoeller also predicted that retention was favored over inversion by 4.0 kcal/mol in the [1,3]-sigmatropic shift because of hyperconjugation, in contradiction to later experiments by Klärner and Adamsky.[21] Semiempirical calculations were also employed to study related "walk" rearrangements where the migrating methylene group was replaced by an oxygen or amino group.[22]

The correct description of possible transition states involved in the "walk" reaction requires a multi-configuration wave function. Complete active space self-consistent -field (CASSCF) studies were reported on the [1,3]-shift ring walk in bicyclo-[2.1.0]pent-2-ene, initially using 4 electrons and 4 orbitals,[23] and later 8 electrons and 8 orbitals,[24] for the complete active space. In contrast to the MINDO/2 calculations,[19] these ab initio calculations predict that inversion is favored in agreement with the Woodward–Hoffmann rules. Using the method described below for the [1,5]-shift, our own 8-electron/8-orbital CASSCF calculation for the [1,3]-shift gave 9.5 kcal/mol favoring the allowed transition state over the forbidden one. However, simpler methods such as unrestricted Hartree–Fock (UHF) or Möller–Plesset (MP) calculations seem to be more commonly applied to norcaradiene[25] or substituted norcaradienes.[26] Haltz et al.[25] also discussed the attack of benzene by methylene to form toluene and cycloheptatriene.

Clearly, there are competitive thermal processes that need to be considered in any experimental or theoretical studies on "walk" rearrangements. The ring-opening reaction in which the internal bond is cleaved can occur at low temperatures in small bicyclic systems. Further, the competitive valence tautomerism of the hydrogens of the monocyclic system, where hydrogens are dispersed over the carbon framework by concerted [1,5]-hydrogen shifts, often can mask the stereochemistry of the process of interest and can only be explored theoretically.

Computational Details

All calculations presented here were obtained using the 6-31G* basis set. Only the lowest energy singlet state was considered. Complete active space self-consistent-field calculations (CASSCF) and multiref-

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erence perturbation corrections (MROPT)[27] to the CASSCF wave function were performed using the HONDO program package.[28] Previous work on the Cope rearrangement[27] showed that MROPT2 gave reasonable results where CASSCF did not, due to lack of dynamic correlation. Some configuration interaction results were obtained with the MELD program.[29] Density functional results using the three-parameter Becke exchange functional and the Lee−Yang−Parr correlation functional (B3LYP), obtained with the Gaussian 94 program package,[30] were used to get preliminary estimates of energies and structures. The B3LYP results were checked for spin stability, and spin unrestricted "singlet" results are reported when this gives a lower energy. Optimized geometries for B3LYP were obtained using the program OPTIMIZE,[31] which takes energies and gradients from Gaussian 94. The choice of orbitals included in CASSCF calculations was based on the orbitals expected to change markedly during the reactions being studied. Consequently, four different sets of active orbitals were used in our theoretical investigation. For convenience of presentation, these sets are labeled CAS(a), CAS(b), CAS(c), and CAS(d).

A set of six active orbitals with six electrons, CAS(a), was chosen as relevant for the thermal ring isomerization from CHT to NCD. This set includes three $\pi-\pi^*$ pairs of orbitals of the CHT ring. With the C_s point group, the dominant configuration of the six active electrons is $(a')^2 (a'')^2 (a')^2$ for CHT, NCD, and the transition state (TS-*iso*, see below), so cleaving of the internal bond is a WH-allowed process.

Sets of eight orbitals were chosen to account for the nondynamic correlation effects in the "walk" rearrangement CAS(b), the [1,5]-suprafacial hydrogen shift CAS(c), and the toluene formation CAS(d). The CAS(b) set includes two $\pi-\pi^*$ pairs of the six-member ring orbitals of norcaradiene, and two $\sigma-\sigma^*$ orbital pairs involving the migrating carbon. The dominant configuration for NCD with C_s symmetry is $(a')^2 (a'')^2 (a')^2 (a'')^2$. Along the reaction path, the molecule has no symmetry, but at either the allowed or forbidden transition state, it again has C_s symmetry with a new mirror plane. At the transition states, one orbital becomes the singly occupied p orbital on the carbon atom which undergoes the rearrangement. This occupied p orbital is of a′ or a″ symmetry depending on whether the transition state is WH-allowed (TS-a) or WH-forbidden (TS-f), respectively. The dominant electron configuration is expected to be $(a')^2 (a')^2 (a'')^2 (a')^2 (a')^0$ for the allowed transition state and $(a')^2 (a')^2 (a'')^2 (a')^1 (a'')^1$ for the forbidden transition state.

The CAS(c) set of 8 electrons and 8 orbitals, chosen for the hydrogen shift, consists of three $\pi-\pi^*$ pairs of orbitals as in the CAS(a) set plus the σ pair of bonding and antibonding molecular orbitals of the C7H8 bond, where H8 undergoes the process of rearrangement (see Figure 1 for atom numbering). The dominant configuration at the starting C_s symmetry of cycloheptatriene is $(a')^2 (a')^2 (a'')^2 (a')^2$. At the transition state (TS-*hyd*), the molecule has C_s symmetry with respect to a different mirror plane and the dominant configuration becomes $(a')^2 (a')^2 (a')^2 (a'')^2$.

(27) Various types of MROPT method differ by the choice of zeroth-order Hamiltonian H_0 in multireference perturbation theory. MROPT1 method takes $H_0 = \sum n_k \epsilon_k$ where the eigenvalues ϵ_k are obtained by diagonalization of the **F** matrix in doubly occupied, singly occupied, and virtual subspaces. Other MROPT methods are generalizations of the MROPT1 method. For details see: Kozlowski, P. M.; Davidson, E. R. *J. Chem. Phys.* **1994**, *100*, 3672. Kozlowski, P. M.; Dupuis, M.; Davidson, E. R. *J. Am. Chem. Soc.* **1995**, *117*, 774.

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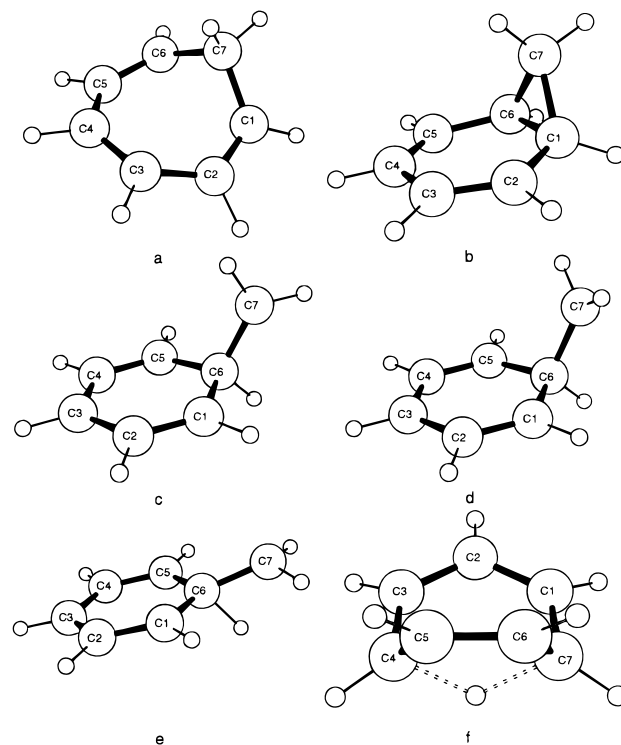(31) Baker, J. OPTIMIZE, a suite of algorithms for geometry optimization.

Figure 1. Numbering of molecular skeletons: (a) 1,3,5-cycloheptatriene, (b) norcaradiene, (c) forbidden TS, TS-f, (d) allowed TS, TS-a, (e) toluene formation TS, TS-t, and (f) TS-*hyd*. Hydrogen atom numbering follows carbon atoms, i.e., H_1 atom is attached to C_1.

Finally, the set of 8 electrons and 8 orbitals chosen for the hydrogen migration to form toluene, CAS(d), consists of five π orbitals on C1−C5, the π orbital on C7, and the $\sigma-\sigma^*$ pair of C6H6 bond orbitals, where H6 undergoes the process of migration. The dominant configuration at C_s symmetry of toluene is $(a')^2 (a')^2 (a'')^2 (a')^2$. At the transition state TS-t, the dominant configuration is $(a')^2 (a')^2 (a'')^2 (a')^2$.

It is possible that polarization functions on hydrogen could be important for transition states involved with hydrogen migration processes. To test the effect of polarization functions on hydrogen some B3LYP calculations were performed with the 6-31G** basis sets and are included in the Supporting Information. The calculated activation energies were changed by less than 0.1 kcal/mol for the walk rearrangement and by less than 1.0 kcal/mol for the hydrogen migration.

Results and Discussion

(a) Isomerization of Cycloheptatriene to Norcaradiene. The structures and energies of norcaradiene, cycloheptatriene, and the transition state for their interconversion, TS-*iso*, have been found with C_s symmetry. Preliminary structures were located and characterized at the B3LYP level of theory using gradients and energies from Gaussian 94 and optimization algorithms implemented in the optimization package OPTIMIZE.[31] These structures were then reoptimized at the CASSCF level of theory with 6 electrons and 6 orbitals, defined as CAS-(a) above, to give the CASSCF geometry. The C_s structures located for norcaradiene and cycloheptatriene are true minima, i.e., no imaginary vibrational frequencies were found. The transition structure located, TS-*iso*, is a true transition structure, i.e., one imaginary frequency has been found at both levels of theory. Figures 1a and 1b show the structures of cycloheptatriene and norcaradiene and Table 1 reports some important geometric parameters at the CASSCF and B3LYP levels of theory. The calculated structure for cycloheptatriene has been compared with electron diffraction data.[3] This comparison shows a very good agreement in all bond lengths and angles. Although a nonplanar

Table 1. Calculated Geometry Parameters of Norcaradiene, Isomerization Transition State (TS-*iso*), and Cycloheptatriene Using 6-31G* Basis Set (Bond Lengths in Å and Bond Angles in deg) and Comparison of Cycloheptatriene with Experimental Data

parameter	norcaradiene B3LYP/**CAS(a)**/*CAS(b)*	TS-*iso* B3LYP/**CAS(a)**	cycloheptatriene B3LYP/**CAS(a)**/*CAS(c)*	exptl [ref 3]
r(C7C1)	1.507/**1.499**/*1.531*	1.485/**1.479**	1.509/**1.512**/*1.511*	1.505
r(C1C2)	1.472/**1.486**/*1.484*	1.417/**1.421**	1.351/**1.347**/*1.347*	1.356
r(C2C3)	1.352/**1.349**/*1.328*	1.381/**1.379**	1.447/**1.467**/*1.467*	1.446
r(C3C4)	1.454/**1.467**/*1.469*	1.420/**1.423**	1.365/**1.355**/*1.355*	1.356
$\angle$(C1C7C6)	62.85/**62.42**/*59.37*	78.19/**81.38**	108.32/**111.20**/*111.73*	∼105
$\angle$(C7C1C2)	120.52/**120.29**/*119.83*	121.84/**121.50**	121.93/**122.87**/*123.14*	121.8
$\angle$(C1C2C3)	122.00/**121.81**/*121.78*	123.37/**123.63**	125.43/**125.29**/*125.52*	127.2
$\angle$(C2C3C4)	121.38/**121.55**/*121.36*	122.36/**123.04**	125.93/**126.18**/*126.31*	119.8
α	111.36/**110.92**/*110.74*	114.45/**114.42**	127.94/**130.94**/*131.87*	130.3[a]
β	171.03/**175.32**/*175.69*	160.77/**161.74**	154.83/**153.98**/*154.66*	156.3[a]

[a] Reference 5.

Table 2. Calculated and Experimental Relative Energies (kcal/mol) of Species Involved in (a) the Isomerization Process, (b) the "Walk" Rearrangement, (c) the 1,5-Suprafacial Hydrogen Shift, and (d) the Formation of Toluene

method	(a) isomerization of cycloheptatriene		(b) "walk" rearrangement		(c) 1,5 suprafacial hydrogen shift	(d) formation of toluene	
	TS-*iso* − CHT	NCD − CHT	TS-f − NCD	TS-a − TS-f (ZPC)[b]	TS-*hyd* − CHT	TS-t − TS-a	toluene − TS-t
experiment	11	4			31		
B3LYP	10.02	6.48	41.20[a]	+0.91[a] (−0.01)	40.57	5.85[a]	90.26[a]
PB3LYP[c]			41.53	−0.66		2.32	85.48
CASSCF	21.63	11.84	35.20	+0.26 (+1.18)	60.19	13.55	94.35
MROPT2	8.90	7.32	44.58	−1.85	38.70	1.87	87.63

[a] Unrestricted B3LYP calculation of transition states. [b] Zero-point correction in parantheses, which needs to be added. [c] Spin projected B3LYP energies using the method of ref 37.

structure for cycloheptatriene has been established experimentally, quantitative values for α and β angles vary significantly with the type of experimental data. Table 1 compares calculated α and β angles with the values determined by X-ray crystallography by Davis and Tulinski.[5] Both angles agree well with these data. Alpha and beta are defined as angles between the C7C1C6 and C1C2C5C6 planes and the C2C3C4C5 and C1C2C5C6 planes of cycloheptatriene, respectively.

All CASSCF energies have been corrected by multireference second-order perturbation theory. The calculated energy difference between the species involved in the isomerization reaction are compared with experimental data[7] and shown in part a of Table 2. The calculated energy difference between NCD and CHT is 6.4, 7.3, and 11.8 kcal/mol for B3LYP, MROPT2, and CASSCF methods, respectively, compared to the approximate experimental value of 4 kcal/mol. The calculated energy difference between the transition state and cycloheptatriene is 10.0, 8.9, and 21.6 kcal/mol for B3LYP, MROPT2, and CASSCF methods, respectively. The values calculated with MROPT2 and B3LYP agree reasonably well with the experimental activation energy of 11 ± 2 kcal/mol.

Since norcaradiene could be present in amounts approaching 2% at room temperature, reliable predictions of the vibrational bands of NCD might result in detection of vibrational signals from norcaradiene in the cycloheptatriene spectrum. Scaled quantum mechanical (SQM) methods[32] were used to refine the B3LYP/6-31G* vibrational force field. Appropriate transferable scale factors were taken from recent studies by Baker et al.[33] The calculated frequencies of cycloheptatriene with greatest intensity are shown in Table 3. A complete list is available in the Supporting Information. Calculations of cycloheptatriene are compared with experimentally determined fundamentals. A direct comparison of calculated (SQM) frequencies with the

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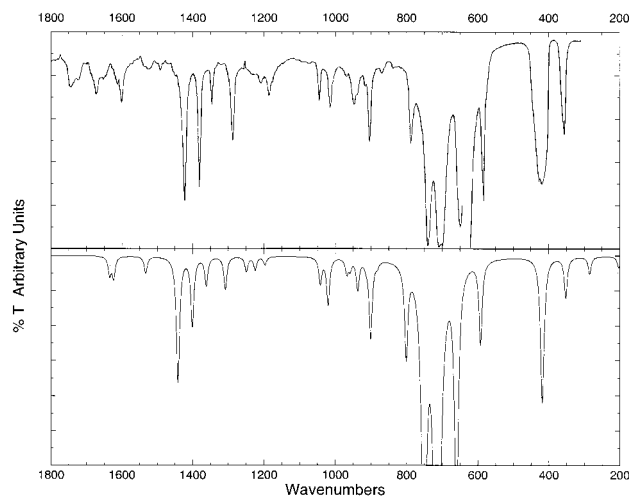(33) Baker, J.; Jarzȩcki, A. A.; Pulay, P. *J. Phys. Chem. A* **1998**, *102*, 1412.

Table 3. Calculated and Experimental Frequencies (cm^{-1}) of 1,3,5-Cycloheptatriene

	CAS(a)	CAS(c)	B3LYP	SQM B3LYP freq	SQM B3LYP IR int.[a]	exptl	assignment
a′	3347	3348	3170	3037	65.14	3027	CH str
	3258	3197	3105	2975	22.54	2966	CH(eq) str
	3193	3016	3011	2885	33.25	2838	CH(ax) str
	755	757	727	715	56.45	712	ring bend + CH rock
	685	681	669	660	13.16	657	ring def + CH$_2$ rock
a″	3354	3354	3177	3044	50.42	3039	CH str
	3335	3335	3155	3023	13.10	3027	CH str
	743	744	764	751	23.94	743	CH rock

[a] IR intensity in km/mol.

experimental IR spectrum[2a] in the "fingerprint" region (200−1800 cm^{-1}) is shown in Figure 2. In general, the calculated SQM frequencies are in good agreement with experimental data. The calculated fundamentals in the 1200−1600 cm^{-1} region still indicate a small but consistent error that shifts the frequencies to about 10 cm^{-1} higher than experimental fundamentals. This error indicates that transferable scale factors for CC stretch and CH wagging are slightly too low for the cycloheptatriene ring vibrations. A selected set of calculated frequencies and intensities of norcaradiene are reported in Table 4. The higher CH stretch fundamentals of norcaradiene might be the easiest to identify in the spectrum of the mixture.

(b) "Walk" Rearrangement of Cycloheptatriene. The skeletal rearrangement of cycloheptatriene is known to occur at temperatures above 370 °C and is formulated with norcaradiene intermediates. Two transition structures on the norcaradiene potential energy surface relevant to the "walk" rearrangement, WH-forbidden (TS-f) and WH-allowed (TS-a), were found within C_s symmetry and are shown in Figures 1c and 1d, respectively. These structures differ approximately by a 90° rotation of the migrating methylene group. The methylene in

Figure 2. Infrared spectrum of cycloheptatriene from 200 to 1800 cm^{-1}: (top) experimental spectrum taken from ref 2a; (bottom) predicted SQM B3LYP/6-31G* spectrum with a Lorentzian band profile with half-width 5 cm^{-1}.

Table 4. Calculated Frequencies (cm^{-1}) of Norcaradiene

| | CAS(a) | CAS(b) | B3LYP | SQM B3LYP | | assignment |
				freq	IR int.[a]	
a′	3376	3353	3199	3066	23.57	CH str
	3351	3332	3175	3042	13.94	CH str
	3328	3180	3157	3025	27.20	CH str
	3307	3091	3146	3014	16.64	CH(eq) str
	1075	1111	1015	981	9.49	6-member ring str
	780	847	746	729	58.63	CH wag + ring str
a″	3363	3369	3188	3055	52.15	CH str
	1171	1115	1070	1041	10.47	CH$_2$ wag

[a] IR intensity in km/mol.

TS-f is "flat" and lies in the mirror plane while the methylene in TS-a is slightly pyramidal. Initially, these structures were located and characterized with B3LYP. Each transition state had one calculated imaginary frequency for the reaction coordinate (186i and 197i for TS-f and TS-a, respectively). Following the reaction coordinate downhill from either transition state leads to norcaradiene. Both of these "singlet" B3LYP calculations had broken spin symmetry indicating that neither transition state wave function could be represented well by a single Slater determinant and the B3LYP energy might not be accurate. The zero-point energies for TS-f and TS-a with this UB3LYP wave function differed by only 0.01 kcal/mol.

After locating these structures with B3LYP calculations, all three species (norcaradiene, TS-f, and TS-a) were reoptimized with the CAS(b) set of orbitals to give CASSCF singlet state geometries and energies appropriate for the "walk" reaction. As expected, the TS-f wave function had ^{1}A″ symmetry and was primarily a single open-shell configuration. The TS-a wave function had ^{1}A′ symmetry and consisted mostly of three configurations. The calculated imaginary frequency for the reaction coordinate at the CASSCF level is 380i and 229i for TS-f and TS-a, respectively. The most important geometry parameters for norcaradiene reoptimized within CAS(b) are listed in Table 1. The zero-point energy correction, based on CASSCF harmonic frequencies, shifts the energy toward TS-f by another 1.2 kcal/mol. The calculated activation entropy was 1.8 cal/mol/K higher for TS-f than for TS-a.

The MROPT2 method of multi-configuration perturbation theory[27] was applied at the CASSCF geometries to see if it would improve upon the CASSCF energies for all three points

on the potential energy surface. The MROPT2 activation energy shown in part b of Table 2 is in close agreement with B3LYP and significantly different from CASSCF. On the other hand, the TS-a − TS-f energy difference evaluated at the CASSCF geometry is negative with MROPT2. Similarly the spin projected B3LYP at the UB3LYP geometry calculations show the WH-forbidden transition state (TS-f) to be higher in energy than the WH-allowed transition state (TS-a). This may be a result of not being able to reoptimize the coordinates for the MROPT2 or PB3LYP methods. Small changes in coordinates due to reoptimization could change the relative energy by a few kilocalories per mole. For example, the CASSCF energy difference at the B3LYP structures increases by 0.5 kcal/mol.

In addition, multireference frozen-core configuration interaction with single- and double-excitation (CISD), using the CASSCF geometry, was applied to these two transition states to see whether this method could be used to calculate the small energy difference between the TS-f and TS-a structures. To be consistent, the ^{1}(a″a′) open shell ROHF configuration was used as the reference for TS-f, while ^{1}(a′a′) and two (a′)^2 configurations were used for TS-a. In both cases, these reference configurations span the minimal two-electron/two-orbital description of bond breaking and reforming between the singly occupied p orbital of the migrating group and the singly occupied molecular orbital (SOMO) of the pentadienyl ring fragment. These CI results are included in the Supporting Information and are quite similar to the other energies shown in Table 2.

A schematic showing the alternative reaction paths for the "in" and "out" hydrogen atoms on the migrating CH$_2$ group is shown in Figures 3a and 3b for the "forbidden" and "allowed" walk processes. On the allowed path, the reaction proceeds with rotation of the CH$_2$, while on the forbidden path, the same hydrogen remains over the ring and the reaction proceeds through inversion. The most important geometry parameters for both transition states are listed in Table 5. The actual Cartesian coordinates and energies for each method are given in the Supporting Information.

There are only minor differences between the CASSCF and B3LYP geometries. With the exception of the C6H6 bond distance, all CH bonds of TS-f are shorter by about 0.01 Å in the CASSCF calculations. There is no significant difference in any angles. In the case of the TS-a state, all CH bonds are shorter in the CASSCF than in the B3LYP calculations. However, the C6C7 distance is 0.03 Å longer in the CASSCF. The CH bonds from CASSCF are probably too short because dynamic correlation is not included.

Perhaps the main difference between the DFT and CASSCF results for the TS-a state can be observed in pyramidalization of the CH$_2$, which is more pyramidal in the CASSCF calculations. The pyramidalization of the methylene group in the TS-a structure opens the possiblility for existence of another form of the TS-a structure, with inverted pyramidalization of the angle (which could also be viewed as a 180° rotation of the methylene group). All attempts to find such a structure for TS-a starting from an inverted geometry converged to the original geometry. It is interesting that the pyramidalization of the methylene group in the TS-a structure points in a different direction than one would expect. That is, the TS-a pyramidalization is inverted from the pyramidalization in NCD when the C7C1 bond breaks.

Since the zero-point energy correction calculated from the CASSCF force field was found to stabilize the TS-f structure slightly, the force constant elements of TS-f and TS-a were compared. To obtain a physically meaningful comparison, both

Table 5. CASSCF and B3LYP Geometry Parameters of TS-a, TS-f, TS-t, and TS-*hyd* Transition States in 6-31G* Basis Set (Bond lengths in Å and Bond Angles in deg)

parameter	TS-forbidden		TS-allowed		TS-t		TS-*hyd*	
	CAS(b)	B3LYP	CAS(b)	B3LYP	CAS(d)	B3LYP	CAS(c)	B3LYP
r(C7H8)	1.073	1.085	1.076	1.086	1.076	1.076	1.440	1.446
r(C6H6)	1.114	1.105	1.089	1.109	1.213	1.165	1.075	1.087
r(C6C7)	1.509	1.510	1.550	1.517	1.504	1.498	1.500	1.502
r(C1C6)	1.513	1.515	1.511	1.514	1.455	1.472	2.495	2.497
r(C1C2)	1.367	1.368	1.367	1.367	1.380	1.375	1.396	1.397
r(C2C3)	1.426	1.419	1.421	1.417	1.407	1.409	1.396	1.397
r(C7C1)	2.478	2.478	2.459	2.450	2.573	2.580	1.423	1.424
r(C5C6)	1.513	1.515	1.550	1.517	1.504	1.498	1.336	1.334
∠(C7C6H6)	107.74	107.25	110.63	110.13	72.17	78.75	121.31	120.92
∠(C5C6C7)	110.17	109.99	106.86	107.86	120.81	120.62	112.87	113.25
α	128.11	127.71	121.00	123.13	163.33	160.53		
CH_2 pyram	0.00	0.00	−17.96	−8.94	+22.41	+19.51		

Table 6. Summary of DFT, CAS, and MROPT2 Calculations with 6-31G* Basis Set

	B3LYP		CASSCF			
state on PES	energy	ZPE	energy	ZPE	MROPT2	exptl [ref]
cycloheptatriene	0.00	0.00	0.00	0.00	0.00	0
norcaradiene	6.48	+0.15	11.84	+0.61	7.32	4 [7]
TS-*iso*	10.02	−0.58	21.63	−0.45	8.90	11 [7]
TS-a	48.60 (47.35)[b]	−3.93	47.30	−3.65	50.05	
TS-f	47.69 (48.01)[b]	−3.92	47.04	−4.83	51.90	
TS-t	54.45 (49.67)[b]	−4.82	60.85	−4.88	51.92	51 [6]
TS-*hyd*	40.57	−3.08	60.19	−3.02	38.70	31 [9]
TS-*inv*	5.24	+0.02				6 [8]
TS-t′	93.20 (89.02)[b]	−6.11				
toluene	−35.81	−0.06	−33.50	−0.17	−35.71	−32 [41]
p-isotoluene	−4.47	−0.46				−10 [41]
norboradiene	20.27	+0.36				14 [41]

[a] Relative energy in kcal/mol. [b] Spin projected B3LYP energies using the method of ref 37.

TS-a and TS-f quadratic Cartesian force fields were transformed into the same set of nonredundant natural internal coordinates.[34] In general, the force constants show high transferability between transition states. There are, however, a few interesting differences. It has been found that the ring CC stretches are slightly stiffer in TS-a than in TS-f. Similarly, the C6H6 stretch is stiffer in TS-a than in TS-f. Only the C6C7 stretch force constant is significantly stronger in TS-f than TS-a. This bond is also shorter in the TS-f structure by about 0.04 Å. This indicates a stronger bond that might lead to stabilization of the TS-f structure over TS-a. Among the angle deformations, there is one negative force constant for TS-a and TS-f. The negative force constant in the TS-a structure corresponds to rotation of the methylene group. In the TS-f structure, the negative value corresponds to pyramidalization of the CH_2 group. As expected, these force constants contribute the most to the normal mode with the imaginary frequency, and define the reaction coordinate for TS-a and TS-f states. Thus, for TS-a, rotation has an imaginary frequency of $229i$ cm^{-1} and pyramidalization has a real frequency of 631 cm^{-1} while for TS-f rotation has a real frequency of 273 cm^{-1} and pyramidalization has an imaginary frequency of $380i$ cm^{-1}.

For a qualitatively correct treatment of a potential surface involving diradical transition states such as TS-a and TS-f as well as TS-t and TS-t′ discussed later in this study, Noodleman[35] and Yamaguchi et al.[36] proposed projecting out the spin-contaminated Xα or UMP energy of the "singlet" state based

on calculations performed on the triplet state. Recently, it has been reported that such a projection of the spin contamination from unrestricted DFT calculations improves the agreement of calculated data with experimental data.[37] Other reports claim that this method should not be used for DFT calculations on diradicals[38] since the exact functionals would yield energies with no spin contamination. The projected energies of TS-a, TS-f, TS-t, and TS-t′ are reported in Table 6 and the Supporting Information. At TS-f, the triplet state lies below the UB3LYP "singlet", so projection raises the estimated energy of the true singlet. At Ts-a, the triplet is higher in energy, so projection lowers the estimated energy of the true singlet. As a result, the sign of the difference between TS-f and TS-a is reversed by this method of spin projection. The UB3LYP calculation approximates the lowest state with $M = 0$ (where M is the eigenvalue of the spin operator S_z[39]). If the arguments against spin projection were applied in the case when the triplet state is the ground state, then the unprojected energy should be regarded as an approximation to the $M = 0$ component of the triplet. If exact functionals were available this would be the same energy as the $M = 1$ component.

It is quite possible that the H6 hydrogen in the TS-a structure easily undergoes a tunneling process to form a transition state (TS-t) for toluene formation. This transition state has been located with unrestricted B3LYP calculations and reoptimized with CASSCF using the set of orbitals adapted for this transition state, CAS(d). Both TS-t and TS-a are true transition states with only one imaginary frequency. Along the coordinate from TS-a

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(37) Goldstein, E.; Beno, B.; Houk, K. N. *J. Am. Chem. Soc.* **1996**, *118*, 6036.
(38) Wittbrodt, J. M.; Schlegel, H. B. *J. Chem. Phys.* **1996**, *105*, 6574.
(39) Jarzęcki, A. A.; Davidson, E. R. *J. Phys. Chem. A* **1998**, *102*, 4742.

to TS-t, the initially imaginary mode A″ becomes real, and an orthogonal mode A′ that was initially real becomes imaginary. The TS-t state was 13.6 and 5.8 kcal/mol (2.3 kcal/mol after spin projection) above the TS-a structure in CASSCF and B3LYP calculations, respectively. The experimental activation energy for the TS-t transition state is 51.1 kcal/mol above the cycloheptatriene ground state, which is similar to the B3LYP calculated 54.4 kcal/mol value (49.6 kcal/mol after spin projection). It is interesting that the pyramidalization in TS-t is reversed from the intuitive direction and from TS-a. That is, the CH_2 is bent toward the migrating H6 hydrogen in TS-t (see Table 5 and Figure 1e).

(c) Suprafacial [1,5]Hydrogen Shift in Cycloheptatriene. One of the most important competitive processes to the "walk" rearrangement is the suprafacial [1,5]hydrogen shift, easily observed experimentally above 100 °C using isotopomers of cycloheptatriene. By studying the potential surface of cyclo-heptatriene with B3LYP, we were able to locate the transition structure corresponding to the hydrogen shift process (a migration from C7 to C4 in the numbering of Figure 1). The C_s structure found is a true transition state, since the calculations of force constants indicate one imaginary frequency equal to 1519i cm^{-1}. The geometry of the transition state (TS-*hyd*) found with B3LYP calculations was used as an initial geometry to find the transition structure at the CASSCF level of calculations. The CAS(c) set of orbitals was used for these calculations. The reoptimized C_s geometry of the transition structure, at the CASSCF level of calculation, is also a true transition state. For consistency of energetic comparisons, the same definition of an active CASSCF space was used to reoptimize the cyclohep-tatriene structure. The most important geometry parameters for reoptimized cycloheptatriene within the CAS(c) orbital set are listed in Table 1. Both optimized structures at the CASSCF level were used for MROPT calculations of multireference per-turbation theory to improve upon the CASSCF energy re-sults. The summary of relative energy differences for these calculations is presented in part c of Table 2. It has been found that the MROPT2 method gives an energy barrier of 38.7 kcal/mol. This energy barrier is comparable with the 40.6 kcal/mol result found with B3LYP. The CASSCF energy barrier is significantly higher. The experimental study of the [1,5]-suprafacial hydrogen shift gave the height of the barrier at about 31 kcal/mol,[9] which is still 8.0 kcal/mol less than the lowest calculated result.

Table 5 presents the most significant geometry parameters for the transition state (TS-*hyd*) found for the [1,5]hydrogen shift. There are no large differences in geometry between the CASSCF and B3LYP results. The TS-*hyd* state shown in Figure 1f has a "boat" conformation where two carbon atoms share the "pseudoaxial" hydrogen, which undergoes the rearrangement process. This result is in agreement with frequency calculations of cycloheptatriene, where the "axial" hydrogen stretch has the lowest frequency among all CH stretches (see Table 3). Interestingly, this stretch in the norcaradiene molecule changes and becomes the highest fundamental frequency (Table 4).

(d) CHT Isomerizations. Exploration of the C_7H_8 potential energy surface (PES) was extended using just B3LYP to study the interconversion of the "boat" conformation of cyclohep-tatriene and to study the transfer of hydrogen H6 across the ring to form 3-methylene-1,4-cyclohexadiene (*p*-isotoluene). In addition, the energy of norboradiene has been calculated. B3LYP and CASSCF calculations for selected points of the PES are listed in Table 6 and plotted in Figures 4 and 5. Some of these results have already been compared with energies from other
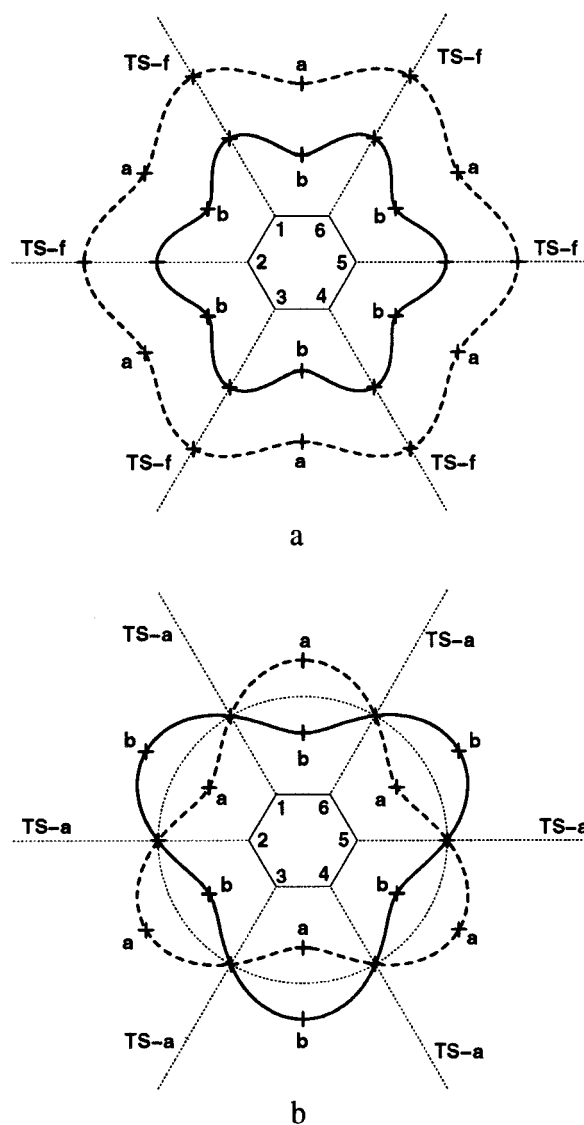

Figure 3. (a) A schematic forbidden path and (b) a schematic allowed path for the "walk" rearrangement.
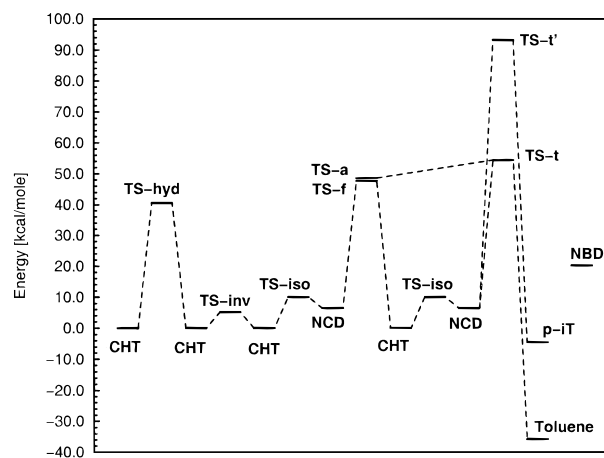

Figure 4. Relative B3LYP/6-31G* energies of calculated structures on the C_7H_8 potential energy surface: CHT, cycloheptatriene; NCD, norcaradiene; NBD, norboradiene.

methods of calculation in Table 2. Every transition state shown in Table 6 has one imaginary frequency, and every minimum has only real frequencies.
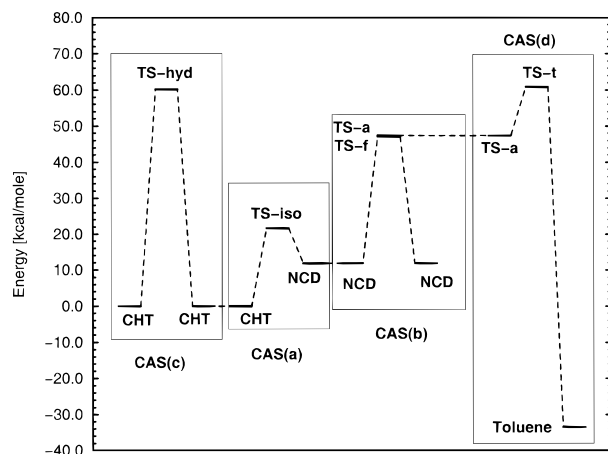
Figure 5. Relative CASSCF energies of calculated structures on the C_7H_8 potential energy surface.

The activation energy of inversion of cycloheptatriene has been determined experimentally by NMR kinetic study and found to be about 6.3 kcal/mol.[8] The calculated transition state found for this process (TS-*inv*) has C_{2v} symmetry and is 5.2 kcal/mol above the ground state of cycloheptatriene. No experimental evidence for the "chair" conformation has been found, but recently the geometry and energy of the "chair" conformation has been reported for a calculation using the Hartree−Fock method.[40] We were not able to reproduce this result and could not find any "chair" minimum using either the HF or the B3LYP formalism.

(e) ***p*-Isotoluene Formation.** The *vicinal* shift of the hydrogen atom from the ring to the methylene group to form toluene has a relatively low activation energy compared with the transfer of this hydrogen across the ring to form *p*-isotoluene. The transition state for this latter process (TS-t′) has been found with C_s symmetry about 86.8 kcal/mol above the ground state of norcaradiene. The energy calculated for *p*-isotoluene is 4.5 kcal/mol lower than that of CHT although the experimental heat of formation of *p*-isotoluene is 10 kcal/mol less than that of CHT.[41] Further, the experimental heat of formation of NBD is 13.8 kcal/mol greater than that of CHT while the B3LYP energy difference is 20.3 kcal/mol. On the other hand, the B3LYP energy of toluene is 35.8 kcal/mol below that of CHT while the experimental heat of formation is 32 kcal/mol below, which is relatively better agreement. Thus, the B3LYP/6-31G* energy difference between these quite different geometrical and electronic structures has an uncertainty of around 6 kcal/mol.

(40) Fedorov, A. V.; Snavely, D. L. *J. Phys. Chem. A* **1997**, *101*, 9042.

(41) Heats of formation were obtained from the Standard Reference Data Program, National Institute of Standards and Technology, using the on-line source at webbook.nist.gov.

Conclusions

The B3LYP results for the "walk" process give the TS-f transition state to be more stable than the TS-a state by about 0.9 kcal/mol. Both paths give a large spin density for a singlet state and the spin-corrected result actually has the oposite sign. Similarly, CASSCF results give TS-f more stable by 0.3 kcal/mol but MROPT2 reverses this when evaluated at the CAS geometry. While these methods all agree that TS-f and TS-a differ in energy by <1 kcal/mol, they are not sufficiently precise to allow the sign of the difference to be predicted. The B3LYP transition state for the isomerization of cycloheptatriene to norcaradiene (TS-*iso*) has been found 10 kcal/mol above the cycloheptatriene ground state. This agrees reasonably well with the experimental activation energy of 11 ± 2 kcal/mol and the MROPT2 value of 9 kcal/mol. As Table 6 shows, the MROPT2 results seem consistently more reliable than CASSCF and quite comparable to B3LYP.

The B3LYP transition state for the [1,5]suprafacial hydrogen shift (TS-*hyd*) has been found about 37 kcal/mol above the ground state of cycloheptatriene after zero-point correction. This result is 6 kcal/mol higher than the experimental data, but is in good agreement with MROPT2 calculations. The calculated B3LYP route for formation of toluene from norcaradiene involves a transition state (TS-t), which is about 43 kcal/mol higher than the ground state of norcaradiene after zero-point correction. The B3LYP relative energies of various stable isomers of C_7H_8 reported in this paper differ from the experimental relative enthalpies by as much as 6 kcal/mol. Thus at points where B3LYP is spin stable, the relative error between greatly different molecular structures is 6 kcal/mol.

The involvement of the allowed transition state of the walk rearrangement in the formation of toluene has been shown to be possible. The scaled quantum mechanical (SQM) force field procedure has been applied to the B3LYP/6-31G* force constant matrix of CHT and NCD. This shows that NCD has some vibrational frequencies that might be detected even in the presence of a large excess of CHT.

Supporting Information Available: Tables of optimized coordinates and energies from all calculations, full tables of scaled frequencies for cycloheptatriene and norcaradiene, and figures comparing force constants for TS-a and TS-f (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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