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Why 6-Methylpentacene Deconjugates but Avoids the Thermally Allowed Unimolecular Mechanism

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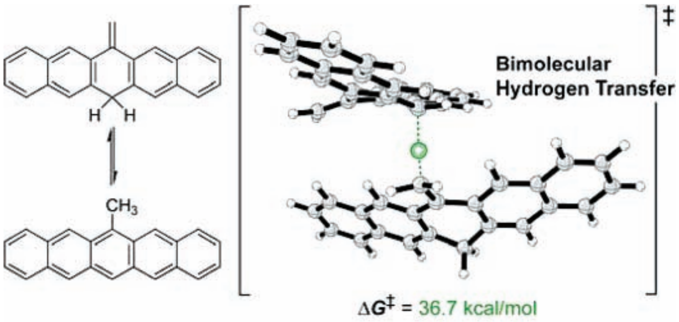
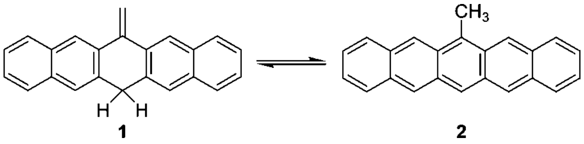
ABSTRACT



Tautomeric equilibria involving hydrogen migration in methylacenes were explored computationally using DFT methods. As the aromatic system becomes more extended, the methylene isomer is predicted to become favored. Reasonable-looking pericyclic sigmatropic hydrogen shifts are found to be energetically prohibitive, and bimolecular mechanisms involving radical pair intermediates are energetically feasible.

The unusual tautomeric equilibrium between 6-methylene-6,13-dihydropentacene (**1**) and 6-methylpentacene (**2**), shown in Scheme 1, was first observed by Clar and Wright in 1949.[1]

Scheme 1. Equilibrium between 6-Methylene-6,13-dihydropentacene (**1**) and 6-Methylpentacene (**2**)



Despite being seemingly less aromatic, the dihydro isomer is strongly favored at room temperature. A small portion of the fully aromatic methylpentacene isomer is formed when a solution of the hydrocarbon is heated to 200 °C, as shown by the appearance of a red−violet color due to strong ultraviolet absorption bands of **2**. The relative stability of the two isomers has been attributed to a decrease in resonance energy upon benzannulation,[2] although mechanisms for the interconversion process have yet to be proposed. Although the interconversion observed by Clar and Wright could be acid-catalyzed,[1] thermal mechanisms may also occur in the absence of acid. The most direct pathway for this reaction is a [1,5] sigmatropic hydrogen shift, which was suggested by Dreiding et al. to be a facile route for a similar reaction involving the conversion of toluene to 3-methylene-1,4-

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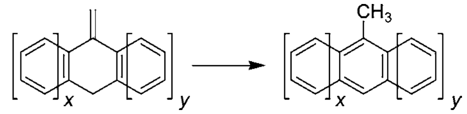
cyclohexadiene (*p*-isotoluene),[3] a reaction first reported by Plieninger to occur easily at room temperature.[4] *p*-Isotoluene was later found to give toluene and dimers in solution with second-order kinetics and activation parameters suggesting radical reactions.[5] Similarly, the conversion of *o*-isotoluene and 5-methylene-1,3-cyclohexadiene to toluene[6] and dimers[5,7] has been reported to occur with second-order kinetics in solution, and *m*-isotoluene (or homofulvene) polymerizes upon heating.[3] Other substituted isotoluenes were found to give aromatic products involving a radical pathway.[8] We show that sigmatropic hydrogen shifts in *p*-isotoluene and larger methylenedihydroacenes are energetically prohibitive and predict that a bimolecular radical chain mechanism occurs under thermal conditions; the mechanism is consistent with prior experimental work and recent experiments on methylpentacene.[9]

Dihydro derivatives of various polycyclic aromatic hydrocarbons (PAH) have been found to undergo different types of hydrogen-transfer reactions.[10] A general stepwise nonchain radical mechanism was established to explain various hydrogenation and dehydrogenation reactions.[10a,b] Hydrogen transfer was also found to be involved in the formation of graphitic species and other disproportionation byproducts from PAHs[10c−e] likely involved in defect formation in pentacene thin films.[10e] Given the increasing evidence for hydrogen transfer involving PAHs, and even though the interconversion of **1** and **2** originally observed by Clar and Wright is likely acid-catalyzed,[1] it is reasonable to suspect that the equilibrium of **1** and **2** could also involve a hydrogen-transfer mechanism that would account for possible dimeric products observed recently.[9] Such a mechanism would account for the second-order kinetics observed for the isomerization of *p*-isotoluene.

The equilibrium between **1** and **2** has been studied using DFT methods.[11] The experimentally observed appearance of some of **2** at 200 °C indicates that the ΔG of **1** is slightly below that of **2** at that temperature and several kilocalories/mole lower at 25 °C. The B3LYP-calculated reaction energies and activation energies for [1,5] hydrogen shifts are summarized in Table 1 for toluene through 6-methylpentacene (**2**). Free energies of reaction decrease in magnitude from $\Delta G = -31.8$ kcal/mol for toluene to $\Delta G = -7.3$ kcal/mol for 5-methyltetracene. For 6-methylpentacene, the equilibrium is predicted to reverse, disfavoring the fully aromatic system. The B3LYP/6-311+G(d,p) enthalpy of reaction (ΔH) agrees with experiments and predicts **2** ($x = 2$, $y = 2$) to be less stable by 1.1 kcal/mol. The free energy of reaction (ΔG) also predicts **2** to be less stable, but only slightly (0.2 kcal/mol). Methylacene **2** is calculated to be entropically favored by $\Delta S = 3.0$ cal/mol K at 298 K and by $\Delta S = 3.3$ cal/mol K at 473 K. This corresponds to $\Delta\Delta G = -0.6$ kcal/mol from $\Delta G = 0.2$ kcal/mol at room temperature to $\Delta G = -0.4$ kcal/mol at 473 K. The higher entropy of **2** is a consequence of the easy out-of-plane librations of the pentacene coupled strongly with rotation of the methyl group.[12] The shift in the relative stability of the two isomers is correctly predicted to occur at pentacene in the series of acenes.

Table 1. B3LYP/6-31G(d) Reaction and Activation Energies for [1,5] Hydrogen Shifts (298 K)[a]



x	y	ΔH	ΔG	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$
0	0	−30.8	−31.8	70.4	71.4
1	0	−24.5	−23.9	67.4	68.9
1	1	−11.0	−11.9	66.2	67.1
2	1	−5.6	−7.3	67.2	67.1
2	2	−0.2 (1.1)[b]	−1.1 (0.2)[b]	67.0	67.9

[a] Energies reported in kcal/mol. [b] B3LYP/6-311+G(d,p) energies are in parentheses.

The trends in free energies of activation for [1,5] hydrogen shifts are steady and within the range of $\Delta G^{\ddagger} = 67.1$ and $\Delta G^{\ddagger} = 71.4$ kcal/mol, as listed in Table 1. The activation energy for a [1,5] hydrogen shift in **1** is predicted to be extraordinarily high at $\Delta G^{\ddagger} = 67.9$ kcal/mol. This is attributed to a strained geometry in the transition structure. Even though the ground-state minimum of **1**, shown in Figure 1, adopts a bent structure (∼145°) that makes it seemingly poised for a [1,5] hydrogen shift, the methylene carbon remains significantly far (4.14 Å) from the hydrogen. As seen in structure **TS-1-5**, the C2−C3−C4 angle must decrease from 151° in **1** to 85° in the transition structure. When compared to the geometries of systems where [1,5] hydrogen shifts are ideal, such as cyclopentadiene[13] and (*Z*)-1,3-pentadiene,[13c−f,14] this is a significant distortion from the

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(9) NMR data consistent with the formation of dimers support our predictions that the mechanism occurs intermolecularly. Full details will be reported in due course.

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(11) All calculations were carried out using the Gaussian 03 program (Frisch, M. J. et al., *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford CT, 2004. Full ref listed in Supporting Information). Geometries were optimized using the hybrid density functional B3LYP with the 6-31G(d) basis set and, in specified cases, B3LYP/6-311+G(d,p). For a detailed description of the computational procedure, see Supporting Information.

(12) A hindered rotor approximation for rotation of the methyl group in **2** was applied for thermal corrections and entropy calculations. However, it is suspected that strong coupling between rotation of the methyl group and other skeletal vibrations leads to overcorrection of the partition function and, in turn, entropy and free energy. Consequently, the relative energies of **2** do not contain hindered rotor approximations. For a detailed description of the hindered rotor analysis, see Supporting Information.

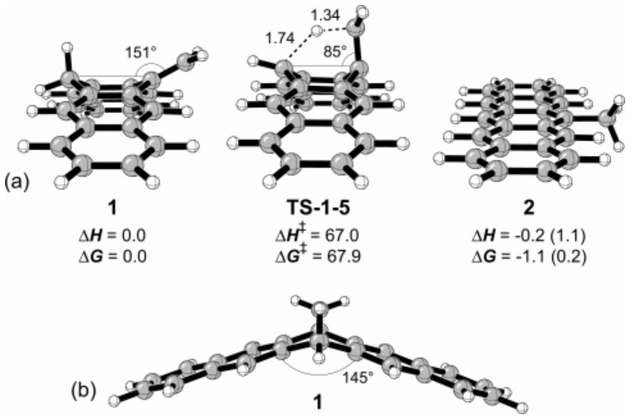


Figure 1. B3LYP/6-31G(d) ground-state minima and transition structure for a [1,5] hydrogen shift shown (a) down the long axis and (b) from the side of the pentacene backbone. B3LYP/6-311+G-(d,p) energies are shown in parentheses. Energies are reported in kcal/mol.

minimum. These effects are observed in [1,5] hydrogen shifts calculated for toluene through 6-methylpentacene, as shown in Table 1.

Alternative intramolecular mechanisms that lead to a formal [1,5] shift and would potentially circumvent the geometric demands of a [1,5] shift mechanism include a series of [1,2] or [1,3] hydrogen shifts. The reaction and activation energies for these pathways have been calculated, in addition to the direct [1,5] sigmatropic hydrogen shift pathway. The B3LYP/6-31G(d) $\Delta G^{\ddagger}$ for the initial [1,2] shift in **1** is 67.7 kcal/mol, and free energies of activation for subsequent [1,2] shifts are in general just as high or even higher. A [1,3] shift occurring with suprafacial stereochemistry is a thermally forbidden process and requires substantial twisting of the acene backbone. For example, $\Delta G^{\ddagger}$ for the initial forbidden [1,3] shift (**TS-1-3**) in **1** is an insurmountable 96.3 kcal/mol, thereby eliminating all reasonable mechanisms involving intramolecular hydrogen shifts.

An intermolecular mechanism consisting of bimolecular hydrogen transfer and radical formation is proposed in Scheme 2. This mechanism involves initiation by hydrogen transfer between two molecules of **1** via a molecular disproportionation step to form two radicals, **3** and **4**. The radical adduct **4** undergoes hydrogen transfer as a radical chain propagation step to regenerate a radical and to form product **2**. The reaction is then terminated by radical disproportionation to form two methyl isomers.

B3LYP/6-31G(d) energies for the distinct forward and reverse steps of this mechanism are listed in Table 2. The initiation step is predicted to be rate determining with $\Delta G^{\ddagger} = 36.7$ kcal/mol corresponding to **TS-1**. This step is substantially endergonic with $\Delta G = 14.9$ kcal/mol. The gas-phase geometry for bimolecular hydrogen transfer in the initiation reaction corresponding to **TS-1** is shown in Figure 2. The two molecules orient perpendicular to each other and at an angle allowing the methylene group to approach the hydrogen while minimizing repulsion between the two π systems. The σ bond of the hydrogen being abstracted elongates to 1.56 Å, and the forming bond of the methyl group becomes 1.25 Å.

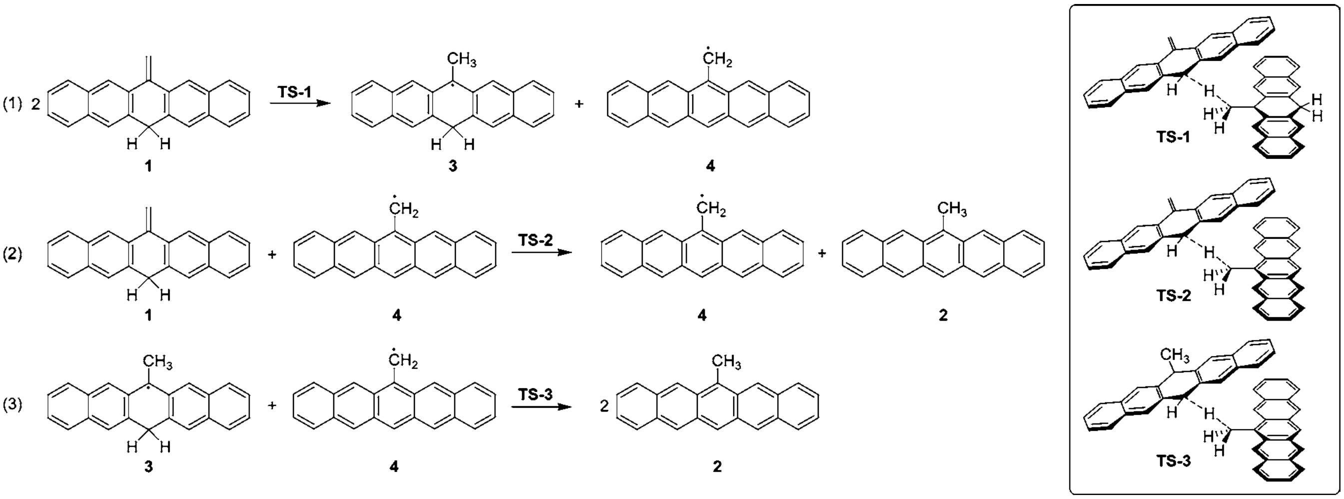
Table 2. B3LYP/6-31G(d) Reaction and Activation Energies and Entropies for Bimolecular Hydrogen Transfer (298 K)[a,b]

reaction	ΔH	ΔG	ΔS	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$
(1)	16.7	14.9	5.8	25.5	36.7	−37.6
−(1)	−16.7	−14.9	−5.8	8.8	21.8	−43.4
(2)	−0.2	−1.1	3.2	17.2	28.7	−38.5
−(2)	0.2	1.1	−3.2	17.4	29.8	−41.7
(3)	−17.1	−19.2	0.7	11.8	24.1	−41.4
−(3)	17.1	19.2	−0.7	28.7	41.3	−42.0

[a] See Scheme 2. [b] Energies are reported in kcal/mol, and entropies are reported in cal/mol K. Reverse reactions are indicated with a minus sign.

The subsequent hydrogen-transfer and disproportionation reactions are exergonic ($\Delta G = -1.1$ and $\Delta G = -19.2$ kcal/

Scheme 2. Proposed Mechanisms Involving Bimolecular Hydrogen Transfer Radical Formation



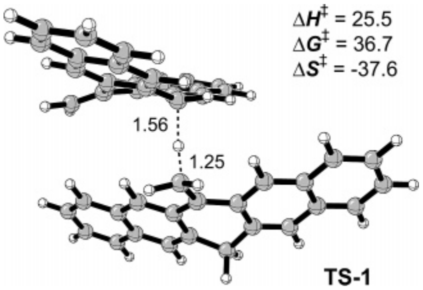


Figure 2. B3LYP/6-31G(d) transition structure **TS-1** for initial radical formation by bimolecular hydrogen transfer. Energies are reported in kcal/mol, and entropies are reported in cal/mol K.

mol, respectively) and require lower activation energies. Transition structure **TS-2** occurs with $\Delta G^{\ddagger} = 28.7$ kcal/mol, and **TS-3** occurs with $\Delta G^{\ddagger} = 24.1$ kcal/mol. The geometries of **TS-2** and **TS-3** are quite similar to **TS-1** and, therefore, are not shown here. Free energies reflect the entropic consequences of a bimolecular mechanism. Activation entropies for these bimolecular processes range from −37.6 to −41.4 cal/mol K for the forward reactions involving **TS-1**−**TS-3**. The energetics for the backward reactions also indicate that the mechanism is reversible. The reverse reaction of the termination step ($\Delta G^{\ddagger} = 41.3$ and $\Delta G = 19.2$ kcal/mol) is energetically comparable to the initiation step, and the remaining reverse reactions are exergonic or near thermoneutral with low activation energies.

Equilibria involving other methylacenes are proposed to occur through such intermolecular bimolecular hydrogen transfer mechanisms. Intramolecular mechanisms involving sigmatropic hydrogen shifts are energetically unfavorable pathways. A mechanism involving radical pair intermediates and bimolecular hydrogen transfer can account for product formation with reasonable reaction and activation energies. These mechanisms are reversible and are energetically feasible pathways that avoid the geometric and energetic demands of intramolecular hydrogen shifts.

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Supporting Information Available: Details of the computational procedure, Cartesian coordinates, spin contamination values for open-shell structures, electronic energies, and thermal corrections of ground states and transition states. This material is available free of charge via the Internet at http://pubs.acs.org.

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