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Tautomerization of Some Methylacenes and the Role of Reverse Radical Disproportionation

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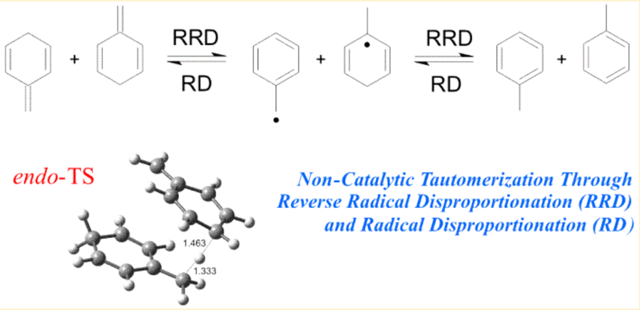
S Supporting Information

ABSTRACT: The thermokinetics for the tautomerization of a series of methylenedihydroacenes to the corresponding methylacenes (toluene to 6-methylpentacene) have been investigated by means of CBS-QB3 calculations. Only for 6-methylpentacene does the methylenedihydro form predominate at room temperature. The obtained equilibrium ratios are consistent with various theoretical methods, but the agreement with the scarce experimental data is only qualitative. The noncatalyzed thermal tautomerization of the methylenedihydroacene in an inert solvent may proceed by means of a reverse radical disproportionation reaction (RRD) as the rate-determining step. The benzylic BDE(C−H)s and the hydrogen atom affinities (HA) of the tautomers have been used to calculate the reaction enthalpy, $\Delta_{\mathrm{RRD}}H$. It appears that the $E_{\mathrm{a,RRD}}$ is substantially higher than $\Delta_{\mathrm{RRD}}H$. This implies that the opposite reaction (and the tautomer forming step), a radical−radical disproportionation (RD), is an activated process. This is an often ignored or overlooked kinetic feature. The consequence is that although the RRD reaction may be kinetically feasible at elevated temperatures, the products are not the tautomers but rather dimers stemming from radical−radical recombination reactions, with *p*-isotoluene as a clear exception. It is further shown that the RRD self-reaction of phenalene is too slow at 298 K, despite claims to the contrary.



INTRODUCTION

The effect of benzannulation on the equilibrium between methylacenes (**1**−**5**) and their methylenedihydroacene tautomers (**1t**−**5t**) (Scheme 1) was reported for the first time in a seminal paper by Clar in 1949.[1] Therein, it was established that in a nonpolar solvent and at room temperature 6-methylpentacene (**5**) exists (almost) exclusively as the tautomeric methylene-6,13-dihydropentacene (**5t**), whereas for methylacenes with fewer *β*-fused rings the aromatic entity prevails. This conclusion has been reached on the basis of the change of the UV absorbance upon heating of a solution containing a single tautomer. According to the literature, the experiment with 6-methylpentacene has never been repeated afterward. Various experimental[2] and computational[3] studies have followed in an effort to understand in detail the relationship between aromaticity (resonance enthalpy), the number of annulated rings, and the tautomeric equilibrium ratios.

Recently, we have computationally studied the tautomerization (keto−enolization) of hydroxyl-substituted naphthols and 9-anthrols employing the CBS-QB3 model chemistry.[4] It has been found that the calculated equilibrium ratio between anthrone and 9-anthrol in a non-hydrogen-bonding solvent is in excellent agreement with experiment.[4] Next to benzannulation, the tautomeric ratio in solution can be influenced significantly through the formation of intra- and intermolecular hydrogen bonds.[4] Despite the fact that the thermodynamics of the keto−enolization for the hydroxyarenes may now be well understood, the precise mechanism and, therefore, the rates are difficult to predict. In general, the presence of an acid appears to be a prerequisite for a facile transformation. A similar mechanistic uncertainty holds for the tautomerzation of methylacenes. For example, from a thermodynamic perspective, 3-methylene-1,4-cyclohexadiene (*p*-isotoluene, **1t**) is supposed to be a rather unstable compound with regard to its tautomer, toluene (**1**), due to the aromatic stabilization of the latter. However, in solution the noncatalyzed conversion of **1t** to **1** is relatively slow.[5] Conversely, in solution the disubstituted pentacene derivative 6,13-dipropylpentacene (**6**) does not convert to its tautomer **6t** (eq 1), as is the case for **5**, even at temperatures of around 373 K.[2e]

The mechanism for the tautomerization can be envisaged as a two-step process and is shown in Scheme 2. First, a hydrogen atom is shuttled between two methylenedihydroacenes, thereby generating two benzyl/cyclohexadienyl-type radicals. This rate-determining bimolecular reaction is referred to as "reverse radical disproportionation" (RRD).[6] Second, the forward radical disproportionation (RD) yields the two methylacenes.

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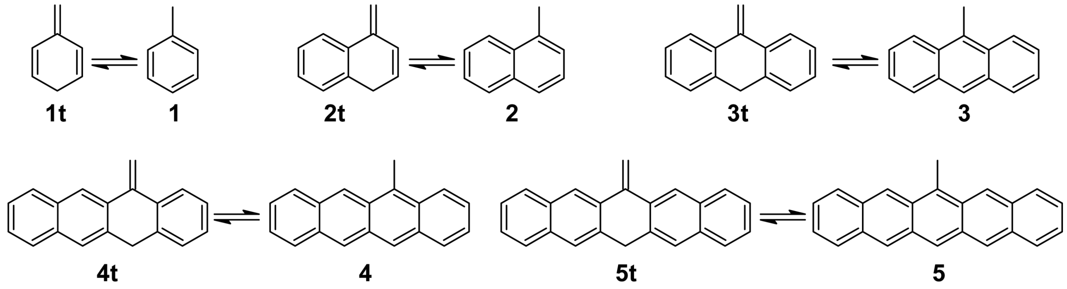
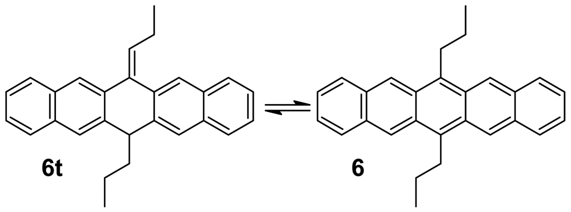
Scheme 1. Tautomeric Equilibria of Methylacenes





(1)

These hydrogen atom shuttling reactions have been identified in high-temperature processes involving the cleavage of strong chemical bonds during coal liquefaction, the desubstitution of chlorinated hydroxyarenes, and the uncatalyzed hydrogenation of C═C and C═N bonds.[6−8] However, there exists great uncertainty regarding the magnitude of the activation enthalpy for the RRD reaction, $E_{\text{a,RRD}}$, which hampers any attempt to predict the corresponding rates and to assess the importance of such a reaction in the tautomerization process. At first approximation, one can assume that the E_{aRRD} is close to reaction enthalpy for RRD, $\Delta_{\text{RRD}}H$, since the enthalpic barrier for the opposite radical disproportionation (RD), $E_{\text{a,RD}}$, is close to zero. This microscopic equilibrium consideration has been well documented for a large body of radicals and can be found in almost any textbook on radical chemistry. However, in a computational study on the tautomerization of a series of *β*-fused methylacenes (**1**, **3**, and **5**), unexpectedly high values for $E_{\text{a,RD}}$, were found.[3c] An experimental investigation on the tautomerization of some methylacenes seems to support the computational kinetic results, but the major observed products were not the tautomers.[2c] In an attempt to resolve these matters, we have studied, by employing CBS-QB3 calculations, the thermokinetic features of the tautomerization for the series of compounds displayed in Scheme 1. To gain insight in the hydrogen atom donor ability, the carbon−hydrogen bond dissociation enthalpies, BDE(C−H)s, for the various species (molecules and radicals) involved have been computed. Transition-state calculations have been conducted for some systems. These data may allow to evaluate the proposed mechanistic option(s).

■ RESULTS AND DISCUSSION

Tautomeric Ratios of Methylacenes. In Table 1, the CBS-QB3-computed free energies (Δ_tG), enthalpies (Δ_tH), and entropies (Δ_tS) for tautomerization have been compiled for a series of methylacenes consisting of toluene (**1**), 1-methylnaphthalene (**2**), 9-methylanthracene (**3**), 5-methyltetracene (**4**), and 6-methylpentacene (**5**). Here, the tautomerization is defined as the transformation of a methylenedihydroacene (**xt**) to a methylacene (**x**), i.e., **xt** ⇌ **x**. The Δ_tS (and Δ_tG) data have been adjusted to correct for the contribution by internal and external rotational symmetry (see the Supporting Information). The thermodynamic data ($\Delta_fG°$, $\Delta_fH°$, $S°$) for the individual and auxiliary compounds obtained by the CBS-QB3 calculations are listed in Table S1 of the Supporting Information together with experimental $\Delta_fH°$s from the literature. Table S1 shows that CBS-QB3 overestimates slightly, by 1−2 kcal mol^{-1}, the experimental enthalpies of formation; larger discrepancies may well be associated with erroneous experimental data (see, for example, footnote *m* in Table S1). In the case of the 6-methylpentacene system **5t** ⇌ **5**, the CCSD(T) step of the CBS-QB3 computational sequence turned out to be too time-consuming for our computer resources. Fortunately, there exists an excellent linear correlation (see Table S2) between the thermodynamic quantities (Δ_tG and Δ_tH) obtained by the full CBS-QB3 sequence and by the much lower computational time demanding (U)B3LYP/CBSB7 geometry optimization and frequency steps of the composite CBS-QB3 method, leading to extrapolated "CBS-QB3" values for the tautomerization **5t** ⇌ **5** of Δ_tG = 2.5 kcal mol^{-1} and Δ_tH = 2.4 kcal mol^{-1}. The thermodynamic data obtained by several other theoretical methods also have been included in Table 1. According to the CBS-QB3 computations, the increase in the enthalpies of tautomerization, Δ_tH, upon benzannulation from toluene to 6-methylpentacene is 31.6 kcal mol^{-1}. Notably, this result is very close to the 30.4 kcal mol^{-1} proposed by Clar in 1949 and obtained without any computational resources.[1] Clearly, the most important contribution to Δ_tH is the (partial) gain/loss of the aromatic resonance enthalpy (RE)[9−11] as has been observed for the enthalpy of ketonization for a series of hydroxyarenes (phenol, 1-naphthol, and 9-anthrol).[4] An analogous enthalpic dependence is expected to be the dominant factor in the dehydrogenation for the corresponding dihydroacenes (Scheme 3). Therefore, the enthalpy of dehydrogenation, $\Delta_{\text{dehydr}}H$, for compounds **7**−**11** has also been computed at the CBS-QB3 level of theory. The results are collected in Tables S2 and S3,

Scheme 2. Reverse Radical Disproportionation and Radical Disproportionation

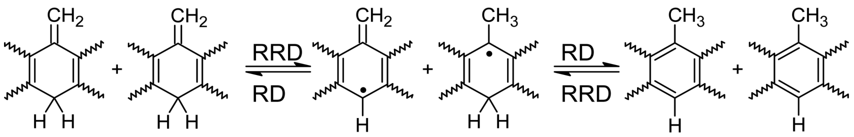
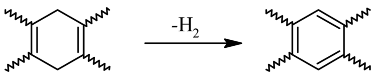


Table 1. Δ_tG, Δ_tH, and Δ_tS for Tautomerization of Methylacenes 1−5[a]

	Δ_tG[b]	Δ_tH[b]	Δ_tS[b]	Δ_tH[c]	Δ_tH[d]	Δ_tH[e]	Δ_tH[f]
1t ⇌ **1**	−29.6	−29.2	1.4	−30.8	−32.3	−21.9	[−38.8]
2t ⇌ **2**	−21.3	−22.6	−4.2	−24.5	−23.0	−15.9	[−34.1]
3t ⇌ **3**	−8.4	−8.7	−1.0	−11.0	−9.9	−1.2	[−25.5]
4t ⇌ **4**	−4.2	−3.9	1.2	−5.6	−4.1		[−18.4]
5t ⇌ **5**	2.5[g]	2.4[g,h]	−0.2[g]	−0.2	2.6	8.9	[−8.4]
6t ⇌ **6**	6.5[g]	6.0[g,h]	−1.6[g]				
1−**5**[i]		−31.6		−30.6	−34.9	−30.8	−30.4

[a]In (k)cal mol^{-1} (K^{-1}), at T = 298 K, see Scheme 1. [b]This work, at the CBS-QB3 level of theory. [c]B3LYP/6-31G(d) calculations.[3c] [d]SCF-MO theory calculations.[3b] [e]Semiempirical MNDO calculations.[2d] [f]According to an aromatic resonance concept, without the "aliphatic" resonance.[1a] [g]Calculated from linear correlations (r^2 > 0.9999) between the two sets (for **1**−**4**) of computational data (CBS-QB3 and B3LYP/CBSB7, see Table S2). [h]According to MNDO calculations, Δ_tH(**5t**⇌**5**) = 8.9 and Δ_tH(**6t**⇌**6**) = 13.0 kcal mol^{-1}.[2e] [i]Change in Δ_tH between toluene and 6-methylpentacene.

Scheme 3. Dehydrogenation of Some Linear Dihydroaromatics



7-11 **12-16**

7/**12**: 1,4-cyclohexadiene/benzene

8/**13**: 1,4-dihydronaphthalene/naphthalene

9/**14**: 9,10-dihydroanthracene/anthracene

10/**15**: 5,12-dihydrotetracene/tetracene

11/**16**: 6,13-dihydropentacene/pentacene

showing that the $\Delta_{dehydr}H$s range from −7.0 (1,4-cyclohexadiene to benzene, **7** → **12**) to 27.8 kcal mol^{-1} (6,13-dihydropentacene to pentacene, **11** → **16**) and that they are generally in good agreement with the experimental reaction enthalpies. A rather satisfying linear relationship can be derived between the enthalpy of tautomerization, Δ_tH, of the methylenedihydroacences and the enthalpy of dehydrogenation, $\Delta_{dehydr}H$, of the related dihydroacenes following $\Delta_tH = 0.91 \times \Delta_{dehydr}H - 23.4$ ($r^2 = 0.997$). This underscores that in both processes, tautomerization and dehydrogenation, about the same amount of aromatic stabilization enthalpy is gained. Interestingly, the enthalpy of dehydrogenation of 6,13-dihydropentacene (**11**) is now (almost) identical to the $\Delta_{dehydr}H$ for conversion of cyclohexane to cyclohexene, thus clearly demonstrating the high reactivity (e.g., in addition reactions) of the center ring of pentacene.[12]

The tautomeric equilibrium ratios are determined by Δ_tG and not only by Δ_tH. It may be expected that the molecular entropy increases in the conversion of the methylenedihydroacene to the methylacene due to the formation of an internal (free) methyl rotor. At first approximation, the contribution of a free rotating methyl group to the molecular entropy, S^0, at 298 K, can be estimated as 5.8 cal mol^{-1}K^{-1}.[13] In the calculations, the methyl group is treated as a one-dimensional rotor, and after correction for the internal and external rotations CBS-QB3 computes for the series **1t**−**5t**, excluding **2t**, a Δ_tS of about |1−2| cal mol^{-1} K^{-1}. Experimentally, it is found that the methyl group in toluene (**1**) is essentially a free rotor with a rotational barrier, $\Delta_{rot}G^‡$, of less than 0.02 kcal mol^{-1}.[14] The methyl group in 1-methylnaphthalene (**2**) is a hindered rotor with a $\Delta_{rot}G^‡$ = 2.3 kcal mol^{-1}[15,16] as observed by experiment. Because of this hindrance, the entropy for the tautomerization decreases: Δ_tS(**2t**⇌**2**) = −4.2 cal mol^{-1} K^{-1}. Again for 9-methylanthracene (**3**), a low experimental rotational barrier of $\Delta_{rot}G^‡$ = 0.3 kcal mol^{-1} is found.[16,17] The rotation of the methyl group in **3**[18] and higher methylacenes[3c] is coupled to the out-of-plane bending mode of the aromatic ring system. These low vibrational and rotational frequency modes are large contributors to S^0; hence, erroneous handling by a computational method may well lead to an unreliable Δ_tS and consequently an inaccurate tautomeric equilibrium ratio.

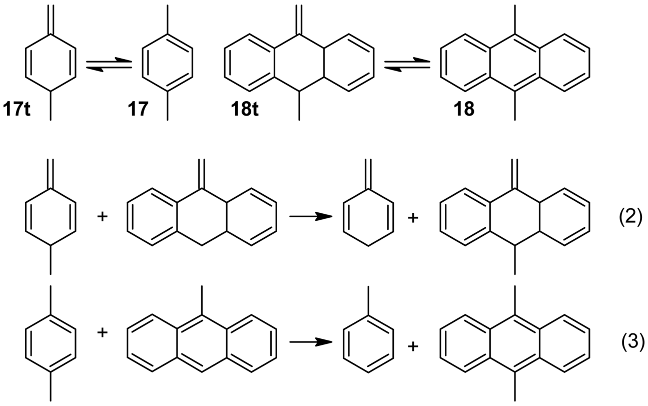
Although the CBS-QB3 method is expected to provide quite accurate thermodynamic data (within 1−2 kcal mol^{-1}), the computational results seem to be only in fair agreement with the findings from experimental studies.[1,2d] It has been claimed that at room temperature 6-methylene-6,13-dihydropentacene (**5t**) and not 6-methylpentacene (**5**) is thermodynamically the most stable conformer, i.e., Δ_tH and Δ_tG > 0, while for the methylacenes **1**−**4** the aromatic entity largely prevails (vide infra), consonant with the computational results.[1] The tautomerization of **4t** ⇌ **4** and **5t** ⇌ **5** have been investigated by means of UV spectroscopy. From the UV spectrum of 5-methyltetracene (**4**) dissolved in alcohol at room temperature, it has been concluded that only a small fraction of the tautomer **4t** is present.[19] If the percentage of **4t** is arbitrarily set at 1%, Δ_tG_{exp}(**4t**⇌**4**) is calculated to be −2.7 kcal mol^{-1} at 298 K, in reasonable agreement with the Δ_tG of −4.2 kcal mol^{-1} obtained by CBS-QB3, which corresponds to a fraction of 0.08% for **4t**.[19] When a solution of **5t** dissolved in 1,2,4-trichlorobenzene or 1-methylnaphthalene is heated up to 473 K in the absence of air, the pale yellow color turns to violet-red; the related change of the UV spectrum indicates the formation of 6-methylpentacene (**5**).[1,20] From these observations, the percentage of **5** has been estimated as ≤1% at 473 K. This in turn leads to Δ_tG_{exp}(**5t**⇌**5**) ≥ 4.3 kcal mol^{-1}, to be compared with the calculated Δ_tG(**5t**⇌**5**) of 2.5 kcal mol^{-1} (see Table S2) at that temperature. Our computations suggest that under equilibrium conditions the percentage of **5** increases from 1.5 to 6.5% over a temperature range of 298 to 473 K.[21]

The differences between theory (gas phase) and experiment (liquid phase) may originate from the interactions of the solvent with the two tautomeric species. A sizable solvent effect has been found for the tautomeric equilibrium ratio for 9-anthrone ⇌ 9-anthrol due to the formation of a 1:1 hydrogen-bonding complex between the solute (carbonyl and/or hydroxyl) and the hydrogen bond accepting and/or donating solvent.[4] It seems rather unlikely that the same holds for the all-carbon molecules of the present study. Compounds with benzylic hydrogens such as toluene, 1-methylnaphthalene, or 9-methylanthracene do not form 1:1 hydrogen-bonded complexes with a hydrogen bond accepting solvent,[22] leaving only a dissimilarity in the global solvation between the two tautomers as a possibility. The effect of solvation by 1,2,4-trichlorobenzene (ε_r = 5.7) on the **5t** $\rightleftharpoons$ **5** equilibrium has briefly been explored by B3LYP/CBSB7 computations in combination with the PCM continuum solvation model. It was found that the Δ_tG at 298 K changes only marginally (a decrease of 0.1 kcal mol^{-1}) upon solvation, meaning that there is no significant difference in the solvation energies for the species involved. Therefore, until further refinement is possible, the percentage of **5** at 298 K under fully equilibrated conditions is (much) higher than anticipated by the single experimental study.[1]

The enthalpies of tautomerization for some methylenedihydroacenes have been determined in the gas phase by measuring the (difference in the) acidities of the tautomers.[2d] These experiments have yielded Δ_tH's of −24.0 ± 1.8, −15.8 ± 1.8, and −5.1 ± 1.8 kcal mol^{-1} for **1t** $\rightleftharpoons$ **1**, **2t** $\rightleftharpoons$ **2**, and **3t** $\rightleftharpoons$ **3**, respectively, thus differing by 4−7 kcal mol^{-1} from the Δ_tH's obtained by CBS-QB3 (see Table 1). However, gas-phase acidity experiments may not be the most reliable instrument in this case. For instance, the same methodology has yielded for the tautomerization of 2,5-cyclohexadienone to phenol a Δ_tH = −10.0 ± 3.0 kcal mol^{-1},[23a] while other (computational) methods have afforded much lower values (Δ_tH = −17.0[23b] and −17.7 kcal mol^{-1}[14]). In the liquid phase, the heats of solution for the individual compounds **2t**, **2** and **3t**, **3** in CCl_4 at 298 K have been determined by calorimetry.[2d,24] The Δ_tH's for **2t** $\rightleftharpoons$ **2** and **3t** $\rightleftharpoons$ **3** derived in this way are −15.0 ± 2.0 and −3.4 ± 4.0 kcal mol^{-1}, respectively, i.e., 5−7 kcal mol^{-1} higher than the CBS-QB3 results. The large error margins may be associated with the unknown heats of vaporization (for **2t**, **2**) or sublimation (for **3t**, **3**). In any case, the experimental Δ_tH(**3t** $\rightleftharpoons$ **3**) suggests that it may be feasible to observe the tautomer **3t** by, e.g., NMR spectrometry when starting from **3**.[21,25] However, this appears not to be the case, which is corroborated by the equilibrium ratio for **3**/**3t** of about 10^6 at 298 K found in this study (see Table 1). Recently, the synthesis and tautomerization of 6,13-dipropylpentacene (**6**) (eq 1) has been reported.[2e] The computations reveal that the equilibrium **6t** $\rightleftharpoons$ **6** relative to **5t** $\rightleftharpoons$ **5** has been shifted further toward the 6-propylidene-13-propyl-6,13-dihydropentacene (**6t**) (see Table 1), with an increase in Δ_tH of about 3.6 kcal mol^{-1}.

The origin of the enhanced preference for the dihydro tautomer can be demonstrated by analyzing the change of the $\Delta_fH°$s for the tautomeric species in which a hydrogen atom is replaced by a methyl group (Scheme 4). Replacing C4−H (**1t**) by C4−Me (**17t**) leads to a decrease in Δ_tH(**17t**$\rightleftharpoons$**17**) relative to Δ_tH(**1t**$\rightleftharpoons$**1**) of −1.3 kcal mol^{-1}. Conversely, substituting C10−H (**3t**) by C10−Me (**18t**) yields an increase of Δ_tH(**18t**$\rightleftharpoons$**18**) relative to Δ_tH(**3t**$\rightleftharpoons$**3**) of 2.6 kcal mol^{-1}, meaning that the equilibrium is shifted toward the methylenedihydro derivative. The main reason for this change is the repulsive interaction between the methyl substituent at the sp^2 carbon and the adjacent C−H moieties as illustrated by reactions 2 and 3 with enthalpies of reaction of Δ_rH = −1.0 and 2.9 kcal mol^{-1}, respectively. Hence, the tautomeric equilibrium can be altered not only by extended benzannulation but also by the introduction of bulky groups at the carbon atom in opposite position to the methylene group.

Scheme 4

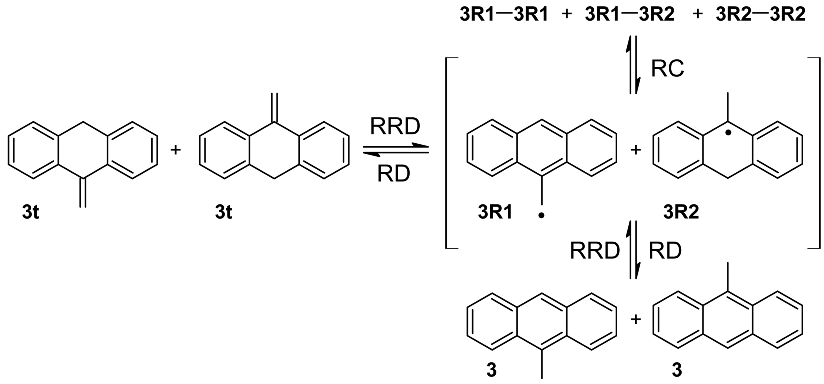


With a Δ_tG of 6.5 kcal mol^{-1} (see Table 1), a **6**/**6t** ratio of about 2 × 10^{-5} is predicted at 298 K. However, it has been reported that **6**, dissolved in $CDCl_3$ and kept under nitrogen, does not convert to **6t** at room temperature.[2e] Similarly, a dilute solution of **6** (ca. 4 mM) in mesitylene remains unaffected when heated up to 423 K.[2e] Under those conditions, the tautomerization to **6t** occurs readily only in the presence of an organic acid.[2e,26]

Further benzofusion at the [*b*] side of the methylacene leads to an increasingly favorable thermodynamic driving force toward the tautomeric methylenedihydroacene. However, the apparently slow kinetics for the self-reaction hamper the equilibration.

Tautomerization by Reverse Radical Disproportionation. The noncatalytic tautomerization of a methylenedihydroacene to a methylacene in an inert solvent is likely to proceed through a two-step mechanism. The conversion of 9-methylenedihydroanthracene (**3t**) into 9-methylantracene (**3**) is presented in some detail in Scheme 5. The initial reverse radical disproportionation, RRD, reaction between two molecules **3t** involves a transfer of a benzylic hydrogen atom to the exocyclic olefinic moiety, yielding two distinct hydroaromatic radicals: **3R1** and **3R2**. In the subsequent radical disproportionation, RD, a hydrogen atom is shuttled between the incipient radicals leading to two 9-methylanthracenes (**3**). After a singlet−triplet interconversion, an alternative second pathway for radicals **3R1** and **3R2** consists of a (reversible) radical recombination, RC, resulting in the formation of various dimeric compounds.[27] Generally, it is assumed that the activation energy/enthalpy of the RRD reaction, $E_{a,RRD}$ (= $\Delta_{RRD}H^{\ddagger} + RT$), is close to the reaction enthalpy, i.e., $E_{a,RRD} \cong \Delta_{RRD}H$.[8,28] This implies that the activation energy for the backward reaction (a radical−radical disproportionation), $E_{a,RD}$, approaches zero. A minor enthalpic barrier (1−3 kcal mol^{-1}) for the RD reaction imposed by the temperature dependence of the solvent's viscosity (diffusion control) must be taken into account. Alternatively, from a series of related experimental studies it can be deduced that $E_{a,RRD} = -8.4 + 0.98 \times \Delta_{RRD}H$.[29] That means that the activation enthalpy is, rather unexpectedly, lower than the reaction enthalpy. In 1990, linear correlations between activation enthalpy and reaction enthalpy have been proposed to follow $E_{a,RRD} = 9 + 0.82 \times \Delta_{RRD}H$ and $E_{a,RD} = 9 + 0.18 \times \Delta_{RD}H$ ($\Delta_{RRD}H = -\Delta_{RD}H$).[30] However, the experimental data to support these thermokinetic equations appear

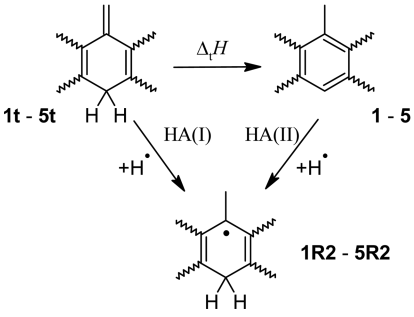
Scheme 5. Noncatalytic Tautomerization through Reverse Radical Disproportionation (RRD) and Radical Disproportionation (RD)



rather obscure. Clearly, there exists a considerable uncertainty regarding the relationship between E_{aRRD} and $\Delta_{RRD}H$.

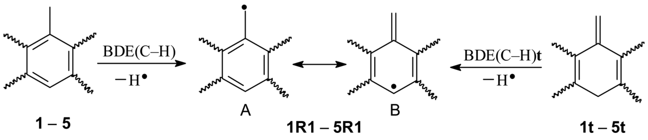
In any case, in order to predict the E_{aRRD}s for the methylenedihydroacenes and the methylacenes, the $\Delta_{RRD}H$s needs to be known, and they have been computed by CBS-QB3. The $\Delta_{RRD}H$ consists of two components: the reaction enthalpy involving the addition of a hydrogen atom (hydrogen affinity, HA) and the bond dissociation enthalpy of the hydrogen atom donor, BDE(C−H). First, the HAs of the tautomers have been calculated. This quantity is defined as the enthalpy of addition for a hydrogen atom to the exocyclic methylene carbon in the methylenedihydroacene, HA(I) or to the aromatic carbon atom opposite to the C−CH_3 moiety in the methylacene, HA(II), as illustrated in Scheme 6. The HAs are correlated through Δ_tH = HA(I) − HA(II). The results are summarized in Table 2. The HA(I)s for the methylenedihydroacenes vary only slightly from −52.2 (**1t**) to −48.1 (**5t**) kcal mol^{-1}, and the HA(I)s for **3t**, **4t**, and **5t** are almost identical. For these compounds, the increments in the heats of formation due to benzofusion at the [*b*] side for both the molecule and the adduct radical are identical (see Table S1), which explains why there is no variation in the HA(I)s. In Scheme S1, the Mulliken (α) spin densities in the product radicals ***x*R2** (x = 1−5) are visualized. The major spin density in the radical species is located on the benzylic carbon and varies marginally from 0.556 (**1R2**), 0.569 (**2R2**), 0.619 (**3R2**), 0.598 (**4R2**), to 0.577 (**5R2**).

Scheme 6. Hydrogen Affinities



The HA(II) changes from −23.1 (toluene) to −50.6 kcal mol^{-1} (6-methylpentacene). The increment can be associated with the amount of resonance enthalpy consumed in the addition of a hydrogen atom to the methylacene. The computed hydrogen affinities for the methylacenes and for the corresponding unsubstituted acenes (**12**−**16**) are almost identical (see Table 2). For benzene and naphthalene, the hydrogen affinities are in excellent agreement with the experimental values (see Table 2). Next, the hydrogen atom donor abilities of the tautomers have been calculated. They are expressed as the benzylic bond dissociation enthalpies for the methylenedihydroacenes, BDE(C−H)**t**, and for the methylacenenes, BDE(C−H), yielding the benzylic radical species ***x*R1** (see Scheme 7). The results are compiled in Table 2. The BDEs are interrelated through the equation Δ_tH = BDE(C−H)**t** − BDE(C−H). Inspection of Table 2 shows that the BDE(C−H)s in methylenedihydroacenes **1t** and **2t** are extremely low, at 61.5[31] and 67.7[32] kcal mol^{-1}, respectively (vide infra). For comparison, the BDE(C−H) in 9,10-dihydroanthracene, an often used high-temperature hydrogen atom donor solvent, is 80.9 kcal mol^{-1} (CBS-QB3; experimental: 79.9 kcal mol^{-1}, see Table S1). The number of experimental benzylic BDEs reported in the literature is rather limited. From a gas-phase study, the relative (to toluene) benzylic BDE(C−H)s, ΔBDE(C−H), for 1-methylnaphthalene (**2**), and 9-methylanthracene (**3**) can be deduced as −2.9 and −7.8 kcal mol^{-1}, respectively.[33a] A liquid phase study has yielded for 9-methylanthracene a ΔBDE(C−H) of −5.3 kcal mol^{-1}.[33b] The CBS-QB3 computed ΔBDE(C−H) for **2** and **3** are −0.4 and −5.3 kcal mol^{-1}, respectively. These data agree with results from other computational methods.[35] Further analysis of the data shows that a substantial fraction of the ΔBDE(C−H) for **3** is due to the enthalpic destabilizing effect in the molecule by the methyl group.[35] The Mulliken (α) spin densities for the benzylic radical species (***x*R1**) are depicted in Scheme S2. The distribution of the unpaired spin densities reveals that the delocalization largely confined to the ring carrying the benzylic carbon.[37] The spin density on the benzylic carbon in the radical decreases sharply from 0.788 (**1**), 0.695 (**2**), 0.466 (**3**), 0.282 (**4**), to 0.150 (**5**), concomitantly with a similar increase of the spin density at the ring carbon opposite to the exocyclic methylene group.

Scheme 7. Bond Dissociation Enthalpies



Thus, for 5-tetracenylmethyl (**4R1**) and 6-pentacenylmethyl (**5R1**), the major contribution to the distribution of the unpaired

Table 2. CBS-QB3-Calculated Hydrogen Affinities, HA(I) and HA(II), for Tautomeric Species, Their Benzylic BDE(C−H)'s, and the Reaction Enthalpies for Reverse Radical Disproportionation ($\Delta_{RRD}H$)[a]

	$C_6H_5CH_3$ (**1**)	1-$C_{10}H_7CH_3$ (**2**)	9-$C_{14}H_9CH_3$ (**3**)	5-$C_{18}H_{11}CH_3$ (**4**)	6-$C_{22}H_{13}CH_3$ (**5**)
HA(I)	−52.2	−52.1	−48.7	−48.3	−48.1[b]
HA(II)	−23.1, −22.8[c]	−29.5, −29.5[d]	−40.0, −39.3[e]	−44.4, −43.9[f]	−50.6,[b] −49.9[g]
BDE(C−H)**t**[h]	61.5	67.7	76.6	79.5	81.1
BDE(C−H)	90.6[i]	90.2	85.3	83.4	78.7[b]
$\Delta_{RRD}H(1)$[j]	9.3	15.6	27.9	31.2	33.0
$\Delta_{RRD}H(2)$[j]	67.5	60.7	45.3	39.0	28.1

[a] In kcal mol^{-1} at $T = 298$ K; see Schemes 6 and 7 and Table S1. By definition, Δ_tH = HA(I) − HA(II) and Δ_tH = BDE(C−H)**t** − BDE(C−H); see Table 1. [b] Derived from linear correlations between CBS-QB3 and (U)B3LYP/CBSB7 results for compounds **1**−**4**, $\mathrm{HA(II)}_{\mathrm{CBS\text{-}QB3}} = 0.8824 \times \mathrm{HA(II)}_{\mathrm{CBSB7}} - 0.810$ ($r^2 = 0.9995$), $\mathrm{BDE(C{-}H)}_{\mathrm{CBS\text{-}QB3}} = 0.7714 \times \mathrm{BDE(C{-}H)}_{\mathrm{CBSB7}} + 22.516$ ($r^2 = 0.9844$). [c] The HA for benzene; expt −22.2 ± 0.9 kcal mol^{-1}.[39] [d] The HA for C1 in naphthalene; expt −29.0 ± 0.5 kcal mol^{-1}.[40] [e] The HA for C9 in anthracene. [f] The HA for C5 in tetracene. [g] The HA for C6 in pentacene and is derived from a linear correlation between CBS-QB3 and (U)B3LYP/CBSB7 results for compounds **12**−**15**; $\mathrm{HA(II)}_{\mathrm{CBS\text{-}QB3}} = 0.8930 \times \mathrm{HA(II)}_{\mathrm{CBSB7}} - 0.520$ ($r^2 = 0.9997$). [h] BDE(C−H)**t** refers to the (allylic/benzylic) BDE(C−H) in the methylenedihydro derivatives. [i] For comparison, the experimental BDE(C−H) in toluene is 89.8 ± 0.6 kcal mol^{-1}.[34b] [j] RRD reaction (1) **xt** + **xt** → **xR1** + **xR2** with $\Delta_{RRD}H(1)$ = BDE(C−H)**t** + HA(I). RRD reaction (2) **x** + **x** → **xR1** + **xR2** with $\Delta_{RRD}H(2)$ = BDE(C−H) + HA(II), **x** = **1**−**5**. See Schemes 1 and 6.

spin is represented by resonance form B. The BDE(C−H) decreases, and the BDE(C−H)**t** increases with decreasing benzylic spin density though not in a linear relationship (Figure S1) as has been observed previously for cyclic delocalized radicals.[34a]

Finally, with the data compiled in Table 2, the reaction enthalpies for the RRD reactions, $\Delta_{RRD}H$, can now be derived with the consistent set of HAs and the BDE(C−H)s. The $\Delta_{RRD}H$ for the RRD reaction between two methylene-dihydroacenes (***x*t** + ***x*t**) is given by $\Delta_{RRD}H$ = BDE(C−H)***x*t** − HA(1)***x*t** (see Table 2). When assuming that $E_{a,RRD} \cong \Delta_{RRD}H$, the $E_{a,RRD}$ is predicted to increase from 9.3 (**1t**), 15.6 (**2t**), 27.9 (**3t**), 31.2 (**4t**) to 33.0 (**5t**) kcal mol^{-1}. Experimentally, the dynamics for the thermal reactions of **1t**, **2t**, and **3t** (1 M in benzene) have been studied by NMR spectrometry at around 380 K.[2c] In all cases, the decay of the reactant follows second-order kinetics with pre-exponential factors of log A_{RRD} (M^{-1} s^{-1}) = 8−9, suggesting loose transition states, similar to those found for hydrogen atom abstraction reactions by a carbon centered radical from, e.g., a hydrocarbon. The activation energies ($E_{a,RRD}$) were found as 21.8 ± 0.3 (**1t**), 22.3 ± 0.8 (**2t**), and 27.1 ± 0.1 (**3t**) kcal mol^{-1}, respectively. *The observed kinetic behavior excludes an unimolecular 1,5-sigmatropic thermal hydrogen shift as the mechanism for tautomerization.*[41] Interestingly, the thermolysis of **1t** in benzene yields toluene (45%) and dimeric products (55%). On the other hand, the thermal reaction of **2t** or **3t** in benzene affords only dimers and oligomers and the expected 1-methylnaphthalene, **2**, or 9-methylanthracene, **3**, could not be detected.[2c] The experimental $E_{a,RRD}$s for **1t** + **1t** and **2t** + **2t** do not correspond with the computed values when assuming $E_{a,RRD} \cong \Delta_{RRD}$H. Thus, the agreement for **3t** + **3t** of 27.1 (expt) versus 27.9 (calcd) kcal mol^{-1} must be considered as rather fortuitous (see Table 2). The E_{aRRD} of 9.2 kcal mol^{-1} (or even lower[29]) for **1t** + **1t** combined with the experimental log A_{RRD} (M^{-1} s^{-1}) = 8.1 implies a rate constant for RRD of ≥20 M^{-1} s^{-1} at 298 K. Therefore, the half-life for **1t** in a 1 M solution is expected to be 0.06 s or less. Practically, this means that the purification of *p*-isotoluene, **1t**, at elevated temperatures or even NMR recordings at room temperature would never have been possible.[5] However, since **1t** exists as a reasonably stable compound at room temperature, it needs to be concluded that the RRD self-reaction of **1t** (and probably for other methylene-dihydroacenes as well) is much slower than anticipated on the basis of reaction enthalpy considerations only.

The incipient radicals (see Scheme 5) lead to the formation of products from disproportionation and recombination, and the overall bimolecular rate constant for disappearance, k_d, is given by $k_d = k_{RD} + k_{RC}$.[42] In the absence of substantial steric interactions, the k_d in the liquid phase is generally larger than 10^9 M^{-1} s^{-1}, meaning that these reactions occur at or near the diffusion-controlled limit.[42,43] The modest temperature dependence of k_d can be associated with the temperature dependence of the viscosity of the solvent.[42] On the other hand, it has been hypothesized that the radical−radical disproportionation is an activated process to be compared with the hydrogen atom abstraction by a radical from a closed-shell molecule, and therefore, an enthalpic activation barrier is expected to be present.[44] The intrinsic activation barrier for a hypothetical thermoneutral disproportionation reaction may be as high as 8.5 kcal mol^{-1}.[45] The ratio between disproportionation and recombination (k_{RD}/k_{RC}) in the liquid phase and in the gas phase has been studied for a large number of radicals.[42] Various features have been suggested to determine this ratio, such as the relative geometries of the radical pairs required for the disproportionation and the recombination reactions and the reorientation of the radicals in the pair.[42,46] There exists a distinct difference between k_{RD}/k_{RC} for the self-reaction of alkyl radicals[51] and for hydroaromatic (benzylic type) radicals. For example, the k_{RD}/k_{RC} (on a per hydrogen basis and around 330 K) changes from 0.3 (*tert*-butyl) to 0.0045 (cumyl) which cannot be explained on the basis of geometry or thermodyamic consideration.[42,47] The variation in k_{RD}/k_{RC} for the hydroaromatic radicals has been associated with the change in exothermicity for the RD reaction: a less exothermic RD leads to an decrease in k_{RD}/k_{RC}.[48b] This implies that when accepting the disproporationation as an activated process, the $E_{a,RD}$ is likely to increase, which is reminiscent of an Evans−Polanyi relationship between $E_{a,RD}$ and $\Delta_{RD}H$.[48b] Inspection of Table 3 shows that on going from **1** to **5** $\Delta_{RD}H$ ($-\Delta_{RRD}H$) for methylacene formation increases from −67.5 (**1**) to −28.1 (**5**) kcal mol^{-1}. Therefore, it seems likely that the formed radical pairs ***x*R1** + ***x*R2** (*x* = 1−5) almost exclusively recombine, with the exception of **1R1** and **R2**. Indeed, disproportionaton products could not be detected for the thermal reactions of **2t** and **3t**.

Transition State for Reverse Radical Disproportionation. In an effort to understand further the relationship between $E_{a,RRD}/\Delta_{RRD}H^{\ddagger}$ and $\Delta_{RRD}H$ in a more direct way, additional CBS-QB3 calculations have been carried out on energetics of the transition state for the hydrogen atom transfer.

Table 3. CBS-QB3-Calculated RRD Activation Parameters for 1t + 1t ⇌ [TS], 1 + 1 ⇌ [TS], 2t + 2t ⇌ [TS], 1t + $^3O_2$ ⇌ [TS], and 1 + $^3O_2$ ⇌ [TS] Reactions[a,b]

	$\Delta_{RRD}G^{\ddagger}$	$\Delta_{RRD}H^{\ddagger}$	$\Delta_{RRD}S^{\ddagger}$	$\Delta_{RRD}H$
1t + **1t** ⇌ $[TS]_{endo}$	31.4	19.1	−41.1	9.2
1t + **1t** ⇌ $[TS]_{endo}$[c]	34.7	19.3	−40.6	9.2
1t + **1t** ⇌ $[TS]_{exo}$	37.5	27.4	−33.9	9.2
1 + **1** ⇌ $[TS]_{exo}$	101.2	91.2	−33.6	67.6
2t + **2t** ⇌ $[TS]_{endo}$[d]	30.0	16.5	−45.3	15.6
1t + $^3O_2$ ⇌ $^3[TS]$	31.7	22.6	−30.5	7.2[e]
1 + $^3O_2$ ⇌ $^3[TS]$	47.3	38.0	−31.0	36.3[e]

[a] In (k)cal mol^{-1} (K^{-1}), at T = 298 K. The thermodynamic quantities obtained by computations always refer to the standard state of 1 atm. To convert to the standard state of 1 M at 298 K the following corrections[13] are required: $\Delta_{RRD}G^{\ddagger}_{1M} = \Delta_{RRD}G^{\ddagger}_{1\ atm} - 1.893$ [$= \Delta nRT \ln(R'T)$], $\Delta H^{\ddagger}_{1M} = \Delta H^{\ddagger}_{1\ atm} + 0.592$ [$= -\Delta nRT$], $\Delta S^{\ddagger}_{1M} = \Delta S^{\ddagger}_{1\ atm} + 8.3$ [$= -\Delta nR \ln(R'T) - \Delta nR$] with R' = 0.082 L atm mol^{-1} K^{-1}, and $\Delta n = -1$ (the change in molarity). [b] The kinetic parameters for k_{RRD} (M^{-1} s^{-1}) in the Arrhenius format are $A_{RRD} = (ekT/h)\exp(\Delta S^{\ddagger}_{1M}/R)$ and $E_{a,RRD} = \Delta H^{\ddagger}_{1M} + RT$.[13] [c] At 380 K, a comparison with data at 298 K shows that $\Delta C_{p,RRD} \cong 0$. With the rotation symmetry numbers σ (see the Supporting Information), the reaction pathway degeneracy (RPD) can be determined. Hence, the prexponential factor (A_{RRD}) for, e.g., **1t** + **1t** ⇌$[TS]_{endo}$ needs to be multiplied by $\sigma(\mathbf{1t}) \times \sigma(\mathbf{1t})/\sigma(\mathbf{TS}) = 2 \times 2/1 = 4$.[49] With log A_{RRD} (M^{-1} s^{-1}) = 7 and $E_{a,RRD}$ = 20.8 kcal mol^{-1}, k_{RRD} is 1.1×10^{-5} M^{-1} s^{-1} at 380 K. With only the thermodynamic data at 298 K, $k_{RRD} = 8.8 \times 10^{-6}$ M^{-1} s^{-1} at 380 K. [d] The thermodynamic parameters for the **2t** + **2t** ⇌ $[TS]_{endo}$ yield log A_{RRD} (M^{-1} s^{-1}) = 5.4 (RPD = 1), $E_{a,RRD}$ = 18.0 kcal mol^{-1}; hence, $k_{RRD} = 9.6 \times 10^{-6}$ M^{-1} s^{-1} at 380 K. [e] Includes −4.2 kcal mol^{-1} for the intermolecular hydrogen bond between the two product radicals (benzyl and hydroperoxyl).

In the case of the RRD reaction between two *p*-isotoluene (**1t**) species, two transition-state structures have been found in which the allylic hydrogen atom is transferred to the carbon of the exocyclic methylene group: a head-to-tail (extended, *exo*)[50] and a sandwich-type (compact, *endo*) transition structure (Figure 1, top), with the latter as the lowest energy conformer. According to the CBS-QB3 calculation an enthalpy of activation $\Delta_{RRD}H^{\ddagger}$ of 19.1 kcal mol^{-1} is found. For the RRD between two toluene (**1**) molecules, yielding also radicals **1R1** and **1R2**, only an *exo*-TS has been localized with an (unrealistic) barrier of $\Delta_{RRD}H^{\ddagger}$ = 91.2 kcal mol^{-1} ($\Delta_{RRD}H$ = 67.6 kcal mol^{-1}). Numerous attempts to locate an *endo*-TS failed, not only by CBS-QB3 but also by a variety of other DFT and ab initio (MP2) methods and basis sets. All geometry optimizations starting from an *endo* arrangement of the reactants eventually converged either back toward two toluene (**1**) molecules or to radicals **1R1** and **1R2**. This strongly indicates that for the **1** + RRD reaction an *endo* arrangement is associated with an enthalpic barrier that is close to the reaction endothermicity. Experimentally, the k_{RRD} for the **1t** + **1t** reaction has been determined as $3.6 \pm 0.4 \times 10^{-5}$ M^{-1} s^{-1} at 380 K (the medium reaction temperature).[2c] The computed k_{RRD} (1.1×10^{-5} M^{-1} s^{-1}) is only slightly at variance with the experiment (see Table 3, footnote *c*). The difference is mainly caused by the deviation in the pre-exponential factors: log A (M^{-1} s^{-1}) = 8.1 ± 0.2 (experimental)[2c] and 7.0 (Table 3). The $E_{a,RRD}$'s of 21.8 ± 0.3 (by experiment)[2c] and 20.8 kcal mol^{-1} (by theory, see Table 3, footnote *b*) at 380 K are in rather satisfying agreement. For the hydrogen transfer reaction **2t** + **2t** ⇌ [TS] ⇌ **2R1** + **2R2** the *endo* transition structure could be located (see Figure 1). However, comparison between experimental (log A (M^{-1} s^{-1}) = 8.5 ± 0.7, $E_{a,RRD}$ of 22.3 ± 0.8 kcal mol^{-1})[2c] and computational (log A (M^{-1} s^{-1}) = 5.4; $E_{a,RRD}$ of 18.0 kcal mol^{-1}, see Table 3) data indicates that the only experimental and calculated rate constants are in reasonable agreement at 380 K, but no convergence is found for the kinetic parameters.

The foregoing results clearly demonstrate that there exists an appreciable activation barrier for the **1R1** + **1R2** RD reaction toward two *p*-isotoluenes, with an $E_{a,RD}$ of 11.5 kcal mol^{-1} ($E_{a,RD} = E_{a,RRD} - \Delta_{RRD}H$). Conversely, for the RD reaction leading to two toluenes the $E_{a,RD}$ is close to zero. This is in agreement with the experimental observation that the thermal **1t** + **1t** reaction yields toluene and dimers in about equal amounts. The radical−radical recombination is a process with-

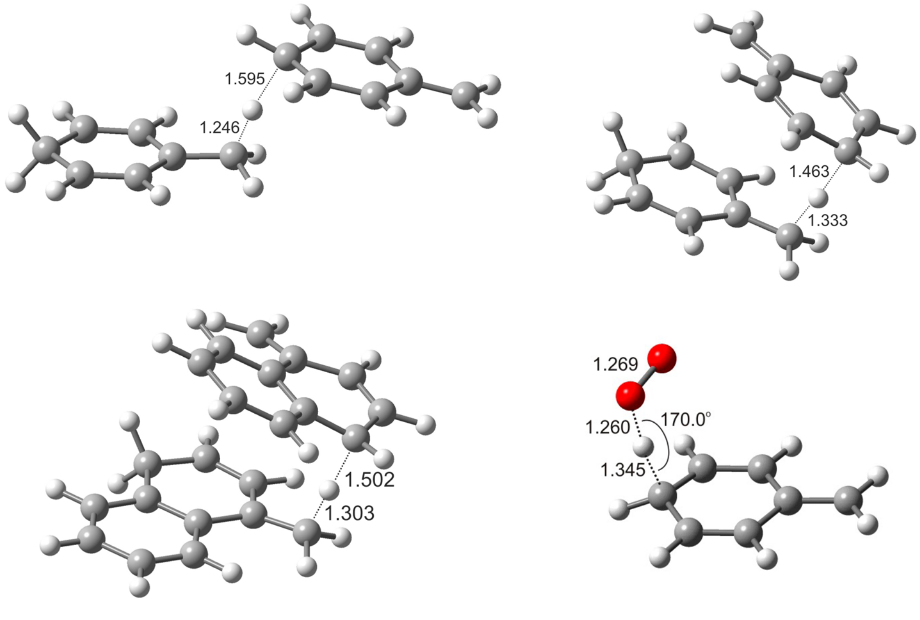


Figure 1. Transition states for RRD reactions of *p*-isotoluene + *p*-isotoluene (top, *exo* and *endo*), 1-methylene-1,4-dihydronaphthalene +1-methylene-1,4-dihydronaphthalene (bottom left) and *p*-isotoluene + $^3O_2$ (bottom right). Bond lengths in Å.

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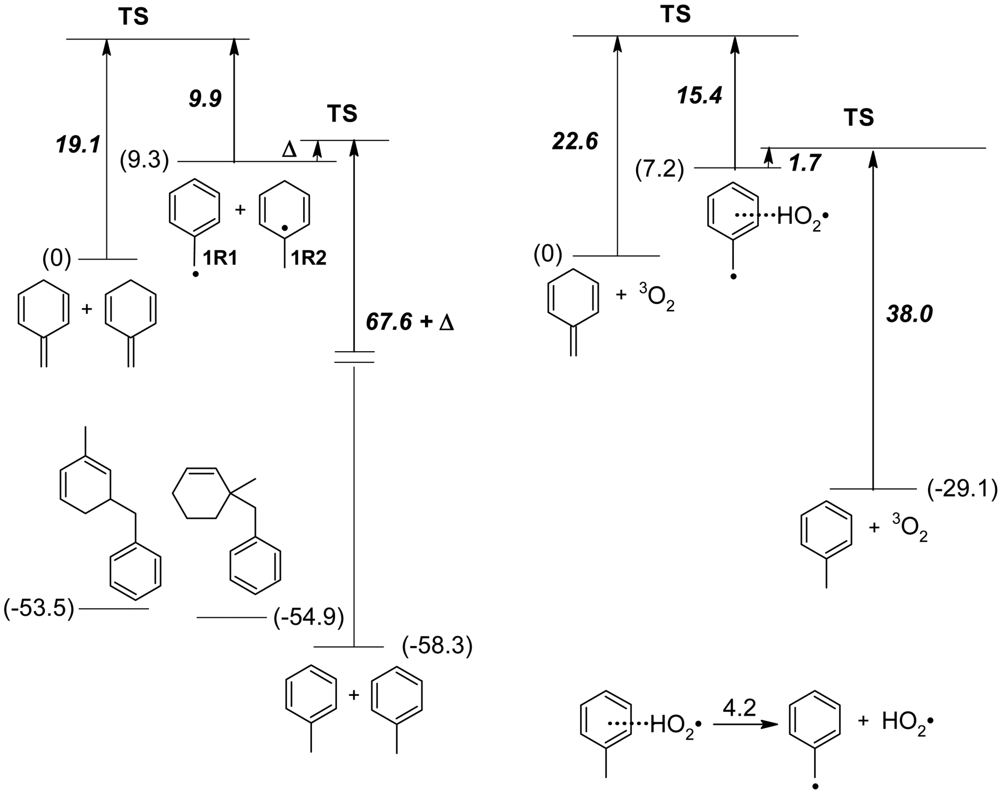
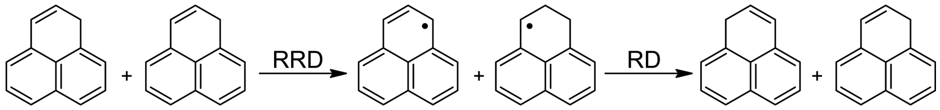
Scheme 8. Enthalpy Diagrams for Various RRD and RD Reactions of *p*-Isotoluene (**1t**) and Toluene (**1**)[a]



[a]The CBS-QB3-computed $\Delta_{RRD}H^{\ddagger}$'s (italics) and the (relative) Δ_rH's and Δ_fH's are all at 1 atm standard state at 298 K.

Scheme 9. Tautomerization of Phenalene



out an enthalpic barrier (vide supra), and the same holds now for the RD reaction to two toluenes. In Scheme 8, the enthalpy diagram for the interconversion of **1t** into **1** by RRD is presented. With 1-methylene-1,4-dihydronaphthalene (benzo-*p*-isotoluene, **2t**) an $E_{a,RD}$ = 2.4 kcal mol^{-1} is calculated for the **2R1** + **2R2** reaction back to the reactants, which is 9 kcal mol^{-1} lower than that for **1R1** + **1R2**. There seems to be no straightforward explanation for this difference in the behavior of the two systems. Probably the computed TS for the **2t** + **2t** RRD is "too tight".

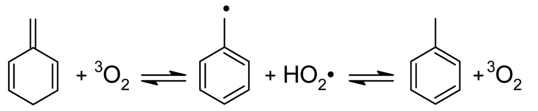
Transition-state calculations with larger methylacenes are beyond our computational resources. In a study at a low level of theory, B3LYP/6-31G(d), the kinetic and thermodynamic parameters for the RRD/RD reactions involving **1t**, **3t**, and **5t** have been reported.[3c] The raw data presented in the Supporting Information of ref 3c have been converted into enthalpic parameters, and they are summarized in Table S4. For the **1t** + **1t** RRD reaction it can be inferred that $E_{a,RRD}$ = 23.7 kcal mol^{-1} at 380 K, and the RRD reaction is almost thermoneutral with $\Delta_{RRD}H$ = 2.0 kcal mol^{-1}. The $E_{a,RRD}$ agrees reasonable well with the CBS-QB3 result (see Table 3); however, the geometry of the optimized TS structure in ref 3c is not disclosed. For the **1** + **1** RRD reaction the $E_{a,RRD}$ was found to be 64.3 kcal mol^{-1}. This means that the enthalpic barrier for the radical disproportionation of **1R1** + **2R1** to two *p*-isotoluenes amounts to 21.7 kcal mol^{-1}, while for the RD to two toluenes only 0.7 kcal mol^{-1} is required (see Scheme 8). Although the two computational methods provide quite similar results for the Δ_fH's, see Table 1, inspection of Table S4 reveals large differences between the two sets of computational results when open- shell species (radicals) are involved, which hampers a detailed analysis. Only in a qualitative way can it be concluded from Table S4 that there are appreciable enthalpic barriers for radical−radical disproportionation reactions and that the $E_{a,RD}$ increases when the reaction becomes less exothermic (the Evans−Polanyi relationship). Hence, on the basis of the thermokinetic rationale presented in this work, it seems obvious that the tautomerization of methylenedihydroacenes cannot occur through a RRD self-reaction (with the exception of *p*-isotoluene, **1t**). Such reactions, even when occurring, would yield essentially (only) recombination products. The reported color change in the 1949 study of a solution of methylene-6,13-dihydropentacene, **5t**,[1] with the concomitant formation **5**, therefore needs to be attributed to the presence of a trace amount of an acid acting as a catalyst.

The various tautomers of 1-methylphenalene have been observed in a NMR study at 298 K.[51] It has been hypothesized that the tautomerization proceeds through a RRD mechanism.[52] The migration of the double bond in (the model) phenalene sets in with a RRD reaction between two phenalene molecules (Scheme 9).

Calculations at the (U)B3LYP/6-311+G(2dp)//(U)B3LYP/6-31G(d,p) level of theory have afforded a $\Delta_{\text{RRD}}H$ = 14.4 kcal mol^{-1} together with an $E_{a,\text{RRD}}$ = 28.8 kcal mol^{-1} (see Table 3, footnote *b*) for a sandwich-type transition state.[52] Consequently, for the second step, a radical−radical disproportionation (RD), the enthalpic barrier, $E_{a,\text{RD}}$, becomes as high as 13.2 kcal mol^{-1}.[52] It needs to be noted that the $\Delta_{\text{RRD}}H$ strongly depends on the applied level of theory (vide supra). With the more sophisticated CBS-QB3 method the RRD is 6.4 kcal mol^{-1} more endothermic ($\Delta_{\text{RRD}}H$ = 20.8 kcal mol^{-1}).[53] In any case, with the computations once more an appreciable activation barrier for the RD reaction is found. This means that the lowest energy pathway for the incipient radicals after RRD constitutes of an array of recombination reactions and does not lead to the tautomeric product(s). Moreover, the Arrhenius parameters which can be derived from the computational data (log A_{RRD} (M^{-1} s^{-1}) = 6.2) imply a k_{RRD} of about 4.6×10^{-15} M^{-1} s^{-1} at 298 K, thus clearly indicating that this reaction pathway cannot be of any physical meaning at ambient temperature.

In another study, the self-reaction of phenalene in the presence of an excess of 9,10-dihydroanthracene in diphenyl ether and at around 500 K has been reported.[54] The kinetic parameters for the rate-determining RRD reaction (log A_{RRD} (M^{-1} s^{-1}) = 5.1, $E_{\text{a,RRD}}$ = 18.5 kcal mol^{-1}[54]) are quite at variance with the aforementioned computational results. The parameters for the thermal self-reaction of phenalene have been derived from a complex mechanistic scheme.[53] Thus, the unusually low *A* factor for the hydrogen atom transfer reaction suggests some flaws in the assessment of the data. In conclusion, despite claims of the contrary,[52] it is kinetically and mechanistically unfeasible that the tautomerization of 1-methylphenalene at room temperature follows a RRD pathway. Rather, the interconversion must be suspected to be an (acid) catalyzed process.[51]

The benzylic C−H bonds in the methylenedihydroacenes **1t** and **2t** are rather weak with BDE(C−H)s of of 61.5[31] and 67.7[32] kcal mol^{-1}, respectively (see Table 2). Therefore, these compounds are expected to be quite susceptible toward oxygen even at ambient temperature. The first step of this process consists of a RRD with a hydrogen atom transfer from, e.g., **1t** to triplet oxygen, eq 4:



(4)

For the direct reaction of molecular oxygen with hydrocarbons, it has always been assumed that the activation energy is close to the reaction enthalpy (vide supra).[56] The $\Delta_{\text{RRD}}H^\ddagger$ and $\Delta_{\text{RRD}}H$ for the RRD reactions of dioxygen with **1t** and **1** have been computed by CBS-QB3. The results are summarized in Table 3, the transition structure is displayed in Figure 1, and a graphical representation of the reaction pathways is shown in Scheme 8. The two product radicals hydroperoxyl ($HO_2^\bullet$) and benzyl form an intermolecular hydrogen-bonded complex with a hydrogen bond strength of 3.6 kcal mol^{-1}.[57] At 298 K, the $E_{a,\text{RRD}}$ of 23.8 kcal mol^{-1} for the **1t** + O_2 RRD is much larger than the $\Delta_{\text{RRD}}H$ of 7.2 kcal mol^{-1}, similar to the **1t** + **1t** RRD. This offers a rationale why **1t** is not exceptionally reactive toward molecular oxygen.[58] Eq 4 suggests that oxygen may act as a catalyst for the tautomerization of *p*-isotoluene. However, this is probably not the case. After hydrogen atom transfer but before diffusion out of the solvent cage the benzyl radical most likely is trapped by a second molecule of oxygen present in the wall of the cavity to form a benzylperoxyl radical.[60] Interestingly, for the hydrogen atom abstraction from toluene by oxygen the computations suggest $E_{a,\text{RRD}} \cong \Delta_{\text{RRD}}H$ (see Scheme 8). Currently, we are investigating the transition states for the reaction of oxygen with various prototype (phenolic) compounds.

The calculation at the CBS-QB3 platform have shown how the energetics of polyaromatics and derivatives are changing upon benzannulation at the [*b*] side. For 6-methylpentacene and beyond, the methylenedihydro tautomer is the most stable conformer. In the same series of polyaromatics, the reactivity (hydrogen atom affinity) of the central aromatic carbon atoms increases substantially. The reverse radical disproportionation (RRD) reaction has often been proposed as an initiation reaction in radical processes occurring at high temperatures. The RRD between two closed-shell molecules dictates (in part) the equilibrium pool of radicals. These steady-state conditions require only knowledge of the (computed) equilibrium free energy data. However, when the RRD reaction becomes the rate-determining step, insight into the dynamics for the back reaction is required. As demonstrated here, the radical−radical disproportionation appears to be an activated process, at least for hydroaromatic radicals.

■ COMPUTATIONAL DETAILS

Quantum-chemical computations on the CBS-QB3[61] level of theory were performed with the Gaussian 09 suite of programs.[62] All geometries were optimized to stationary points (no imaginary frequencies for ground state structures, one imaginary frequency for transtion states). Zero-point vibrational energies (ZPVE) were scaled by a factor of 0.99.

■ ASSOCIATED CONTENT

Supporting Information

Three tables with CBS-QB3 and B3LYP/CBSB7 computed and experimental thermochemical data for methylarenes, methylarene tautomers, and auxiliary compounds. B3LYP/6-31G(d)-computed thermochemical data from the literature. Two schemes with spin densities for benzylic and hydroaromatic radicals. A figure showing the relationship of benzylic spin densities and C−H bond dissociation enthalpies. A discussion of the relation between aromatic resonance enthalpy and heat of tautomerization. Evaluation of the entropies with consideration of the symmetry numbers of the compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01275.

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Notes

The authors declare no competing financial interest.

■ DEDICATION

This paper is dedicated to the memory of Prof. Reiner Sustmann (1939−2014).

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(5) Compound **1t** has been purified by preparative GC at a column temperature of about 60 °C[2a−c] and with a chromatographic retention time for **1t** of 23 min.[2a] At room temperature, the facile tautomerization of **1t** occurs only in the presence of a catalyst (sulfuric acid).[2a]

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(18) According to the CBS-QB3 calculations, the global minimum structure for **3** consists of the methyl group with two hydrogens almost staggered and one hydrogen twisted 16.6° out of the plane of the aromatic ring. For the rotational transition state, two rotamers have been identified, one with two hydrogen staggered and one fully eclipsed and the other with one hydrogen in the plane perpendicular to the aromatic ring; its free energy is 0.03 kcal mol^{-1} lower. These transition structures are lower in enthalpy than the global minimum but higher in free energy, with $\Delta_{\mathrm{rot}}G^{\ddagger}$ = 0.84 kcal mol^{-1}; experimentally$\Delta_{\mathrm{rot}}G^{\ddagger}$ = 0.3 kcal mol^{-1}.[17b]

(19) Unfortunately, the wording in ref 1a,b is ambiguous with respect to the equilibrium concentration range of **4t** in the alcoholic solvent. In ref 1b, it is stated that in alcohol as the solvent the tautomer **4t** is present "...in an appreciable proportion...", which would suggest a percentage of **4t** clearly above 1%, whereas in ref 1a, p 509, referring to the same experiment, the claim (in German) about **4t** is "...dass es in geringem Prozentsatz auch in einer schwach absorbierenden Methylen-Form...". This can be understood to refer also to a concentration significantly less than 1%.

(20) Upon cooling, tautomer **5** disappears again, and this cycle seems to be repeatable 12−15 times while a polymeric material is formed simultaneously.[1b]

(21) Reference 3a reports the equilibrium amounts for **3t** ⇌ **3**, **4t** ⇌ **4**, and **5t** ⇌ **5**, calculated with the use of the estimated (increase in) resonance energies: 0.2% (**3t**), 14% (**4t**), and 96% (**5t**) at 291 K. The percentage of **5** increases from 4% at 291 K to 13% at 491 K. The authors have noted the disagreement with the work of Clar (ref 1) claiming ≤1% of **5** at 491 K.

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(24) In liquid-phase calorimetric experiments, it has been implicitly assumed that the tautomerization of **2t** or **3t** occurs within the time frame (minutes) of the measurement. It is noteworthy that the heat evolved did not change in the presence or absence of several equivalents of an acid (CF_3CO_2H). Therefore, it has been concluded that the tautomerization is already catalyzed due to *trace impurities* in CCl_4.[2d]

(25) According to ref 2d, the NMR spectrum (200 MHz) of a $CDCl_3$ solution of 9-methylanthracene (**3**) has been recorded at 298 K with a trace of CF_3CO_2H. After averaging about 11000 spectra collected over a period of 9 h it is claimed that "...Although there were several signals that grew into the spectrum in the region of the expected sp^3 methylene signal at 3.7 ppm, none could be unequivocally assigned to tautomer **3t**". This observation led to an estimated upper limit for $\Delta_{\mathrm{t}}G$ of −3.7 kcal mol^{-1}, still about 5 kcal mol^{-1} higher than the CBS-QB3 value (see Table 1).

(26) Camphor-10-sulfonic acid has been used. The tautomerization is found to be a second-order reaction depending on the concentrations of **6** and the acid.

(27) The radical−radical disproportionation, RD, can occur either inside the initial solvent cage or the species first diffuse into the bulk solution followed by a re-encounter. For similar reactions such as the RRD between α-methylstyrene and a hydrogen donor (e.g., 9,10-dihydroanthracene) it has been demonstrated by isotope labeling that that diffusion of the geminate radical pair out of the initial solvent cage prevails.[6]

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(29) From Table 4 and Figure 6 in ref 6, a linear correlation can be derived for the RRD reactions of α-methylstyrene with nine different benzylic-type hydrogen atom donors, obeying $\Delta_{\mathrm{RRD}}H^{\ddagger} = -8.4 + 0.97 \times \Delta_{\mathrm{RRD}}H$ (kcal mol^{-1}) (r^2 = 0.87); hence, $\Delta_{\mathrm{RRD}}H^{\ddagger} < \Delta_{\mathrm{RRD}}H$. The $\Delta_{\mathrm{RRD}}H$'s (ranging from 30 to 42 kcal mol^{-1}) presented in Table 4 of ref 6 are based on a combination of experimental and estimated enthalpic data. The exothermic isomerization 1-butene to 2-butene in the presence of 1,3-butadiene may proceed through formation by RRD of two methylallyl radicals. The *endo*-TS is calculated by CBS-QB3 as being 7.7 kcal mol^{-1} lower than the enthalpy level of the two radical, meaning $\Delta_{\mathrm{RRD}}H^{\ddagger} < \Delta_{\mathrm{RRD}}H$.

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(31) A further refinement by means of the isodesmic reaction **1t** + 1,4-cyclohexadienyl → **1R1** + 1,4-cyclohexadiene with the CBS-QB3-computed $\Delta_{\mathrm{r}}H$ = 12.8 kcal mol^{-1} (see Table S1) and combined with the experimental BDE(C−H) of 76.8 kcal mol^{-1} in 1,4-cylohexadiene leads to BDE(C−H) of 64.0 kcal mol^{-1} for **1t** (CBS-QB3 direct: 61.5 kcal mol^{-1}).

(32) A further refinement by means of the isodesmic reaction **2t** + 1,4-dihydronaphthalene-1-yl → **2R1** + 1,4-dihydronaphthalene with the CBS-QB3-computed $\Delta_{\mathrm{r}}H$ = 8.9 kcal mol^{-1} (see Table S1) and combined with the experimental BDE(C−H) of 78.1 kcal mol^{-1} in 1,4-dihydronaphthalene leads to BDE(C−H) of 69.2 kcal mol^{-1} for **2t** (CBS-QB3 direct: 67.7 kcal mol^{-1}).

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