Tridehydrobenzenes

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Reactivity of an Aromatic σ,σ,σ-Triradical: The 2,4,6-Tridehydropyridinium Cation**

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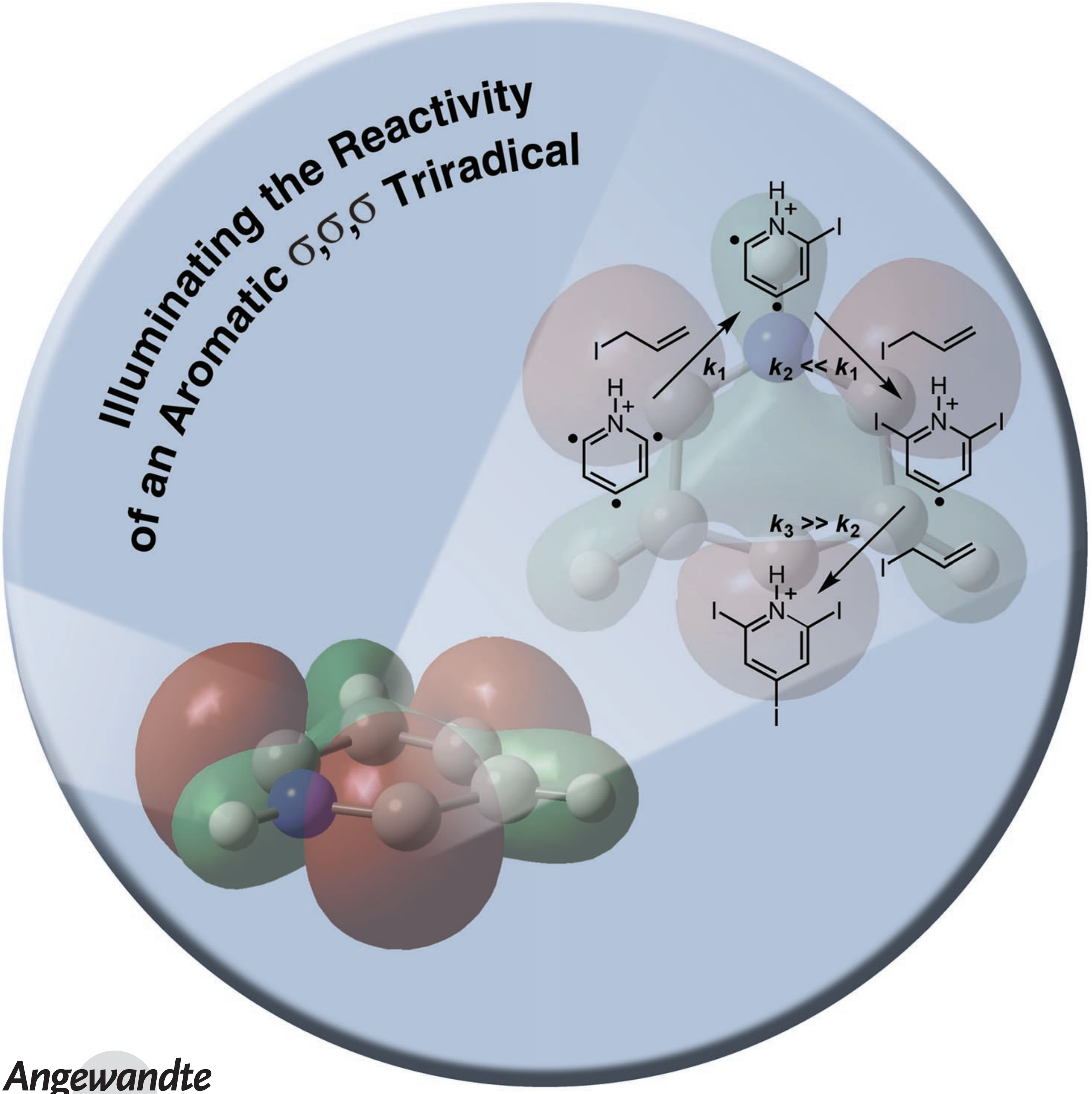

Certain σ-type, carbon-centered mono- and biradicals, the dehydro- and didehydroarenes, play an important role in organic synthesis, development of new organic materials, and the biological activity of organic compounds.[1,2] Therefore, numerous investigations have focused on their properties.[1–5] In contrast, the related σ,σ,σ-triradicals (tridehydroarenes) remain elusive. Almost all studies carried out on tridehydroarenes are computational in nature owing to the difficulty in studying such highly reactive species experimentally.[6] To the best of our knowledge, the only experimental studies reported for tridehydroarenes are thermochemical measurements on 1,3,5-tridehydrobenzene by Wenthold et al.[7] and IR detection of 1,2,3-tridehydrobenzene by Sander et al.[8] The chemical properties of tridehydroarenes appear to be entirely unexplored.

We report here a kinetic reactivity study on a positively charged tridehydroarene, the 2,4,6-tridehydropyridinium cation (**5**). The gas-phase reactions of this triradical are compared to those of two related, previously unreported σ,σ-biradicals, 2,4-didehydropyridinium cation (**3**) and 2,6-didehydropyridinium cation (**4**), as well as two σ-monoradicals, 4-dehydropyridinium cation (**1**) and 2-dehydropyridinium cation (**2**).

Triradical **5** was found to form products similar to those of the mono- and biradicals (Table 1). However, it reacts with most reagents more efficiently than the biradicals and at about equal efficiency as the monoradicals. This behavior can be understood based on a detailed examination of the reactivities of **1**–**4**.

The monoradicals (**1** and **2**) react rapidly with all the reagents studied. They predominantly abstract a H atom from tetrahydrofuran (THF), HCN and CN groups from *tert*-butyl isocyanide, an I atom from allyl iodide, and a SCH_3 group from dimethyl disulfide, as expected.[5,9] Monoradical **2** is slightly more reactive than **1** (Table 1), which may be explained by its higher electrophilicity, quantified here by the (calculated) vertical electron affinity (EA) (**1**: 5.84 eV; **2**: 6.59 eV; UBLYP/aug-cc-pVDZ//UBLYP//cc-pVDZ).[10] For an electrophilic radical, an increase in the EA can lead to a more polar, and hence lower-energy, transition state, thus enhancing its reactivity.[11]

Addition of a second radical site to monoradical **1** or **2** to generate the singlet biradical **3** results in decreased reactivity. The stabilizing interaction between the two electrons (revealed by the magnitude of the singlet–triplet (S-T) gap, i.e., the energy difference between the lowest-energy singlet and triplet states) has been used to rationalize this kind of behavior.[12,13] Part of this interaction is thought to be lost in the transition state of radical reactions owing to a necessity to partially uncouple the biradical electrons.

Based on the above discussion, a larger S-T gap is expected to result in slower radical (but not necessarily nonradical) reactions for singlet biradicals.[3,5] The S-T gaps of **3** and **4** are calculated to be -20.0 kcal mol^{-1} and -10.0 kcal mol^{-1}, respectively (BD(T)/cc-pVDZ//UBPW91/cc-pVDZ). Based on these values, **4** is expected to be more reactive than **3**. The calculated vertical EAs of **3** and **4** are 6.46 eV and 7.23 eV, respectively (UBLYP/aug-cc-pVDZ//MCSCF/cc-pVDZ), again suggesting that **4** should be more reactive than **3**. Indeed, **4** was found to react faster than **3** with all reagents studied. It is even more reactive than the monoradicals toward three of the four reagents studied. However, the dominating reaction for **4** (but not for **1**, **2**, or **3**) is proton transfer (which is calculated to lead to a *triplet* biradical), a nonradical reaction that does not require uncoupling of the biradical electrons. Hence, the high reactivity of **4** must arise from its relatively high acidity and not from its low S-T gap. Unfortunately, the fast proton-transfer reactions of **4** prevent a comparison of the efficiencies of the radical reactions of **4** with those of **1**–**3**.

The types of reactions observed for the two biradicals (with the exception of proton transfer) are similar and indicate the presence of two radical sites (e.g., two consecutive I atom abstractions from allyl iodide molecules and two SCH_3 group abstractions from dimethyl disulfide molecules). Most of these reactions were also observed for the monoradicals; however, the reactions with THF are an exception. While the monoradicals predominantly undergo H atom abstraction from THF, the biradicals abstract H_2O, CH_2O, C_2H_4O, and H^- faster than they abstract H atoms.

Triradical **5** transfers a proton to the two most basic reagents only, which suggests that it is more acidic than biradical **3** but less acidic than biradical **4**. This observation is supported by the EA calculated for **5** (7.01 eV; UBLYP/aug-cc-pVDZ//UBLYP/cc-pVDZ). Further, its reactivity reveals the presence of three reactive radical sites as it abstracts three SCH_3 groups from dimethyl disulfide molecules, three H atoms from THF molecules, and three I atoms from allyl iodide molecules. However, the three radical sites are not equally reactive. For example, the first and third I atom abstractions occur faster than the second. This finding suggests that the first I atom is abstracted by the radical at the 6-position to generate 2,4-didehydro-6-iodopyridinium cation (Scheme 1). This *meta*-benzyne analogue can be expected to be much less reactive than its 2,6-isomer since **4** is much more reactive than **3**, and addition of an I substituent does not greatly influence the reactivity of this type of a biradical. This expectation was verified by isolating the first I atom abstraction product and allowing it to react with allyl iodide. A remarkably similar reactivity to that of **3** was observed (I abs: 53 %, (2°) I abs, (2°) C_3H_5 abs; C_3H_5 abs: 34 %, (2°) I abs, (2°) C_3H_5 abs; C_3H_4 abs: 13 %; reaction efficiency: 14 %). Furthermore, facile proton transfer, the

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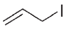
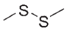
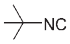
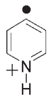
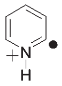
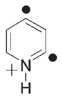
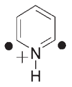
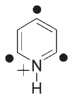
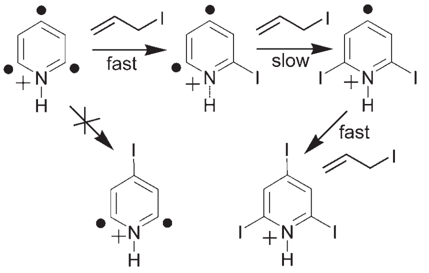
Table 1: Reaction efficiencies[a] and branching ratios[b] for primary products.

	Reagents			
Radical				
 **1**	H abs 81% CH_2 abs 8% C_2H_3 abs 6% CHO abs 3% C_2H_3O abs 2%	I abs 92% C_3H_5 abs 8%	SCH_3 abs 100%	HCN abs 64% (2°) HCN abs (2°) C_4H_8 abs CN abs 36%
	Eff = 28%	Eff = 53%	Eff = 75%	Eff = 90%
 **2**	H abs 100%	I abs 84% C_3H_5 abs 16%	SCH_3 abs 94% H abs 5% $SSCH_3$ abs 1%	CN abs 94% (2°) C_4H_8 abs HCN abs 6% (2°) C_4H_8 abs
	Eff = 76%	Eff = 69%	Eff = 79%	Eff = 93%
 **3**	H^- abs 36% CH_2O abs 26% C_2H_4O abs 20% H_2O abs 14% 2×H abs 4%	I abs 49% (2°) I abs (2°) C_3H_5 abs C_3H_5 abs 42% (2°) I abs (2°) C_3H_5 abs C_3H_4 abs 9%	SCH_3 abs 73% (2°) SCH_3 abs (2°) $SSCH_3$ abs $SSCH_3$ abs 23% (2°) SCH_3 abs $HSCH_3$ abs 4%	HCN abs 54% (2°) C_4H_8 abs H^+ trans and dissoc 46%
	Eff = 28%	Eff = 15%	Eff = 47%	Eff = 82%
 **4**	H^+ trans 78% (2°) THF add H_2O abs 10% H^- abs 5% CH_2O abs 4% 2×H abs 3%	H^+ trans 54% I abs 36% (2°) I abs C_3H_5 abs 6% (2°) I abs (2°) C_3H_5 abs C_3H_4 abs 4%	H^+ trans 65% (2°) SCH_3 abs SCH_3 abs 17% (2°) SCH_3 abs $HSCH_3$ abs 8% e^- abs 8% $SSCH_3$ abs 2%	H^+ trans and dissoc 75% C_4H_8 abs 15% HCN abs 10% (2°) C_4H_8 abs
	Eff = 85%	Eff = 34%	Eff = 93%	Eff = 98%
 **5**	H^+ trans 39% 2×H abs 25% (2°) H abs (2°) CH_2 abs (2°) C_2H_3 abs H^- abs 17% H_2O abs 16% (2°) H abs H abs 3%	I abs 76% (2°) C_3H_5 abs (2°) C_3H_4 abs (3°) I abs (2°) I abs (3°) C_3H_5 abs (3°) I abs CH_2 abs 13% C_3H_5 abs 6% C_3H_4 abs 5%	SCH_3 abs 100% (2°) $HSCH_3$ abs (2°) $SSCH_3$ abs (2°) SCH_3 abs (3°) SCH_3 abs	H^+ trans and dissoc 98% HCN abs 2%
	Eff = 74%	Eff = 53%	Eff = 72%	Eff = 98%

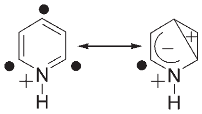
[a] Reaction efficiencies[3,5] (Eff) are reported as $k_{reaction}/k_{collision} \times 100\%$. The reaction efficiency is the percentage of collisions leading to a reaction. [b] abs = abstraction, trans = transfer, dissoc = dissociation, add = addition; secondary and tertiary products are noted as (2°) and (3°), respectively, and are listed under the primary and secondary products that produce them.



Scheme 1.

reaction characteristic of **4**, was not observed. This finding unambiguously rules out the 2,6-isomer.

A likely ionic resonance structure[14] of **5**, structure **6**, explains the different rates observed for the three I atom abstractions. This structure indicates a stronger coupling between the radical sites at positions 2 and 4 (or 4 and 6) than at 2 and 6, and suggests that the radical site at position 6 (or 2) should be more reactive than the others. The second I atom abstraction is slow as a result of the strong spin–spin coupling between the



5 **6**

remaining radical sites. However, once the second I atom is abstracted, a phenyl radical (analogous to **1** and **2**) is produced that undergoes a fast I atom abstraction.

The triradical **5** is calculated to have a doublet ground state (D-Q gap: $-26.8\,\text{kcal}\,\text{mol}^{-1}$; BD(T)/cc-pVDZ//UBPW91/cc-pVDZ), which explains why it undergoes radical reactions faster than the analogous biradical **3** whose reactions are hindered by its singlet ground state (based on a comparison of reactions with allyl iodide and dimethyl disulfide where no proton-transfer reactions were observed; note that deprotonation of **5** is calculated to generate a doublet triradical). The triradical reacts with allyl iodide and dimethyl disulfide at about the same efficiency as the monoradicals. Apparently, the large EA of **5** counterbalances most of the radical reactivity hindering effect caused by the coupling of the three unpaired electrons.

Experimental Section

The precursors of monoradicals **1** and **2** were purchased from Sigma Aldrich Co. and used as received. The precursors of the biradicals **3**[15] and **4**[16] and the triradical **5**[16,17] were synthesized using reported methods. The mono-, bi-, and triradicals were generated in a dual-cell Fourier-transform ion cyclotron resonance mass spectrometer by using previously reported methods.[5,9] Sustained off-resonance irradiated collision-activated dissociation[18] was used to cleave C–I bonds in the protonated precursors. After isolation, **1–5** were allowed to react with reagents for varying periods of time to determine the second-order reaction rate constants (k_{exp}) and reaction efficiencies ($k_{\text{exp}}/k_{\text{collision}}$) as described previously.[3,5,19] The absolute values are estimated to be accurate only within ±50%, but the relative values are much more accurate (±10%). The structures of all the radical species were confirmed by using structurally diagnostic reactions.[5,9] All DFT, coupled-cluster, and MCSCF calculations were carried out with the Gaussian 98[20] and MOLCAS[21] electronic structure program suites.

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