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Quantum Chemical Characterization of the Structures, Thermochemical Properties, and Doublet–Quartet Splittings of Tridehydropyridinium Cations

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Structural and energetic properties are predicted for the six tridehydropyridinium cation isomers in their lowest-energy doublet and quartet states by using density functional, multireference second-order perturbation, and coupled-cluster theories. Doublet–quartet splittings and triradical stabilization energies are examined to gain insight into the degree of interaction between the three radical centers, with comparison being made to analogous tridehydrobenzenes.

Introduction

Certain σ -type, carbon-centered mono- and biradicals, the dehydro- and didehydroarenes, play an important role in organic synthesis, the 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 due to the difficulty in studying such highly reactive species experimentally.^{6–8} The few experimental studies on tridehydroarenes that have been reported include thermochemical measurements on 1,3,5-tridehydrobenzene⁹ and matrix isolation and spectroscopic characterization of 1,2,3-tridehydrobenzene¹⁰ and perfluoro-1,3,5-tridehydrobenzene.¹¹ However, none of these experimental studies have permitted characterization of the chemical properties (i.e., reactivities) of the tridehydroarenes.

Recently, we reported¹² an experimental study on the reactivity of the 2,4,6-tridehydropyridinium cation (a positively charged analogue of 1,3,5-tridehydrobenzene) in a Fourier transform ion cyclotron mass spectrometer. Interestingly, the reactivity of this triradical more closely resembles that of related monoradicals rather than related biradicals. As part of our continuing studies on charged analogues of the tridehydroarenes and in order to better understand the effects of charge and the presence (or absence) of heteroatoms on the structures and energetics of aromatic σ,σ,σ -triradicals, we report here a systematic computational characterization of all six isomers of the tridehydropyridinium cation (i.e., protonated tridehydropyridine). With the exception of the 2,4,6-tridehydropyridinium cation, these triradicals have not been examined previously.

Computational Methods

Molecular geometries for all species were optimized at the multiconfigurational self-consistent field (MCSCF) and density functional (DFT) levels of theory using the correlation-consistent

polarized valence-double- ζ (cc-pVDZ¹³) basis set.¹⁴ The MCSCF calculations were of the complete active space (CASSCF) variety¹⁵ and included (in the active space) the full π space for each molecule and, for each of the monoradicals, biradicals, and triradicals, the nonbonding σ orbital(s). The DFT calculations were of two types. Both used the gradient-corrected exchange functional of Becke,¹⁶ which was combined either with the gradient-corrected correlation functional of Lee, Yang, and Parr¹⁷ (BLYP) or that of Perdew et al.¹⁸ (BPW91). All DFT geometries were verified to correspond to local energy minima by computation of analytic vibrational frequencies, and these (unscaled) frequencies were used to compute zero-point vibrational energies (ZPVE) and 298 K thermal contributions ($H_{298} - E_0$) for all species.¹⁹ DFT calculations for doublet states of monoradicals, triplet states of biradicals, and quartet and doublet states of triradicals employed the unrestricted formalism; total spin expectation values for Slater determinants formed from the optimized Kohn–Sham orbitals did not exceed 0.76, 2.02, 3.79, and 0.88 for doublet monoradical, triplet biradical, quartet triradical, and doublet triradical states, respectively. For singlet biradicals, the DFT “wave function” was allowed to break spin symmetry by using an unrestricted formalism.²⁰ Total spin expectation values for Slater determinants formed from the optimized Kohn–Sham orbitals in these cases ranged widely between 0.0 and 1.0. Geometry optimization using the unrestricted formalism has been shown to give more accurate geometries for a number of relevant aromatic biradicals.^{20–23}

To improve the molecular orbital calculations, dynamic electron correlation was also accounted for by using multireference second-order perturbation theory^{24,25} (CASPT2) for the MCSCF reference wave functions; these calculations were carried out for the BLYP-, BPW91-, and MCSCF-optimized geometries. Some caution must be applied in interpreting the CASPT2 results since this level of theory is known to suffer from a systematic error proportional to the number of unpaired electrons.²⁶ Estimates of the thermodynamic quantities E_0 and H_{298} were derived by adding to these electronic energies ZPVE and the sum of ZPVE and ($H_{298} - E_0$), respectively, where the latter were derived from the DFT calculations.

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Coupled-cluster calculations for single-configuration reference wave functions expanded in Brueckner²⁷ (BD(T)) orbitals were also carried out for all species by using the correlation-consistent polarized valence-triple- ζ (cc-pVTZ¹³) basis set and including all single and double excitations and a perturbative estimate for triple excitations. Brueckner orbitals eliminate contributions from single excitations in the coupled-cluster ansatz, and this alleviates instabilities²⁸ associated with very large singles' amplitudes in the more common CCSD(T) method that have previously been observed for aromatic biradicals having low degrees of symmetry.^{20c} The BD(T)/cc-pVTZ calculations were of the single-point variety and were carried out by using the BPW91/cc-pVDZ-optimized geometries. The BD(T) calculations employed a restricted Hartree–Fock (RHF) reference for closed-shell molecules and an unrestricted Hartree–Fock (UHF) reference for open-shell molecules.

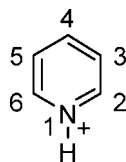
For the doublet states of the triradicals, the MCSCF calculations indicate that the wave functions for these molecules are dominated by a single configuration in which the lowest-energy nonbonding molecular orbital is doubly occupied and the next highest in energy nonbonding molecular orbital is singly occupied (i.e., CI coefficients for this particular configuration range from 0.79 to 0.92). Thus, the single-configuration reference methods employed here (DFT, BD(T)) are expected to provide reasonable descriptions of the wave functions for these molecules.

Calculations were carried out for pyridinium cation (C_{2v}), benzene (D_{6h}), the phenyl radical (C_{2v}), the three isomeric dehydropyridinium cations (DPs; C_s or C_{2v}), the six isomeric dihydropyridinium cations (DDPs; C_s or C_{2v}), the three isomeric dihydrobenzenes (DDBs; C_{2v} or D_{2h}), the three isomeric tridehydrobenzenes (TDBs; C_s or C_{2v}), and the six isomeric tridehydropyridinium cations (TDPs; C_s or C_{2v}). For the DDPs and DDBs, separate calculations were performed for both the lowest-energy singlet and triplet states. For the TDBs and TDPs, separate calculations were performed for both the lowest-energy doublet and quartet states.

All multireference and single-reference calculations were carried out with the MOLCAS²⁹ and Gaussian 98³⁰ electronic structure program suites, respectively.

Results

Geometries. Complete geometric information for the monoradicals, biradicals, triradicals, and related molecules, obtained using the BPW91, BLYP, and MCSCF methods, is provided in the Supporting Information. For the pyridinium cations, the atom numbering scheme is as follows:



For the quartet states of all six isomeric triradicals, the BPW91 geometries give the lowest energies at the CASPT2 level. This is also the case for the triplet states of the six DDPs, the doublet states of the three DPs, the singlet state of pyridinium cation, the doublet states of 3,4,5-TDP and 2,3,6-TDP, and the singlet states of 2,3-DDP, 2,5-DDP, 2,6-DDP, and 3,4-DDP. For the doublet states of 2,3,4-TDP, 2,3,5-TDP, 2,4,5-TDP, and 2,4,6-TDP, however, the BLYP geometries yield slightly lower energies (by 0.13–0.36 kcal/mol) at the CASPT2 level. In

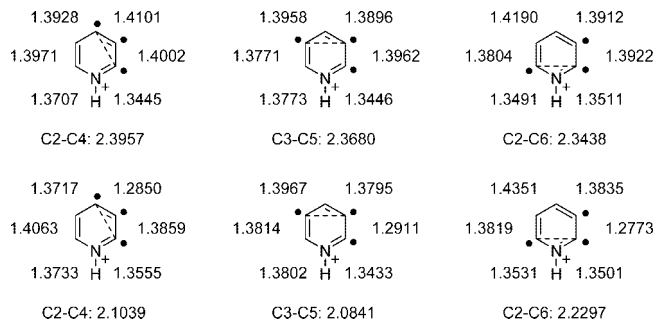


Figure 1. Calculated heavy-atom bond lengths (Å) for the quartet states (top) and doublet states (bottom) for 2,3,4-TDP, 2,3,5-TDP, and 2,3,6-TDP obtained at the BPW91/cc-pVDZ level of theory.

addition, for the singlet states of 3,5-DDP and 2,4-DDP, the MCSCF geometries yield slightly lower energies (by 1.33–1.89 kcal/mol) at the CASPT2 level. The high quality of BPW91/cc-pVDZ geometries, in general, has been noted before.^{20c,22,23a,31,32} It derives in part from canceling errors associated with the approximate functional and the relatively modest basis set size.³³ This favorable cancellation of errors makes BPW91/cc-pVDZ a very economical choice for computing aromatic biradical and triradical structures. On the basis of these observations and for the sake of brevity and consistency, we will focus any discussion of geometrical data primarily on results obtained at the BPW91 level, except in those cases where consideration of other geometries provides additional useful information. Calculated heavy-atom bond lengths for the quartet and doublet states of the six isomeric TDPs, obtained using the BPW91 method, are shown in Figures 1 and 2.

Thermochemical Data. Electronic energies and selected thermochemical quantities were computed for the six isomeric TDPs, the six isomeric DDPs, the three isomeric DPs, the three isomeric TDBs, the three isomeric DDBs, benzene, the phenyl radical, and the pyridinium cation by using the BLYP and BPW91 density functional models and the CASPT2 and BD(T) methods, in conjunction with either the cc-pVDZ basis set or the cc-pVTZ basis set (BD(T) method only).

Zero-point vibrational energies (ZPVEs) and 298 K thermal contributions to the enthalpy were computed for each molecule from the unscaled vibrational frequencies determined at either the BPW91 or the BLYP level. Results from the BPW91 calculations were combined with the CASPT2/cc-pVDZ//BPW91/cc-pVDZ and BD(T)/cc-pVTZ//BPW91/cc-pVDZ total energies to derive 0 K energies, E_0 , for each TDP doublet and quartet state. For the TDPs, all energies are listed in Table 1 relative to the lowest-energy doublet state (either 2A_1 or 2B_2 depending on the theoretical level) of the 3,4,5-isomer (i.e., the global minimum relative to all other tridehydroisomers and states). ZPVEs and 298 K thermal contributions for the six TDPs and all other molecules are provided as Supporting Information.

Table 2 lists the doublet–quartet splittings, ΔE_{D-Q} , given by $[E_0(\text{doublet}) + (H_{298} - E_0)] - [E_0(\text{quartet}) + (H_{298} - E_0)]$, obtained with the four different levels of theory for the TDPs. The values of ΔE_{D-Q} for the corresponding tridehydrobenzenes are provided for comparison—the tridehydrobenzenes are iso-electronic with the TDPs but do not incorporate a (protonated) nitrogen atom in the aromatic system.

A useful perspective on the relative thermodynamic stabilities of the TDPs derives from consideration of the enthalpy changes for the isodesmic hydrogen atom transfer from the pyridinium cation to a triradical cation to give the corresponding biradical and monoradical cations.

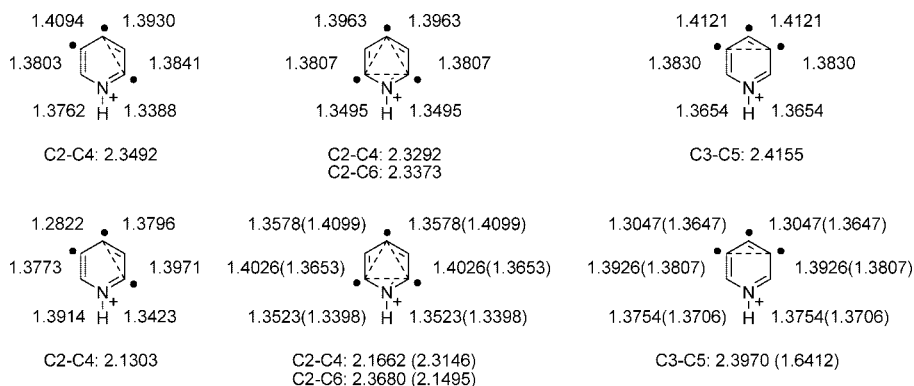
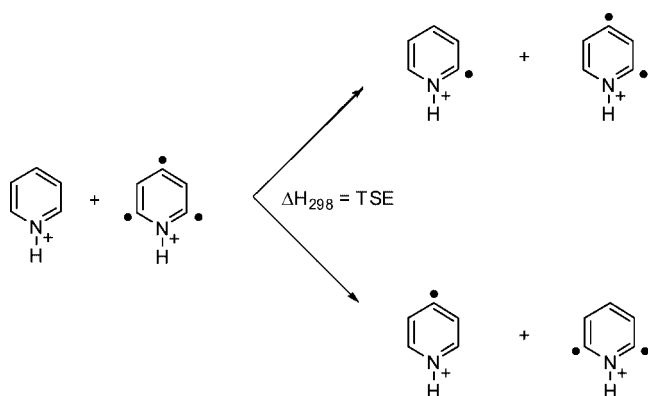


Figure 2. Calculated heavy-atom bond lengths (Å) for the quartet states (top) and doublet states (bottom) for 2,4,5-TDP, 2,4,6-TDP, and 3,4,5-TDP obtained at the BPW91/cc-pVDZ level of theory. For the doublet states of 2,4,6-TDP and 3,4,5-TDP, the first values are for the 2B_2 states; values in parentheses are for the 2A_1 states.

TABLE 1: Relative State Energies (kcal/mol) for *m,n,o*-Tridehydropyridinium Cations

	2,3,4	2,3,5	2,3,6	2,4,5	2,4,6 ^a	3,4,5 ^a
	relative E_0 (BPW91//BPW91) ^b					
doublet	3.0	9.7	15.1	5.0	9.6 (2B_2) 26.2 (2A_1)	0.0 (2A_1) ^c 1.3 (2B_2)
quartet	48.4	43.1	43.8	42.8	42.0	49.5
	relative E_0 (BLYP//BLYP) ^d					
doublet	2.2	9.0	14.2	4.3	9.4 (2B_2) 25.5 (2A_1)	0.0 (2B_2) ^e 1.9 (2A_1)
quartet	49.7	44.5	45.2	44.1	44.0	50.8
	relative E_0 (CASPT2//BPW91) ^f					
doublet	2.2	10.0	13.0	3.1	8.8 (2B_2) 20.7 (2A_1)	0.0 (2B_2) ^g 3.8 (2A_1)
quartet	43.3	39.4	39.9	39.0	38.1	44.6
	relative E_0 (BD(T)//BPW91) ^h					
doublet	1.6	11.2	14.1	3.2	13.2 (2B_2) 24.3 (2A_1)	0.0 (2B_2) ⁱ 2.6 (2A_1)
quartet	47.8	43.6	44.3	43.0	42.5	48.8

^a The symmetry of the quartet state is 4B_2 . ^b BPW91/cc-pVDZ//BPW91/cc-pVDZ + BPW91/cc-pVDZ ZPVE. ^c Absolute energy (including ZPVE), $-246.552061 E_h$. ^d BLYP/cc-pVDZ//BLYP/cc-pVDZ + BLYP/cc-pVDZ ZPVE. ^e Absolute energy (including ZPVE), $-246.492662 E_h$. ^f CASPT2/cc-pVDZ//BPW91/cc-pVDZ + BPW91/cc-pVDZ ZPVE. ^g Absolute energy (including ZPVE), $-245.857673 E_h$. ^h BD(T)/cc-pVTZ//BPW91/cc-pVDZ + BPW91/cc-pVDZ ZPVE. ⁱ Absolute energy (including ZPVE), $-246.098659 E_h$.



The enthalpy changes associated with these isodesmic reactions are termed the triradical stabilization energies (TSEs), as they provide a direct indication of the stabilization ($TSE > 0$) or destabilization ($TSE < 0$) involved when all three radical sites are present in the same molecule. Because the radical sites are generally not stereochemically equivalent, a given triradical has two or three TSE values, each associated with a different separation; this is illustrated above for 2,4,6-TDP, which has two TSEs. TSE values were computed at the four different levels of theory for the doublet and quartet states of each TDP from the 298 K enthalpies and are listed in Tables 3 and 4 along

with the corresponding values for the tridehydrobenzenes provided for comparison.

Discussion

Our focus here is not to provide any detailed dissection of the performance of the various theoretical levels but rather to assess qualitative differences (if any) between the tridehydropyridinium cations (TDPs) and the isoelectronic tridehydrobenzenes (TDBs). We address these chemical issues next and defer a brief discussion of theoretical issues to the end of this article. We have chosen to simplify our discussion by restricting ourselves in general to making comparisons of thermochemical properties between molecules at a single level of theory, namely, the BD(T)/cc-pVTZ//BPW91/cc-pVDZ level, although other levels are presented in certain instances for comparison purposes. Finally, we note that it is not possible to calculate heats of formation for the TDPs due to the lack of appropriate experimental reference data for the biradicals and monoradicals found in the TSE isodesmic equations.³⁴

3,4,5-Tridehydropyridinium Cation (3,4,5-TDP). At all levels of theory, the ground (doublet) state of 3,4,5-TDP is calculated to be the global minimum relative to all of its tridehydroisomers and states (Table 1). Previous calculations on the tridehydrobenzenes have shown that the ground state (2A_1) of 1,2,3-TDB is the global minimum relative to all tridehydrobenzene isomers and states,⁸ although the 2B_2 (excited)

TABLE 2: Calculated D–Q Splittings (kcal/mol) for *m,n,o*-Tridehydropyridinium Cations

level	2,3,4	2,3,5	2,3,6	2,4,5	2,4,6 ^a	3,4,5 ^a
BPW91//BPW91 ^{h,c}	–45.4	–33.4	–28.7	–37.8	–32.4 (² B ₂) –15.8 (² A ₁)	–49.5 (² A ₁) –48.2 (² B ₂)
BLYP//BLYP ^{h,d}	–47.5	–35.5	–31.0	–39.8	–34.6 (² B ₂) –18.5 (² A ₁)	–48.9 (² A ₁) –50.8 (² B ₂)
CASPT2//BPW91 ^{h,c}	–41.1	–29.4	–26.9	–35.9	–29.3 (² B ₂) –17.4 (² A ₁)	–40.8 (² A ₁) –44.6 (² B ₂)
BD(T)//BPW91 ^{h,e}	–46.2	–32.4	–30.2	–39.8	–29.3 (² B ₂) –18.2 (² A ₁)	–46.2 (² A ₁) –48.8 (² B ₂)
ΔE_{D-Q} (<i>m,n,o</i> -tridehydrobenzene) ^{f,g}						
BPW91//BPW91 ^{h,c}	–52.0 (² A ₁) –46.4 (² B ₂)	–37.8	–37.8	–37.8	–31.9 (² A ₁)	–52.0 (² A ₁) –46.4 (² B ₂)
BLYP//BLYP ^{h,d}	–50.5 (² A ₁) –47.8 (² B ₂)	–39.6	–39.6	–39.6	–33.1 (² A ₁)	–50.5 (² A ₁) –47.8 (² B ₂)
CASPT2//BPW91 ^{h,c}	–43.8 (² A ₁) –42.5 (² B ₂)	–35.3	–35.3	–35.3	–26.1 (² A ₁)	–43.8 (² A ₁) –42.5 (² B ₂)
BD(T)//BPW91 ^{h,e}	–49.5 (² A ₁) –47.0 (² B ₂)	–39.3	–39.3	–39.3	–29.7 (² A ₁)	–49.5 (² A ₁) –47.0 (² B ₂)

^a The symmetry of the quartet state is ⁴B₂. ^b Geometries optimized using the cc-pVDZ basis set. ^c Corrected for zero-point vibrational energy differences at 298 K by using the BPW91 frequencies. ^d Corrected for zero-point vibrational energy differences at 298 K by using the BLYP frequencies. ^e Electronic energies calculated using the cc-pVTZ basis set. ^f For the 2,3,4- and 3,4,5-tridehydropyridinium cations, the corresponding data for 1,2,3-tridehydrobenzene are given; for the 2,3,5- and 2,3,6-tridehydropyridinium cations, the corresponding data for 1,2,4-tridehydrobenzene are given; for the 2,4,6-tridehydropyridinium cation, the corresponding data for 1,3,5-tridehydrobenzene are given. ^g For 1,2,3-tridehydrobenzene and 1,3,5-tridehydrobenzene, the symmetry of the quartet state is ⁴B₂.

TABLE 3: Triradical Stabilization Energies (kcal/mol) for *m,n,o*-Tridehydropyridinium Cations

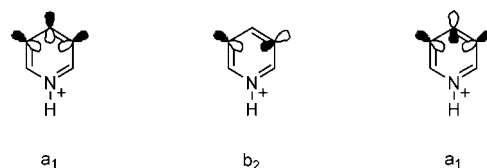
level	state	2,3,4			2,3,5			2,3,6		
		2,3-DDP + 4-DP ^a	2,4-DDP + 3-DP	3,4-DDP + 2-DP	2,3-DDP + 3-DP	3,5-DDP + 2-DP	2,5-DDP + 3-DP	2,3-DDP + 2-DP	2,6-DDP + 3-DP	2,5-DDP + 2-DP
		4-DP ^a	3-DP	2-DP	3-DP	2-DP	3-DP	2-DP	3-DP	2-DP
BPW91//BPW91 ^{h,c}	D	9.8	6.3	4.0	5.3	2.4	20.7	0.6	13.2	16.1
BLYP//BLYP ^{h,d}		9.6	13.6	4.0	4.9	7.1	21.7	0.5	14.3	17.4
CASPT2//BPW91 ^{h,c}		7.9	13.3	1.7	2.5	7.6	16.5	0.0	9.9	14.0
BD(T)//BPW91 ^{h,c,e}		8.4	9.5	1.7	1.3	4.8	20.3	–0.9	13.4	18.1
BPW91//BPW91 ^{h,c}	Q	–11.5	–14.3	–9.8	–4.0	–7.0	–8.3	–3.9	–7.3	–8.2
BLYP//BLYP ^{h,d}		–11.5	–14.1	–9.9	–4.2	–6.9	–8.3	–4.1	–7.3	–8.2
CASPT2//BPW91 ^{h,c}		–9.5	–11.6	–7.7	–3.2	–5.6	–7.0	–3.2	–5.9	–7.0
BD(T)//BPW91 ^{h,c,e}		–10.1	–12.3	–8.3	–3.3	–5.8	–7.2	–3.3	–6.1	–7.2
<i>m,n,o</i> -tridehydrobenzene										
level	state	1,2,3 ^f			1,2,4			1,2,4		
		1,2-DDB + 1,3-DDB + 1,4-DDB + PR ^g	1,3-DDB + 1,4-DDB + PR	1,2-DDB + 1,4-DDB + PR	1,2-DDB + 1,3-DDB + 1,4-DDB + PR	1,3-DDB + 1,4-DDB + PR	1,4-DDB + PR	1,2-DDB + 1,3-DDB + 1,4-DDB + PR	1,3-DDB + 1,4-DDB + PR	1,4-DDB + PR
		PR ^g	PR	PR	PR	PR	PR	PR	PR	PR
BPW91//BPW91 ^{h,c}	D	10.3 (4.7)	18.2 (12.6)	10.3 (4.7)	2.8	10.7	24.9	2.8	10.7	24.9
BLYP//BLYP ^{h,d}		7.9 (5.2)	17.9 (15.2)	7.9 (5.2)	2.6	12.6	25.9	2.6	12.6	25.9
CASPT2//BPW91 ^{h,c}		4.3 (3.0)	17.1 (15.8)	4.3 (3.0)	1.1	13.8	21.9	1.1	13.8	21.9
BD(T)//BPW91 ^{h,c,e}		4.6 (2.1)	18.2 (15.7)	4.6 (2.1)	0.4	13.9	27.3	0.4	13.9	27.3
BPW91//BPW91 ^{h,c}	Q	–10.4	–14.4	–10.4	–3.8	–7.8	–8.9	–3.8	–7.8	–8.9
BLYP//BLYP ^{h,d}		–9.5	–13.2	–9.5	–3.9	–7.6	–8.9	–3.9	–7.6	–8.9
CASPT2//BPW91 ^{h,c}		–8.4	–11.8	–8.4	–3.0	–6.5	–7.8	–3.0	–6.5	–7.8
BD(T)//BPW91 ^{h,c,e}		–9.1	–12.7	–9.1	–3.2	–6.8	–8.1	–3.2	–6.8	–8.1

^a The abbreviations, 2-DP, 3-DP, and 4-DP refer to *m*-dehydropyridinium cations; 2,3-DDP, 2,4-DDP, 2,5-DDP, 2,6-DDP, 3,4-DDP, and 3,5-DDP refer to *m,n*-didehydropyridinium cations. ^b Geometries optimized using the cc-pVDZ basis set. ^c Corrected for zero-point vibrational energy differences at 298 K by using the BPW91 frequencies. ^d Corrected for zero-point vibrational energy differences at 298 K by using the BLYP frequencies. ^e Electronic energies calculated using the cc-pVTZ basis set. ^f For the doublet state, values are for the ²A₁ state; values in parentheses are for the ²B₂ state. ^g The abbreviations, 1,2-DDB, 1,3-DDB, and 1,4-DDB refer to *ortho*-, *meta*-, and *para*-benzyne, respectively; the abbreviation PR refers to the phenyl radical.

state of this molecule is very close in energy.^{6b,c,10b} The relative stability of 1,2,3-TDB, which contains a “ σ -allyl system”, results from the formation of partial bonds between the radical centers. In this molecule, interaction of the radical sites having an *ortho* relationship is stronger than the interaction of the radical sites having a *meta* relationship, but the *ortho* interaction is weaker than that for *ortho*-benzyne due to σ -electron delocalization over all three dehydrocarbon atoms.^{6c} Since similar interactions exist in 3,4,5-TDP, it is not surprising, then, that the ground (doublet) state of this molecule is also the global minimum relative to all of its TDP isomers and states.

The principal electron configuration for the ²B₂ state of 3,4,5-TDP has the lowest-energy nonbonding MO of a₁ symmetry doubly occupied and the nonbonding MO of b₂ symmetry singly occupied (the second nonbonding MO of a₁ symmetry is

unoccupied). For the ²A₁ state, on the other hand, the principal electron configuration has the second nonbonding MO of a₁ symmetry singly occupied instead of the nonbonding b₂ MO.



For this molecule, the calculated energy ordering of the two lowest-lying doublet states (i.e., ²B₂ and ²A₁) depends on the level of theory employed. For example, at the BPW91 level of theory,

TABLE 4: Triradical Stabilization Energies (kcal/mol) for *m,n,o*-Tridehydropyridinium Cations

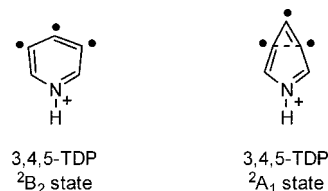
level	state	2,4,5			2,4,6 ^a		3,4,5 ^a	
		2,4-DDP + 3-DP ^b	2,5-DDP + 4-DP	3,4-DDP + 2-DP	2,4-DDP + 2-DP	2,6-DDP + 4-DP	3,4-DDP + 3-DP	3,5-DDP + 4-DP
BPW91//BPW91 ^{c,d}	D	4.5	27.8	2.2	0.3 (−16.3)	16.4 (−0.2)	5.2 (6.5)	8.1 (9.4)
BLYP//BLYP ^{c,e}		11.7	24.5	2.0	7.3 (−8.8)	17.0 (0.9)	5.6 (3.7)	13.4 (11.5)
CASPT2//BPW91 ^{c,d}		12.6	21.1	0.9	7.3 (−4.6)	11.8 (−0.1)	3.7 (−0.1)	15.0 (11.2)
BD(T)//BPW91 ^{c,d,f}		8.1	25.8	0.2	−1.3 (−12.4)	11.9 (0.8)	2.8 (0.2)	13.0 (10.4)
BPW91//BPW91 ^{c,d}	Q	−8.5	−10.0	−4.0	−7.3	−7.9	−11.5	−16.1
BLYP//BLYP ^{c,e}		−8.4	−10.0	−4.2	−7.6	−8.2	−11.5	−15.9
CASPT2//BPW91 ^{c,d}		−7.2	−8.9	−3.3	−5.9	−6.4	−9.2	−13.4
BD(T)//BPW91 ^{c,d,f}		−7.4	−9.1	−3.4	−6.2	−6.8	−9.8	−14.1

<i>m,n,o</i> -tridehydrobenzene								
level	state	1,2,4			1,3,5		1,2,3 ^g	
		1,3-DDB + PR ^h	1,4-DDB + PR	1,2-DDB + PR	1,3-DDB + PR	1,3-DDB + PR	1,2-DDB + PR	1,3-DDB + PR
BPW91//BPW91 ^{c,d}	D	10.7	24.9	2.8	4.9	4.9	10.3 (4.7)	18.2 (12.6)
BLYP//BLYP ^{c,e}		12.6	25.9	2.6	5.9	5.9	7.9 (5.2)	17.9 (15.2)
CASPT2//BPW91 ^{c,d}		13.8	21.9	1.1	5.2	5.2	4.3 (3.0)	17.1 (15.8)
BD(T)//BPW91 ^{c,d,f}		13.9	27.3	0.4	4.7	4.7	4.6 (2.1)	18.2 (15.7)
BPW91//BPW91 ^{c,d}	Q	−7.8	−8.9	−3.8	−7.6	−7.6	−10.4	−14.4
BLYP//BLYP ^{c,e}		−7.6	−8.9	−3.9	−7.9	−7.9	−9.5	−13.2
CASPT2//BPW91 ^{c,d}		−6.5	−7.8	−3.0	−6.0	−6.0	−8.4	−11.8
BD(T)//BPW91 ^{c,d,f}		−6.8	−8.1	−3.2	−6.5	−6.5	−9.1	−12.7

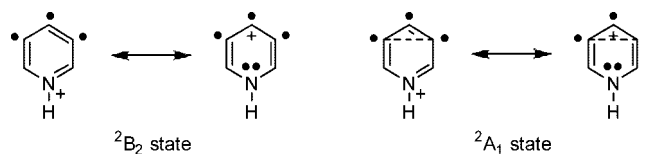
^a For the doublet state, values are for the ²B₂ state; values in parentheses are for the ²A₁ state. ^b The abbreviations, 2-DP, 3-DP, and 4-DP refer to *m*-dehydropyridinium cations; 2,3-DDP, 2,4-DDP, 2,5-DDP, 2,6-DDP, 3,4-DDP, and 3,5-DDP refer to *m,n*-didehydropyridinium cations. ^c Geometries optimized using the cc-pVDZ basis set. ^d Corrected for zero-point vibrational energy differences at 298 K by using the BPW91 frequencies. ^e Corrected for zero-point vibrational energy differences at 298 K by using the BLYP frequencies. ^f Electronic energies calculated using the cc-pVTZ basis set. ^g For the doublet state, values are for the ²A₁ state; values in parentheses are for the ²B₂ state. ^h The abbreviations, 1,2-DDB, 1,3-DDB, and 1,4-DDB refer to *ortho*-, *meta*-, and *para*-benzynes, respectively; the abbreviation PR refers to phenyl radical.

the ²A₁ state is predicted to lie below the ²B₂ state by 1.3 kcal/mol; however, this ordering is reversed at the BLYP, CASPT2, and BD(T) levels of theory, where the ²B₂ state lies below the ²A₁ state by 1.9, 3.8, and 2.6 kcal/mol, respectively (Table 1). An examination of the equilibrium geometries for the ²B₂ and ²A₁ states obtained at the BPW91 level suggests that this method may be overestimating the *meta* interaction between the radical sites at C₃ and C₅ in the ²A₁ state (the C₃–C₅ dehydrocarbon atom separation is calculated to be 1.64 Å). In contrast, at the BLYP level, where the C₃–C₅ dehydrocarbon atom separation is also calculated to be relatively small (1.70 Å), the ²B₂ state lies below the ²A₁ state. A similar effect is also evident for 1,2,3-TDB at the BPW91 level. For this molecule, the calculated C₁–C₃ dehydrocarbon atom separations at the BPW91 and BLYP levels are 1.70 and 1.77 Å, respectively. The ²A₁ state is calculated to lie below the ²B₂ state by 5.6 kcal/mol at the BPW91 level but only by 2.7 kcal/mol at the BLYP level (Table 2). A comparison of the calculated (BPW91) energy differences between the ²B₂ and ²A₁ states for 3,4,5-TDP and 1,2,3-TDB with those obtained at the BD(T) level (the highest level of theory employed; Table 2) suggests that the BPW91 method overestimates the *meta* interaction in the ²A₁ state for these two molecules by about 3–4 kcal/mol. In the case of 3,4,5-TDP, this causes the ²A₁ state to lie below the ²B₂ state at the BPW91 level, but this state ordering does not persist at the higher levels of theory employed here (Table 1).

All of the theoretical methods employed here indicate that the two lowest-energy doublet states for 3,4,5-TDP (i.e., ²A₁ and ²B₂) lie very close in energy (within 1.3–3.8 kcal/mol; Table 1). At the “best” level of theory (BD(T)), the ²B₂ state is calculated to lie below the ²A₁ state by 2.6 kcal/mol. In contrast, for 1,2,3-TDB, the ²A₁ state is calculated to lie below the ²B₂ state by 2.5 kcal/mol (Table 2). This calculated ²A₁–²B₂ energy



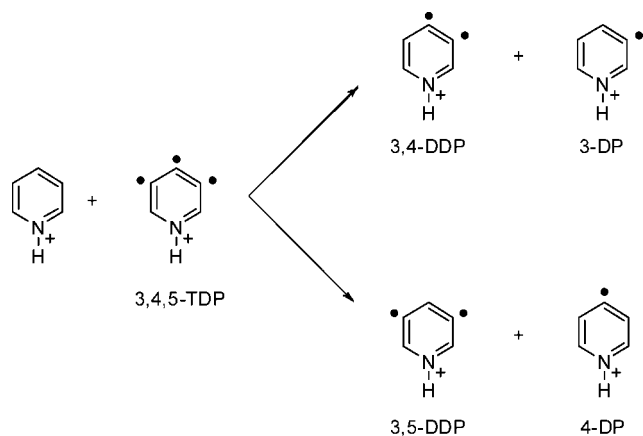
difference for 1,2,3-TDB, as well as the symmetry of the ground state, is in excellent agreement with previous calculations^{10a} and spectroscopic characterization^{10b} of the ground state for this molecule. Thus, interestingly, incorporation of a NH⁺ group into the aromatic ring of 1,2,3-TDB (i.e., to produce 3,4,5-TDP) has a 5 kcal/mol influence on the energy ordering of the low-lying ²A₁ and ²B₂ states. An analysis of the equilibrium geometries (BPW91) and atomic charges (Mulliken) for the ²B₂ and ²A₁ states of 3,4,5-TDP as well as those for the corresponding states of the deprotonated analogue, 3,4,5-tridehydropyridine, suggests that both doublet states of 3,4,5-TDP are stabilized by significant contributions from the resonance structures shown below. These resonance structures, which formally involve an ionized carbene, permit greater charge delocalization away from the nitrogen atom.



For example, for the ²B₂ state of 3,4,5-TDP (Figure 1), the C₂–C₃ and C₅–C₆ bond lengths are about 0.03 Å shorter,

and the N_1-C_2 and C_6-N_1 bond lengths are about 0.04 Å longer, than those for the 2B_2 state of 3,4,5-tridehydropyridine. Moreover, the 2B_2 state of 3,4,5-TDP has a large partial positive charge (+0.134) on C_4 , which is not the case for 3,4,5-tridehydropyridine (−0.005). Similar geometric differences exist for the 2A_1 states of 3,4,5-TDP (Figure 1) and 3,4,5-tridehydropyridine, although the differences are much smaller (i.e., compared to those for the 2B_2 state). For the 2A_1 state of 3,4,5-TDP, the C_2-C_3 and C_5-C_6 bond lengths are only about 0.01 Å shorter, and the N_1-C_2 and C_6-N_1 bond lengths are only about 0.01 Å longer, than those for the 2A_1 state of 3,4,5-tridehydropyridine. In addition, the calculated atomic charges (Mulliken) at C_4 for the 2A_1 states of 3,4,5-TDP and 3,4,5-tridehydropyridine are +0.062 and −0.053. Thus, the resonance structures described above appear to have a greater influence on the structure of the 2B_2 state than on the 2A_1 state for 3,4,5-TDP. Considering the fact that the 2B_2 and 2A_1 states of 3,4,5-tridehydropyridine are calculated (BD(T)) to differ in energy by only about 0.2 kcal/mol, it appears that the resonance contributions for 3,4,5-TDP result in greater stabilization of the 2B_2 state with respect to the 2A_1 state, and this causes the 2B_2 state to lie below the 2A_1 state for this molecule.

At the BD(T) level, the calculated TSEs for the (ground) 2B_2 state of 3,4,5-TDP associated with either the separation of one of the “terminal” radical sites (i.e., at C_3 or C_5 ; to produce 3,4-DDP and 3-DP) or the separation of the “internal” radical site (i.e., at C_4 ; to produce 3,5-DDP and 4-DP) are 2.8 and 13.0 kcal/mol, respectively (Table 4). The fact that these TSEs are positive indicates that the 2B_2 state derives additional stabilization from the presence of the third radical site (compared to the corresponding biradical). In addition, the much larger TSE associated with the latter isodesmic reaction indicates that the *ortho* interaction(s) in this molecule is much stronger than the *meta* interaction. The TSEs for 3,4,5-TDP are similar to those calculated for the 2B_2 state of 1,2,3-TDB (2.1 and 15.7 kcal/mol, respectively; Table 4), which indicates that the presence of the NH^+ group (i.e., in 3,4,5-TDP) has a relatively small effect on the interaction of the radical sites in the 2B_2 state. The significantly smaller TSE associated with the separation of the “internal” radical site for 3,4,5-TDP (13.0 kcal/mol) compared to that of 1,2,3-TDB (15.7 kcal/mol) is likely to result from the contribution of the ionized carbene-type resonance structure for 3,4,5-TDP (a similar resonance structure is not possible for 1,2,3-TDB).



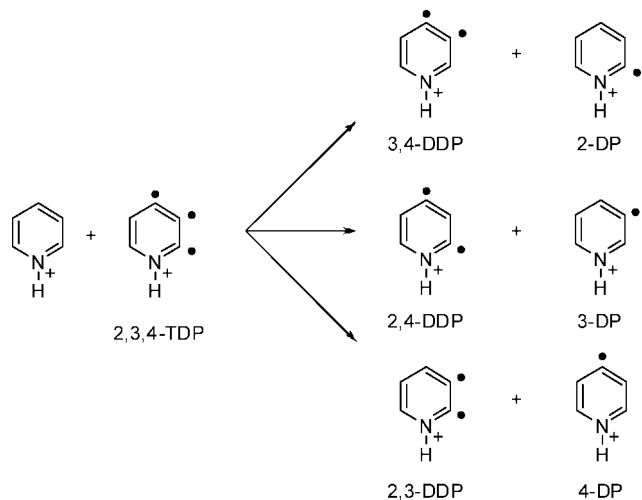
For the (excited) 2A_1 state of 3,4,5-TDP, the calculated (BD(T)) TSEs associated with either the separation of one of

the “terminal” radical sites or the separation of the “internal” radical site are also positive (0.2 and 10.4 kcal/mol, respectively; Table 4), but they are smaller than those calculated for the 2B_2 state by about 2.6 kcal/mol—that is, the $^2B_2-^2A_1$ state energy splitting. These TSEs are considerably smaller than the corresponding TSEs for the 2A_1 state of 1,2,3-TDB (4.6 and 18.2 kcal/mol, respectively; Table 4). Considering the fact that the structures for both molecules are nearly bicyclic, the much smaller TSEs for 3,4,5-TDP may be a result of greater ring strain in this molecule (i.e., due to the presence of the NH^+ group) compared to that for 1,2,3-TDB.

For the (excited) 4B_2 state of 3,4,5-TDP, the calculated (BD(T)) TSEs associated with the separation of either a “terminal” radical site or the “internal” radical site are negative and large (−9.8 and −14.1 kcal/mol, respectively; Table 4). These TSEs are similar to those for the 4B_2 state of 1,2,3-TDB (−9.1 and −12.7 kcal/mol, respectively; Table 4), but they are slightly more negative, suggesting that the NH^+ group (in 3,4,5-TDP) destabilizes the 4B_2 state somewhat compared to 1,2,3-TDB. Hence, while the close proximity of the radical sites stabilizes the low-lying doublet states (i.e., 2B_2 and 2A_1) for both 3,4,5-TDP and 1,2,3-TDB, it strongly destabilizes the 4B_2 states in these molecules due to Pauli repulsion. As a result, the calculated (BD(T)) D–Q splitting (i.e., $^2B_2-^4B_2$) for 3,4,5-TDP is quite large (−48.8 kcal/mol; Table 2), but it is not very different from the calculated D–Q splitting ($^2A_1-^4B_2$) for 1,2,3-TDB (−49.5 kcal/mol; Table 2). Thus, the presence of the NH^+ group in 3,4,5-TDP (compared to that in 1,2,3-TDB) does not have a great influence on the calculated D–Q splitting.

2,3,4-Tridehydropyridinium Cation (2,3,4-TDP). For this triradical, the three radical sites are adjacent to each other (like 3,4,5-TDP), but one of the radical sites is adjacent to the NH^+ group. At all levels of theory, the (ground) $^2A'$ state of 2,3,4-TDP is calculated to be only slightly higher in energy (by 1.6–3.0 kcal/mol) than the ground state of 3,4,5-TDP (Table 1).³⁵ This is not particularly surprising since 2,3,4-TDP, like 3,4,5-TDP, contains a “ σ -allyl system”. However, the calculated (BPW91) structure for the $^2A'$ state of 2,3,4-TDP is quite different from those calculated for the 2B_2 and 2A_1 states of 3,4,5-TDP (Figures 1 and 2). For example, at the BPW91 level, the C_2-C_3 bond length (1.39 Å) for 2,3,4-TDP is much longer than the C_3-C_4 bond length (1.29 Å), the $C_2-C_3-C_4$ bond angle (103.9°) is rather small, and the $N_1-C_2-C_3$ bond angle (123.7°) is rather large. A comparison of this structure with the calculated (BPW91) structures for 3,4-DDP (e.g., C_3-C_4 bond length: 1.27 Å) and 2-DP (e.g., $N_1-C_2-C_3$ bond angle: 124.7°), in particular, suggests that the structure for the $^2A'$ state of 2,3,4-TDP most closely resembles an *ortho*-benzylne (C_3-C_4) and a weakly interacting radical (C_2).

The resemblance of the structure calculated for the $^2A'$ state of 2,3,4-TDP to a molecule that contains an *ortho*-benzylne group and a weakly interacting radical is further supported by the calculated (BD(T)) TSEs for this molecule. For example, the TSE associated with the separation of the C_2 radical site (i.e., to produce 3,4-DDP and 2-DP) is quite small (1.7 kcal/mol), whereas the TSEs associated with the separation of either the C_3 or C_4 radical sites (to produce either 2,4-DDP and 3-DP or 2,3-DDP and 4-DP, respectively) are much larger (9.5 and 8.4 kcal/mol, respectively; Table 3). Since the electronic and geometric structures of the $^2A'$ state of 2,3,4-TDP are so different from those calculated for either 3,4,5-TDP or 1,2,3-TDB, it is not particularly informative to compare the TSEs for 2,3,4-TDP with either of these molecules.



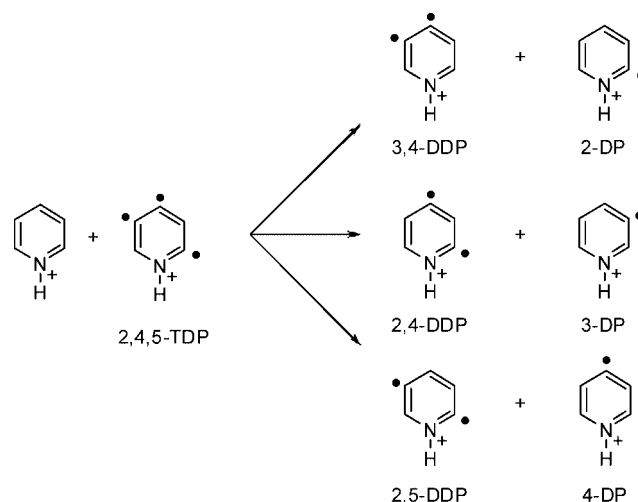
The calculated TSEs for the (excited) $^4A'$ state of 2,3,4-TDP are all negative and large, which is consistent with the strong Pauli repulsion that results from the close proximity of the radical sites (like that for 3,4,5-TDP). Since the calculated (BPW91) geometries for the $^4A'$ state of 2,3,4-TDP and the 4B_2 state of 1,2,3-TDB are similar, it is possible to compare the calculated TSEs for these two molecules. At the BD(T) level, the TSEs associated with the separation of the C_2 , C_3 , and C_4 radical sites for the $^4A'$ state of 2,3,4-TDP are -8.3 , -12.3 , and -10.1 kcal/mol, respectively (Table 3). These TSEs are quite similar to the corresponding TSEs for the 4B_2 state of 1,2,3-TDB (-9.1 , -12.7 , and -9.1 kcal/mol, respectively; Table 3). In contrast to 3,4,5-TDP, where the NH^+ group seems to destabilize the quartet state slightly, the influence of the NH^+ group on the stability of the $^4A'$ state of 2,3,4-TDP is negligible.

Interestingly, even though the calculated (BPW91) structure for the $^2A'$ state of 2,3,4-TDP is very different from those calculated for the doublet states of both 3,4,5-TDP and 1,2,3-TDB; the calculated (BD(T)) D–Q splitting ($^2A' - ^4A'$) for this molecule (-46.2 kcal/mol; Table 2) differs only slightly from the calculated D–Q splittings for 3,4,5-TDP ($^2B_2 - ^4B_2$; -48.8 kcal/mol; Table 2) and 1,2,3-TDB ($^2A_1 - ^4B_2$; -49.5 kcal/mol; Table 2). Thus, like 3,4,5-TDP, the presence of the NH^+ group in 2,3,4-TDP (compared to that in 1,2,3-TDB) appears to have only a minor influence on the calculated D–Q splitting for this molecule.

2,4,5-Tridehydropyridinium Cation (2,4,5-TDP). At all levels of theory, the (ground) $^2A'$ state of this molecule is the next most stable tridehydroisomer (i.e., after 3,4,5-TDP and 2,3,4-TDP).³⁵ The $^2A'$ state of 2,4,5-TDP is calculated to be about 3.1–5.0 kcal/mol higher in energy than the (ground) doublet state of 3,4,5-TDP and about 0.9–2.1 kcal/mol higher in energy than the (ground) doublet state of 2,3,4-TDP (Table 1). The calculated (BPW91) structure of this molecule (Figure 2) indicates that the *ortho*-benzyne (C_4-C_5) interaction dominates, while the *meta* interaction between the dehydrocarbon atoms at C_2 and C_4 is relatively weak (but noticeable). For example, the calculated C_4-C_5 bond length for 2,4,5-TDP (1.28 Å) is nearly identical to the C_3-C_4 bond length (1.27 Å) for 3,4-DDP. Moreover, the C_2-C_4 (*meta*) dehydrocarbon atom separation in 2,4,5-TDP is calculated to be about 2.13 Å, which is 0.12 Å shorter than the corresponding C_2-C_4 separation in 3,4-DDP but 0.26 Å longer than the calculated C_1-C_3 separation for *meta*-benzyne. These structural effects are very similar to those noted before^{6b,c} for the structure of 1,2,4-TDB.

The calculated TSEs for the $^2A'$ state of 2,4,5-TDP are also consistent with a structure that resembles an *ortho*-benzyne

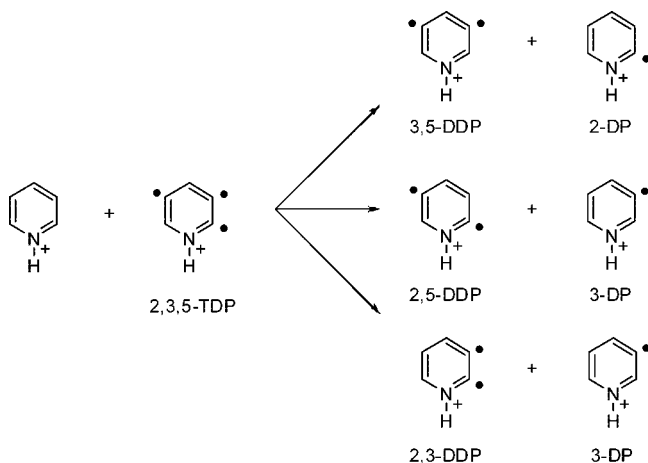
(C_4-C_5) and a weakly interacting radical (C_2). At the BD(T) level, the TSE associated with the separation of the C_2 radical site (to produce 3,4-DDP and 2-DP) is very small (0.2 kcal/mol), whereas the TSEs associated with the separation of either of the C_4 or C_5 radical sites (to produce either 2,5-DDP and 4-DP or 2,4-DDP and 3-DP, respectively) are much larger (25.8 and 8.1 kcal/mol, respectively; Table 4). The TSEs for 2,4,5-TDP are similar to those calculated for the $^2A'$ state of 1,2,4-TDB (0.4, 27.3, and 13.9 kcal/mol, respectively; Table 4), but they are all somewhat smaller. For the (excited) $^4A'$ state of 2,4,5-TDP, the calculated (BD(T)) TSEs for the isodesmic reactions described above are -3.4 , -9.1 , and -7.4 kcal/mol, respectively (Table 4). These TSEs are not very different from those calculated for the $^4A'$ state of 1,2,4-TDB (-3.2 , -8.1 , and -6.8 kcal/mol, respectively; Table 4). Thus, the presence of the NH^+ group in 2,4,5-TDP (compared to that in 1,2,4-TDB) appears to destabilize somewhat the radical sites in the $^2A'$ state but not those in the $^4A'$ state.



At the BD(T) level, the calculated D–Q splitting ($^2A' - ^4A'$) for 2,4,5-TDP is -39.8 kcal/mol (Table 2). For 1,2,4-TDB, the calculated D–Q splitting ($^2A' - ^4A'$) is -39.3 kcal/mol. Even though the presence of the NH^+ group in 2,4,5-TDP (compared to that in 1,2,4-TDB) appears to destabilize the $^2A'$ state, this seems to have very little effect on the calculated D–Q splitting for this molecule.

2,3,5-Tridehydropyridinium Cation (2,3,5-TDP). At the BD(T) level, 2,3,5-TDP in its (ground) $^2A'$ state is the next most stable tridehydroisomer (after 2,4,5-TDP) and lies 11.2 kcal/mol higher in energy than the 2B_2 state of 3,4,5-TDP (the global minimum with respect to all other tridehydroisomers and states; Table 1).³⁵ Like 2,4,5-TDP, the calculated (BPW91) structure for 2,3,5-TDP indicates that the *ortho*-benzyne (C_2-C_3) interaction dominates; however, the *meta* interaction between the dehydrocarbon atoms at C_3 and C_5 for 2,3,5-TDP appears to be somewhat stronger than the corresponding C_2-C_4 (*meta*) interaction for 2,4,5-TDP. For example, the calculated C_2-C_3 bond length for 2,3,5-TDP (1.29 Å) is slightly longer than the C_2-C_3 bond length (1.26 Å) for 2,3-DDP, and the C_3-C_5 (*meta*) dehydrocarbon atom separation for 2,3,5-TDP is about 0.05 Å shorter than the corresponding C_2-C_4 (*meta*) dehydrocarbon atom separation in 2,4,5-TDP (for comparison, the calculated C_3-C_5 dehydrocarbon atom separation for 2,3,5-TDP is about 0.18 Å shorter than the corresponding C_3-C_5 separation in 2,3-DDP and about 0.21 Å longer than the C_1-C_3 dehydrocarbon atom separation for *meta*-benzyne).

For the (ground) $^2A'$ state of 2,3,5-TDP, the calculated (BD(T)) TSE associated with the separation of the C_2 radical site (to produce 3,5-DDP and 2-DP) is 4.8 kcal/mol (Table 3). This TSE is 9.1 kcal/mol smaller than the corresponding TSE for 1,2,4-TDB (13.9 kcal/mol; Table 3) and 3.3 kcal/mol smaller than the corresponding TSE for 2,4,5-TDP (8.1 kcal/mol; Table 4). The relatively small TSE associated with separation of the C_2 radical site for 2,3,5-TDP might, at first, suggest a fairly strong *meta* interaction between the C_3 and C_5 dehydrocarbon atoms; however, it is likely that this particular TSE is affected by not only the C_3 – C_5 interaction but also the proximity of the *ortho*-benzyne group (C_2 – C_3) to the NH^+ group. Previous calculations³¹ have shown that the biradical stabilization energy (BSE) associated with the separation of the C_2 radical site for the 2,3-didehydropyridinium cation (2,3-DDP) is much smaller than that for either *ortho*-benzyne or the 3,4-didehydropyridinium cation (3,4-DDP). A similar effect has also been noted³⁶ for the 2,3-didehydroquinolinium cation (2,3-DDQ). The unusually small BSEs for these types of molecules (i.e., where the *ortho*-benzyne is adjacent to the NH^+ group) have been attributed³¹ to inductive effects that play a role in charge stabilization of similar magnitude to π -delocalization effects. For 2,3,5-TDP, then, the TSE associated with the separation of the C_2 radical site does not provide much insight into the extent of the (*meta*) C_3 – C_5 interaction as this particular TSE is strongly influenced by the proximity of the NH^+ group.



The calculated (BD(T)) TSEs associated with the separation of either the C_3 or C_5 radical sites (to produce either 2,5-DDP and 3-DP or 2,3-DDP and 3-DP) for the $^2A'$ state of 2,3,5-TDP are 20.3 and 1.3 kcal/mol, respectively (Table 3). The latter TSE is similar to that calculated for 1,2,4-TDB (0.4 kcal/mol; Table 3) and indicates that the radical site at C_5 interacts very weakly with the *ortho*-benzyne group (C_2 – C_3). The former TSE, however, is 7.0 kcal/mol smaller than the corresponding TSE for 1,2,4-TDB (27.3 kcal/mol; Table 3). In this case, the smaller TSE for 2,3,5-TDP compared to that for 1,2,4-TDB is likely to be due to the weaker C_3 – C_5 *meta* interaction in 2,3,5-TDP than the corresponding C_2 – C_4 *meta* interaction in 1,2,4-TDB.

For the (excited) $^4A'$ state of 2,3,5-TDP, the calculated (BD(T)) TSEs for the isodesmic reactions described above are -5.8 , -7.2 , and -3.3 kcal/mol, respectively (Table 3). These TSEs are not very different from those calculated for the $^4A'$ state of 1,2,4-TDB (-6.8 , -8.1 , and -3.2 kcal/mol, respectively; Table 3). In this case, however, two of the three TSEs are somewhat larger (i.e., less negative) than those for 1,2,4-TDB, which suggests that the presence of the NH^+ group in

2,3,5-TDP (compared to that in 1,2,4-TDB) stabilizes somewhat the radical sites in the $^4A'$ state of this molecule.

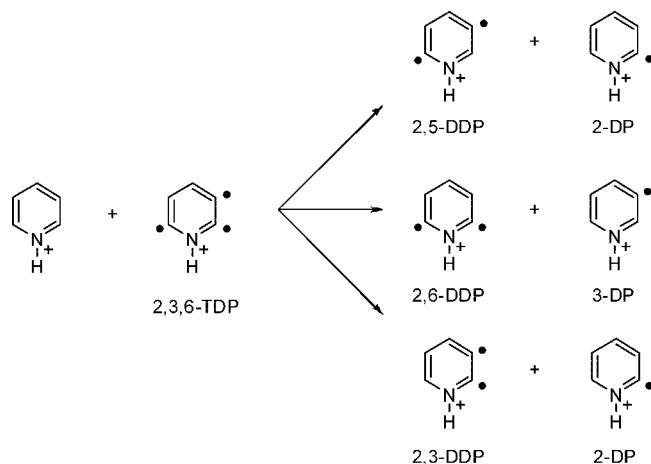
At the BD(T) level, the calculated D–Q splitting ($^2A'$ – $^4A'$) for 2,3,5-TDP is -32.4 kcal/mol (Table 2). For 1,2,4-TDB, the calculated D–Q splitting ($^2A'$ – $^4A'$) is -39.3 kcal/mol. Since the calculated TSEs for the $^4A'$ states of these two molecules are quite similar, the large difference (ca. 7 kcal/mol) in the calculated D–Q splittings is due to the destabilization of the $^2A'$ state that results from the proximity of the *ortho*-benzyne group to the NH^+ group (vide supra).

2,3,6-Tridehydropyridinium Cation (2,3,6-TDP). Even though the (ground) doublet state ($^2A'$) of this molecule³⁵ is calculated to lie above the (ground) doublet states of all of the tridehydroisomers (at all levels of theory; Table 1), it will be discussed next (i.e., before 2,4,6-TDP) because its structure is similar to that for 2,3,5-TDP.

Like 2,3,5-TDP, the calculated (BPW91) structure for 2,3,6-TDP indicates that the *ortho*-benzyne (C_2 – C_3) interaction dominates in this molecule. For example, the calculated C_2 – C_3 bond length for 2,3,6-TDP (1.28 Å) is nearly the same as that for 2,3,5-TDP (1.29 Å), and it is only slightly longer than the calculated C_2 – C_3 bond length (1.26 Å) for 2,3-DDP. Moreover, the calculated C_2 – C_6 (*meta*) dehydrocarbon atom separation for 2,3,6-TDP (2.23 Å) is relatively large and differs from that for 2,6-DDP (2.24 Å) by only about 0.01 Å. The large C_2 – C_6 dehydrocarbon atom separation for 2,3,6-TDP, in particular, suggests that the radical site at C_6 does not interact very strongly with the *ortho*-benzyne group.

For the (ground) $^2A'$ state of 2,3,6-TDP, the calculated (BD(T)) TSE associated with the separation of the C_6 radical site (to produce 2,3-DDP and 2-DP) is small and slightly negative (-0.9 kcal/mol; Table 3). Because this TSE is relatively small and not very different from that calculated for 1,2,4-TDB (0.4 kcal/mol), the interaction of the radical site at C_6 with the *ortho*-benzyne group (C_2 – C_3) must be very weak. However, the fact that this TSE is slightly negative indicates that this weak interaction destabilizes the $^2A'$ state of 2,3,6-TDP to a small degree. The calculated TSE associated with the separation of the C_2 radical site (to produce 2,5-DDP and 2-DP) for the $^2A'$ state of 2,3,6-TDP is 18.1 kcal/mol (Table 3), which is 9.2 kcal/mol smaller than the corresponding TSE for 1,2,4-TDB (27.3 kcal/mol). This difference is nearly identical to that calculated for the separation of the C_2 radical site for 2,3,5-TDP (9.1 kcal/mol) and is likely to result from the same inductive effects that cause the TSE associated with the separation of the radical site at C_2 for 2,3,5-TDP to be unusually small (vide supra). The calculated TSE associated with the separation of the C_3 radical site (to produce 2,6-DDP and 3-DP) for the $^2A'$ state of 2,3,6-TDP (13.4 kcal/mol; Table 3) is only 0.5 kcal/mol smaller than the corresponding TSE for 1,2,4-TDB (13.9 kcal/mol), but it is 6.9 kcal/mol smaller than the TSE associated with the separation of the C_3 radical site for 2,3,5-TDP (20.3 kcal/mol; Table 3). The fact that this particular TSE for 2,3,6-TDP is smaller than that for 2,3,5-TDP is likely due to the much weaker C_2 – C_6 *meta* interaction in 2,3,6-TDP compared to the C_3 – C_5 *meta* interaction in 2,3,5-TDP.

For the (excited) $^4A'$ state of 2,3,6-TDP, the calculated (BD(T)) TSEs for the isodesmic reactions described above are -3.3 , -7.2 , and -6.1 kcal/mol, respectively (Table 3). These TSEs are not very different from those calculated for the $^4A'$ state of 1,2,4-TDB (-3.2 , -8.1 , and -6.8 kcal/mol, respectively; Table 3). However, two of the three TSEs are slightly larger (i.e., less negative) than those for 1,2,4-TDB, which suggests that the presence of the NH^+ group in 2,3,6-TDP



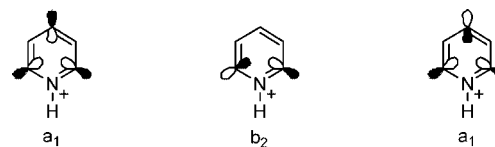
(compared to that in 1,2,4-TDB) stabilizes somewhat the radical sites in the $^4A'$ state of this molecule.

At the BD(T) level, the calculated D–Q splitting ($^2A' - ^4A'$) for 2,3,6-TDP is -30.2 kcal/mol (Table 2). For 1,2,4-TDB, the calculated D–Q splitting ($^2A' - ^4A'$) is -39.3 kcal/mol. Since the calculated TSEs for the $^4A'$ states of these two molecules are quite similar, the large difference (ca. 9 kcal/mol) in the calculated D–Q splittings is due to the destabilization of the $^2A'$ state that results from the proximity of the *ortho*-benzyl group, as well as the radical site at C₆, to the NH⁺ group (vide supra).

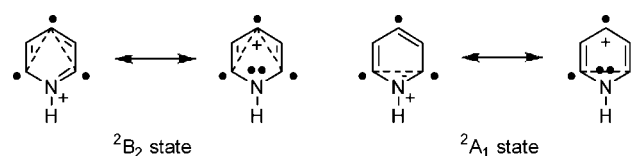
2,4,6-Tridehydropyridinium Cation (2,4,6-TDP). Since this molecule is isoelectronic with 1,3,5-TDB, a brief summary of the theoretical and experimental studies that have been carried out for 1,3,5-TDB may be helpful. Previous calculations for 1,3,5-TDB have shown^{6d} that the quartet state prefers a D_{3h} geometry. At this geometry, there are two degenerate doublet states; however, different Jahn–Teller distortions (i.e., to C_{2v} symmetry) lift the degeneracy of the two doublet states to produce a 2A_1 state and a 2B_2 state.^{6d} A number of previous theoretical studies^{6–9} have predicted that the 2A_1 state is the ground-state of 1,3,5-TDB and that the (excited) 2B_2 state, which lies very close in energy, is a transition state that connects otherwise equivalent 2A minima.^{6d} In addition, all of these theoretical studies have predicted an equilibrium geometry for the 2A_1 state of 1,3,5-TDB that is best described as *meta*-benzyl containing a weakly interacting radical site. This prediction is supported by thermochemical measurements⁹ for 1,3,5-TDB that show that the C–H bond dissociation energy (BDE) at the 5-position of *meta*-benzyl (109.2 ± 5.6 kcal/mol) is nearly the same as the C–H BDE for benzene (112.9 ± 0.5 kcal/mol). Finally, a recent matrix isolation study of perfluoro-1,3,5-TDB has shown that this molecule has a 2A_1 ground state.¹¹

At the BPW91 level, the presence of the NH⁺ group in the aromatic ring of 2,4,6-TDP causes the 2B_2 state of this molecule to be a minimum; that is, unlike 1,3,5-TDB, it is not a transition state connecting equivalent 2A minima. The principle electron configuration for the 2B_2 state of 2,4,6-TDP has the lowest-energy nonbonding MO of a_1 symmetry doubly occupied and the nonbonding MO of b_2 symmetry singly occupied (the second nonbonding MO of a_1 symmetry is unoccupied). For the 2A_1 state, on the other hand, the principle electron configuration has the second nonbonding MO of a_1 symmetry singly occupied instead of the nonbonding b_2 MO.

At all levels of theory, the 2B_2 state is calculated to be the ground state for 2,4,6-TDP with the (excited) 2A_1 state lying



11.1–16.6 kcal/mol higher in energy (Table 1). There appear to be two major factors influencing the energy ordering of the two low-lying doublet states for 2,4,6-TDP. First, an analysis of the equilibrium geometries (BPW91) and atomic charges (Mulliken) for the 2B_2 and 2A_1 states of 2,4,6-TDP suggests that both states are stabilized by a resonance structure that formally involves an ionized carbene (like 3,4,5-TDP; vide supra). This resonance structure permits greater charge delocalization away from the nitrogen atom.



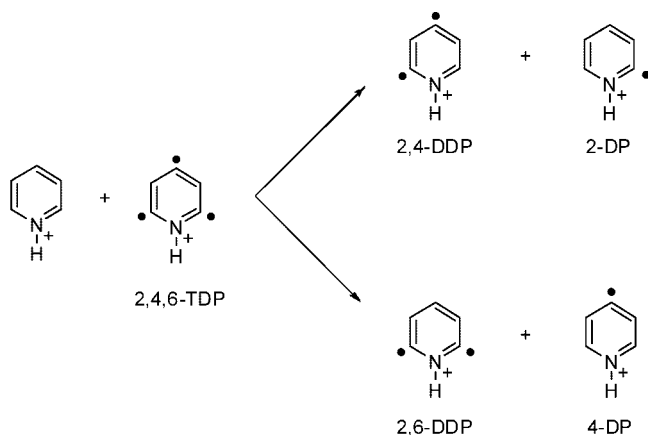
For example, for the 2B_2 state of 2,4,6-TDP, the C₂–C₃ and C₅–C₆ bond lengths are about 0.02 Å shorter, and the N₁–C₂ and C₆–N₁ bond lengths are about 0.05 Å longer, than those for the 2B_2 state of 2,4,6-tridehydropyridine. Moreover, the 2B_2 state of 2,4,6-TDP has a large partial positive charge (+0.180) on C₄, which is not the case for 2,4,6-tridehydropyridine (+0.024). Similar differences exist for the 2A_1 states of 2,4,6-TDP and 2,4,6-tridehydropyridine,³⁷ although they are much smaller (i.e., compared to those for the 2B_2 state). For the 2A_1 state of 2,4,6-TDP, the C₂–C₃ and C₅–C₆ bond lengths are only about 0.01 Å shorter, and the N₁–C₂ and C₆–N₁ bond lengths are about the same as, than those for the 2A_1 state of 2,4,6-tridehydropyridine. In addition, the partial positive charge on C₄ is only about half as large as that for the 2B_2 state. Thus, like 3,4,5-TDP, these resonance structures appear to have a greater (stabilizing) influence on the structure of the 2B_2 state than on that of the 2A_1 state for 2,4,6-TDP.

The second major factor that appears to influence the energy ordering of the two doublet states for 2,4,6-TDP is the C₂–C₆ (*meta*) dehydrocarbon atom separation calculated for the 2A_1 state. At the BPW91 level, the C₂–C₆ dehydrocarbon atom separation is calculated to be 2.15 Å. This dehydrocarbon atom separation is 0.17 Å larger than that calculated for 1,3,5-TDB (1.98 Å) and only 0.19 Å smaller than that calculated for the 4B_2 state of 2,4,6-TDP (2.34 Å). Even though there is a bonding interaction between the C₂ and C₆ dehydrocarbon atoms in the 2A_1 state of both molecules, the extent of this (stabilizing) interaction (i.e., via through-space orbital overlap) appears to be limited by the presence of the NH⁺ group for 2,4,6-TDP; specifically, a smaller C₂–C₆ dehydrocarbon atom separation would lead to a (more) bicyclic structure containing a protonated 2*H*-azirine-type ring, which would introduce a significant amount of bond angle strain. While the charge delocalization afforded by the ionized carbene resonance structure probably offsets this ring strain to some extent, its contribution does not appear to be significant enough to compensate for the relatively weak interaction between the radical sites at C₂ and C₆.

At the BD(T) level, the calculated TSEs for the (ground) 2B_2 state of 2,4,6-TDP associated with the separation of the C₂ radical site (i.e., to produce 2,4-DDP and 2-DP; the C₆ radical



site is equivalent by symmetry) and the separation of the C_4 radical site (i.e., to produce 2,6-DDP and 4-DP) are -1.3 and 11.9 kcal/mol, respectively (Table 4). It is not possible to compare these values with those for 1,3,5-TDB since the 2B_2 state for this molecule is calculated to be a transition state (vide supra). For the 2B_2 state of 2,4,6-TDP, the calculated (BPW91) C_2-C_4 and C_4-C_6 dehydrocarbon atom separations (2.17 Å) are about 0.20 Å smaller than the C_2-C_6 dehydrocarbon atom separation (2.37 Å). This indicates that the C_2-C_4 and C_4-C_6 *meta* interactions are significantly stronger than the C_2-C_6 *meta* interaction. Thus, separation of the C_2 radical site “destroys” only one of the stronger *meta* interactions (i.e., C_2-C_4), whereas separation of the C_4 radical site “destroys” both of the stronger *meta* interactions (i.e., C_2-C_4 and C_4-C_6). This is consistent with the much larger TSE associated with the separation of the C_4 radical site compared to that for the C_2 radical site.



For the 2A_1 state of 2,4,6-TDP, the calculated TSEs associated with the separation of the C_2 and C_4 radical sites are -12.4 and 0.8 kcal/mol, respectively (Table 4). These TSEs are very different from the corresponding TSEs for the 2A_1 state of 1,3,5-TDB (4.7 and 4.7 kcal/mol, respectively; Table 4). For the 2A_1 state of 2,4,6-TDP, the calculated (BPW91) C_2-C_4 and C_2-C_6 dehydrocarbon atom separations are 2.31 and 2.15 Å, respectively (the C_2-C_4 and C_4-C_6 dehydrocarbon atom separations are equivalent by symmetry). The relatively large C_2-C_4 dehydrocarbon atom separation suggests that the interaction between these two particular radical sites is quite weak. This is consistent with the very small TSE associated with the separation of the radical site at C_4 and suggests that the 2A_1 state most closely resembles a *meta*-benzyne containing a weakly interacting radical (like 1,3,5-TDB). The large, negative TSE associated with the separation of the C_2 radical site, then, is likely to be mostly due to the relief of ring strain caused by the presence of the NH^+ group in the aromatic ring (vide supra). Finally, we note that because the electronic structure of the 2A_1 state of 2,4,6-TDP (compared to that for 1,3,5-TDB) is so strongly influenced by the presence of the NH^+ group, it is not possible to compare the TSEs for these two molecules.

For the (excited) 4B_2 state of 2,4,6-TDP, the calculated (BD(T)) TSEs for the isodesmic reactions described above are

-6.2 and -6.8 kcal/mol, respectively (Table 4). These TSEs are not very different from those calculated for the 4B_2 state of 1,3,5-TDB (-6.5 and -6.5 kcal/mol, respectively; Table 4). In addition, the calculated D–Q splitting ($^2B_2-^4B_2$) for 2,4,6-TDP (-29.3 kcal/mol; Table 2) is similar to that ($^2A_1-^4B_2$) for 1,3,5-TDB (-29.7 kcal/mol; Table 2), even though 1,3,5-TDB has a 2A_1 ground state whereas 2,4,6-TDP has a 2B_2 ground state.

Theoretical Disquisition. With few exceptions, the relative state energies calculated at the BPW91, BLYP, CASPT2, and BD(T) levels of theory agree reasonably well for the TDPs. For the quartet states, both DFT methods yield relative energies that are within 0.8 – 1.9 kcal/mol of the BD(T) values (i.e., the “best” level of theory employed here). The CASPT2 method gives relative energies for the quartet states that are 4.0 – 4.5 kcal/mol lower than the BD(T) values, consistent with the usual magnitude of preference that CASPT2 has for high-spin states compared to that for low-spin congeners (recalling that doublet 3,4,5-TDP is serving as the “zero” of energy). Compared to the BD(T) values, the relative energies for the doublet states are more varied at the DFT (1.0 – 3.8 kcal/mol) and CASPT2 (0.1 – 4.4 kcal/mol) levels. In addition, with respect to predictions for the relative state energies of the TDPs, neither DFT method appears to outperform the other.

The calculated D–Q splittings for the TDPs agree reasonably well at all of the levels of theory employed. The DFT and CASPT2 methods give D–Q splittings that are within 1.3 – 5.3 and 0.8 – 5.4 kcal/mol, respectively, of the BD(T) values. However, compared to the BD(T) level, the D–Q splittings calculated at the CASPT2 level are generally somewhat worse (i.e., too small, as expected) compared to those obtained at the DFT levels. Again, neither DFT level seems to fare any better than the other for predicting the D–Q splittings of the TDPs.

The calculated TSEs for the TDPs also agree fairly well at all of the levels of theory employed. For the quartet states, both DFT methods give TSEs that are within 0.8 – 2.0 kcal/mol of the BD(T) values, and the CASPT2 method gives TSEs that are within 0.1 – 0.7 kcal/mol of the BD(T) values. However, compared to the BD(T) values, the calculated TSEs for the doublet states are more varied at the DFT (0.4 – 8.6 kcal/mol) and CASPT2 (0.1 – 8.6 kcal/mol) levels.

Given its reasonably robust many-body treatment of electron correlation, we take the BD(T) method to be preferred for predictions of the relative state energies, D–Q splittings, and TSEs for the TDPs. However, predictions of these thermochemical properties by using the BPW91, BLYP, and CASPT2 methods are generally in good agreement, and in those cases where these particular methods agree less well with BD(T), it is quite possible that more accurate estimates may be associated with values averaged over the various methods. This is, however, a quantitative detail that does not affect the more general qualitative analyses presented above for the individual triradicals.

Conclusions

On the basis of the calculated electronic and geometric structures for the TDPs, these molecules can be grouped into three main types: (1) 3,4,5-TDP, (2) 2,3,4-TDP, 2,4,5-TDP, 2,3,5-TDP, and 2,3,6-TDP, and (3) 2,4,6-TDP. The (ground) doublet state of 3,4,5-TDP is calculated to be the global minimum relative to all of its other tridehydroisomers and states. The presence of the NH^+ group in the aromatic ring of 3,4,5-TDP influences the energy ordering of the two low-lying doublet states due to a contribution by an ionized carbene resonance structure (which permits greater charge delocalization away from the N atom). This resonance structure stabilizes the 2B_2 state

more than the 2A_1 state and leads to a reversal of the energy ordering of these two states compared to that for the isoelectronic species, 1,2,3-TDB. However, the presence of the NH^+ group has little influence on the calculated D–Q splitting for 3,4,5-TDP (compared to that for 1,2,3-TDB).

The calculated equilibrium geometries for the ground $^2A'$ states of 2,3,4-TDP, 2,4,5-TDP, 2,3,5-TDP, and 2,3,6-TDP indicate that these species are best described as *ortho*-benzynes containing a weakly interacting radical site (similar to that for the isoelectronic species, 1,2,4-TDB). It is especially noteworthy that this is the case for 2,3,4-TDP, considering that the three radical sites are adjacent to one another in this molecule. For both 2,3,5-TDP and 2,3,6-TDP, the ground $^2A'$ states are destabilized by about 7–9 kcal/mol due to the proximity of the *ortho*-benzyne and, in the case of 2,3,6-TDP, the radical site at C₂ to the NH^+ group. While this causes the calculated D–Q splittings of these two molecules to be smaller (by 7–9 kcal/mol) than the calculated D–Q splitting for 1,2,4-TDB, the presence of the NH^+ group does not have a significant influence on the calculated D–Q splittings for 2,3,4-TDP or 2,4,5-TDP.

Unlike the isoelectronic species, 1,3,5-TDB, for which the 2B_2 state is calculated to be a transition state, both the 2B_2 and 2A_1 states are calculated to be real minima for 2,4,6-TDP. Whereas the 2A_1 state is calculated to be the ground state for 1,3,5-TDB, the 2B_2 state is calculated to be the ground state (at all levels of theory) for 2,4,6-TDP. The presence of the NH^+ group in the aromatic ring of 2,4,6-TDP influences the energy ordering of the two low-lying doublet states due to a contribution by an ionized carbene resonance structure (which permits greater charge delocalization away from the N atom). This resonance structure stabilizes the 2B_2 state more than the 2A_1 state. In addition, the presence of the NH^+ group in the aromatic ring destabilizes the 2A_1 state by limiting the interaction between the radical sites at C₂ and C₆, and this is not offset to any significant degree by the charge delocalization afforded by the ionized carbene resonance structure. These effects cause the 2B_2 state to lie below the 2A_1 state. Finally, the presence of the NH^+ group has little influence on the calculated D–Q splitting (2B_2 – 4B_2) for 2,4,6-TDP compared to that for 1,3,5-TDB (2A_1 – 4B_2).

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Supporting Information Available: Tables of Cartesian coordinates, zero-point vibrational energies, and 298 K thermal contributions for the TDPs, DDPs, DPs, TDBs, DDBs, the pyridinium cation, benzene, the phenyl radical, 3,4,5-tridehydropyridine, and 2,4,6-tridehydropyridine. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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