

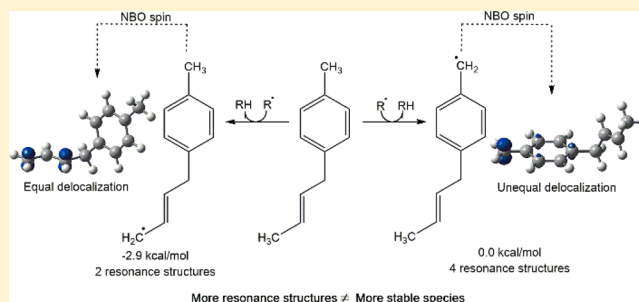
Impact of Conjugation and Hyperconjugation on the Radical Stability of Allylic and Benzylic Systems: A Theoretical Study

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Supporting Information

ABSTRACT: Resonantly stabilized radicals are some of the most investigated chemical species due to their preferential formation in a wide variety of chemical environments. Density functional theory and post-Hartree–Fock calculations were utilized to elucidate the chemical interactions that contribute to the stability of two ubiquitous, resonantly stabilized radicals, allyl and benzyl radicals. The relative stability of these radical species was quantified through bond dissociation energies and relative rotational energy barriers, with a difference of only 0.1 kcal/mol. To clarify and contextualize the energetic results, natural bond orbitals were used to evaluate the atomic spin density distribution in the given molecules. The benzyl radical was found to be ~ 3 kcal/mol less stable than the allyl radical, which was attributed to the inability to efficiently delocalize the spin on a phenyl unit, starkly contrary to general chemistry knowledge. Increasing the degree of π -conjugation and hyperconjugation was shown to benefit allyl radicals to a greater degree than benzyl radicals, again due to more efficient radical delocalization in allyl radicals. This work highlights that more resonance structures do not always lead to a more stabilized radical species, and provides fundamental knowledge about how conjugation and hyperconjugation impact the stabilization of nonbonding electrons in these systems.



1. INTRODUCTION

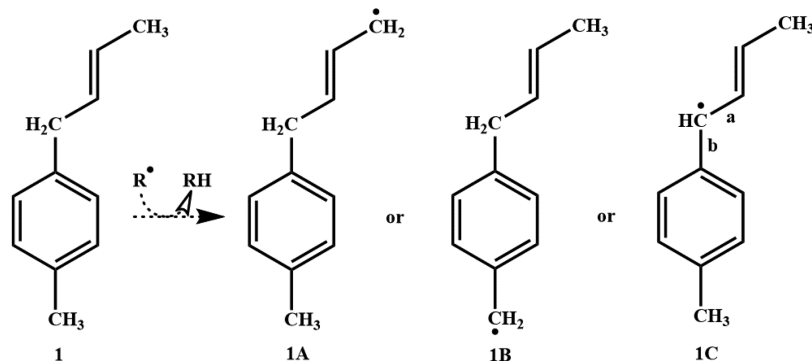
Resonantly stabilized free radicals such as allyl and benzyl radicals, are ubiquitous in many chemical environments and have been detected or implicated as key intermediates in flames,^{1,2} plasmas,^{3,4} and in interstellar space.^{5–9} These transient species are known to participate in a wide variety of chemical reactions including polymerizations,^{10–15} combustions,^{2,16–21} organic syntheses,^{19,22} and in biological and environmental processes.²³ For example, benzyl radicals and their derivatives have shown to be essential intermediates in the oxidation of toluene¹⁷ and methylbenzenes,^{18,21,24} and are implicated in the formation of polycyclic aromatic hydrocarbons (PAHs) in combustion reactions and in the atmospheric processes of earth and other planets.^{8,25–27} Likewise, allylic radicals play specific roles in organic chemistry, including halogenation chemistry,^{28–33} addition chemistry to fullerene structures,^{34,35} and in polymerizations involving multiallyl monomers.^{14,36} Furthermore, allyl and benzyl radicals have allowed a simple framework to comprehend the underlying physical organic concepts governing the stability and reactivity of these compounds, especially concerning the concept of resonance and aromaticity.

Conventional models of resonance have been used to explain a wide variety of topics in organic chemistry, from the investigation of amide rotational barriers^{37,38} to the reactivity of carbonyl compounds.^{37,39,40} Hückel molecular orbital (HMO) theory provided the earliest conceptual framework to understand the resonance in many systems, including the allyl and

benzyl radical. The HMO predicts Hückel energy differences of 0.83β and 0.72β for allyl and benzyl radical, indicating the allyl radical is slightly more stable than the benzyl radical. Delocalization or resonance energies have been used to evaluate the stability of these radicals and are typically quantified through the calculation of CH_2 rotational barriers,^{41–46} referred to as the resonance stabilization energy (RSE), or through the utilization of isodesmic reactions and calculation of relative bond dissociation energies (BDE). Most computational methods used to investigate these radicals involve the linear combination of atomic orbitals molecular orbital theory (LCAO-MO), however the concepts resonance and “electron pushing” are typically conceptualized through valence bond (VB) theory.⁴⁷ VB theory and its refinements, including the block localized wave function (BLW) method,^{48–52} have elucidated the concept of resonance and have been shown to effectively characterize hyperconjugation in some radical systems.^{50,53} Many proponents of VB based resonance studies in π -conjugated radicals, ions and similar resonantly stabilized systems argue rotational barriers only provide crude approximations. They suggest other factors influence chemical stability in the structure, namely, σ -conjugation in the rotated state, geometry relaxation effects, and steric effects, all of which contribute differently to the overall energetics and are difficult to separate from each other

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Scheme 1. Probe Molecule 1 and the Resulting Radicals 1A, 1B and 1C through the Abstraction of a Hydrogen Atom^a

^aThe letters a and b represent the two bonds in 1C available for molecular rotation.

within a consistent framework.⁵² Previous work has shown that steps can be taken in order to eliminate the hyperconjugation effects in the stabilized group through the use of particular isodesmic reactions, demonstrating the RSE method can still provide accurate insight into the relative stability of these systems.⁵⁴

Recent advances in electronic structure calculations have allowed for the accurate determination of RSEs for a variety of allyl and benzyl radical compounds, however; experimental gas phases studies are extremely limited due to the symmetry encountered with benzyl radicals. The singular notable experimental study based on electron paramagnetic resonance (EPR) spectroscopy of the allyl radical rotational barrier in a variety of solvents showed the barrier to be 15.7 ± 1.0 kcal/mol,⁵⁵ while another EPR study measured the rotational barrier of a methylated benzyl radical cations to be 13.4 ± 1.0 kcal/mol.^{56,57} Initial computational work by Hrovat et al. verified these experimental results, reporting the RSE for allyl radical was ~ 2.5 kcal/mol greater than that of the benzyl radical, calculated to be 12.5 ± 1.5 kcal/mol.⁴⁵ Continuing their earlier work, Li et al. showed that the exploration of isodesmic reactions and RSE through CH_2 rotations can be computed with high-accuracy quantum methods such as G4, reporting RSEs for allyl and benzyl radicals to be 13.7 and 11.0 kcal/mol, respectively.⁵⁴ These studies established that the allyl radical is ~ 2.5 kcal/mol more stable than the benzyl radical, nonetheless, the cause for this observation, the specific contributions to the relative stability, and how this stability can be modified remains elusive. The opposite result is perpetuated by many traditional organic chemistry textbooks, which predict the benzyl radical has equal or greater stability than the allyl radical, mostly reasoned on the basis of the number of contributing resonance structures.

Thus, this study aims to comprehend the relative stability of allyl and benzyl radicals using a common precursor (Scheme 1) and the impact of increased π -conjugation and hyperconjugation (Schemes 3–5, vide infra). Previous work has shown that concepts important for allyl and benzyl radical stability, namely resonance, conjugation and hyperconjugation, can be investigated through approaches which compute electron occupations and spin densities such as natural bond orbitals (NBO)^{49,58–60} or the quantum theory of atoms in molecules (QTAIM).^{61,62} These calculations provide relevant knowledge to forward many fields where these resonantly stabilized radicals play a crucial role, and build a framework to facilitate a larger discussion of these radicals through insights

gained by population analyses, which to our knowledge is not discussed in the scientific literature at this point.

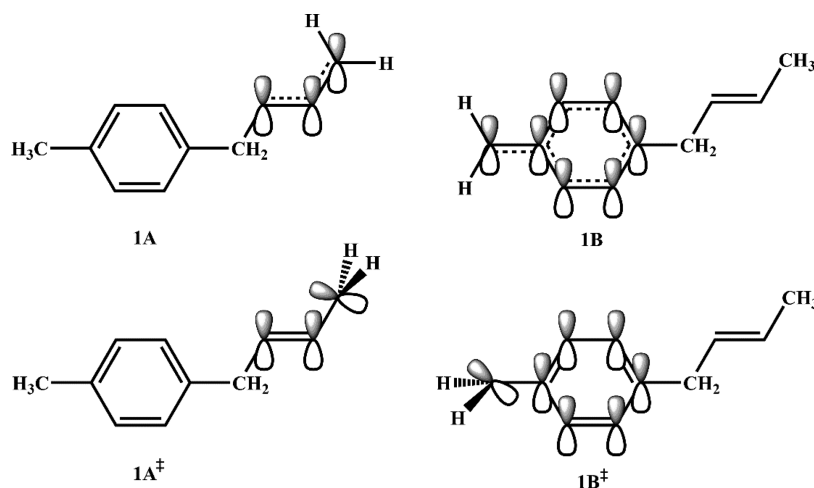
2. COMPUTATIONAL METHODS

Density functional theory (DFT) and post-Hartree–Fock (post-HF) methods were used to optimize and calculate energies for ground state and transition state structures using the Gaussian 09 (D.01)⁶³ suite of programs. The structures of interest were verified as a minimum energy or transition state geometry via frequency calculations. All ground state minima were found to have no imaginary frequencies while transition states had one imaginary frequency corresponding to the degree of freedom of interest.

Two split valence Pople basis sets, namely 6-31+G(d,p) and 6-311G(2d,d,p) (CBSB7), were used to evaluate basis set dependence, while the integral equation formalism variant of the polarizable continuum model (IEF-PCM)⁶⁴ was used to model the impact of solvation (water, methanol, *n,n*-dimethylformamide, chloroform, carbon tetrachloride, and toluene) in these systems. Methods utilized in this study are HF, the popular hybrid density functional, B3LYP,^{65–68} a complete basis set method (CBS-QB3),^{69–71} double hybrid DFT techniques (B2PLYPD3,^{72,73} and B2PLYP⁷⁴) and coupled-cluster method (CCSD(T)).^{75,76} For DFT, double hybrid DFT, and post-HF methods, the wave function was treated as unrestricted (U) and restricted open-shell (RO) to understand the effect of spin contamination on our system. Optimizations with RO wave functions were followed by a numerical frequency analysis to confirm ground state minima. The population of atomic spin densities were obtained via Mulliken population analysis, QTAIM,^{61,77–88} and NBO analysis (NBO 3.1, Gaussian09).⁸⁹

The relative stability of three possible radicals: an allyl radical (1A), a benzyl radical (1B), and a site stabilized by both allyl and benzyl functionalities (1C) originating from compound 1 (Scheme 1) was evaluated using two approaches. The relative stabilization of these three radical sites were assessed by comparing the enthalpy of formation, which is similar to an isodesmic reaction approach where the expectation is typically the cancellation of errors, as both the reactant and product structures have the same number and types of chemical bonds. For example, the relative difference between allyl (1A) and benzyl (1B) radicals can be evaluated by the difference between the total enthalpies of the structures, e.g., the difference between H_{1A} and H_{1B} to produce ΔH_{AB} ($= H_{1A} - H_{1B}$). This approach is exactly the same if one compares the bond dissociation energies of corresponding C–H bonds that produce these radicals. As a result, ΔH_{AB} is referred to as the relative bond dissociation energy (ΔBDE) approach.

It has been suggested that resonance stabilization energy (RSE) afforded through a ΔBDE type approach is not an error proof method.^{48,49,90} The relative magnitude of the resonance stabilization of allyl radicals, cations and anions as well as the benzyl counterparts have been debated widely using this approach.^{41,43,45,54} Since our study is not intended to compute the absolute RSE of the allyl and benzyl

Scheme 2. Rotations of CH₂ Unit in 1A and 1B^a

^aTransition state structures representing the 90° out of plane, nonconjugated p-orbital are denoted as 1A[‡] and 1B[‡].

Table 1. Comparison of Ab Initio Methods and Basis Sets for the Relative Stabilization of Radicals 1A, 1B and 1C^a

method/basis set	1A (S ²)	1B (S ²)	1C (S ²)	ΔH _{AB}	ΔH _{AC}	ΔH _{BC}
B2PLYP-D3/6-31+G(d,p)	0.83	0.83	0.91	-4.1	8.2	12.3
B2PLYP/6-31+G(d,p)	0.83	0.83	0.91	-4.7	7.8	12.5
UB3LYP/6-31+G(d,p)	0.78	0.78	0.79	-2.9	11.1	14.0
UB3LYP/6-311G(2d,d,p)	0.78	0.78	0.79	-2.8	11.8	14.5
ROB3LYP/6-31+G(d,p)	0.75	0.75	0.75	-2.6	11.7	14.3
ROB3LYP/6-311G(d,p)	0.75	0.75	0.75	-2.8	11.8	14.5
ROHF/6-31+G(d,p)	0.75	0.75	0.75	-0.2	7.2	7.4
HF/6-31+G(d,p)	1.40	1.40	1.58	0.5	14.5	13.9
ROCCSD(T)/6-31+G(d,p)//UB3LYP/6-31+G(d,p) ^b	0.75	0.75	0.75	-3.1	7.5	10.6
ROCCSD/6-31+G(d,p)//UB3LYP/6-31+G(d,p) ^b	0.75	0.75	0.75	-2.8	7.4	10.2
ROCCSD(T)/6-31+G(d')//ROB3LYP/6-311G(2d,d,p) ^b	0.75	0.75	0.75	-2.8	7.8	10.6
ROCCSD/6-31+G(d')//ROB3LYP/6-311+G(2d,d,p) ^b	0.75	0.75	0.75	-2.7	7.4	10.1
ROCBS-QB3	0.75	0.75	0.75	-2.6	10.1	12.6
UCCSD(T)/6-31+G(d')//UB3LYP/6-31+G(2d,d,p) ^b	1.34	0.95	1.54	-4.1	5.8	10.0
UCCSD/6-31+G(d')//UB3LYP/6-31+G(2d,d,p) ^b	1.34	0.95	1.54	-3.4	6.4	9.8
UCBS-QB3	1.34	0.95	1.54	-3.4	9.0	12.4

^aAll energy values are enthalpies unless otherwise stated. All values for ΔBDE given in kcal/mol. ^bIndicates the calculation is a single point energy calculation with HF energy shown.

radicals, the ΔBDE approach is sufficient to describe the relative energetic difference between the two radicals. Furthermore, Hrovat and Borden showed that an isodesmic approach was a useful method for computing the relative stability of allyl and benzyl radicals.⁴⁵ It is worth noting that C–H BDE or C–X where X is a heteroatom or organic functionality does not need to be considered in this case, only the relative stability of the radical site is considered. In many previous studies, polarization effects encountered with C–H bond cleavage were found to produced notable errors;⁹¹ however, calculations associated with our unique probe molecule **1** avoids or negates all bond breakages that could be hindered by unwanted effects such as polarization.

As shown in Scheme 2, the rotation effectively eliminates the π-cloud overlap of the methylene carbon, so a comparison of the relative rotational energy barrier (ΔREB) of two radical sites allows for the estimation of the relative RSE of various π-conjugated radicals. As investigated in previous studies, more stable π-conjugated radical sites are observed to have a larger barrier to methylene rotation than less stable radicals.^{41,42,45} To complement the ΔBDE method, the relative difference between the rotational barrier energies (e.g., ΔΔH_{AB}[‡] = ΔH_{1A}[‡] – ΔH_{1B}[‡]) also provide the relative stability of the radical sites. The aforementioned approaches are utilized throughout the text for all systems discussed, with procedural differences noted when necessary.

Entropic effects were ignored and omitted from discussion throughout this manuscript. Gibbs free energy barriers (ΔG[‡]) and relative Gibbs free energies (ΔG) were calculated for all positions considered in molecule **1** (Scheme 1) to understand how entropy impacts ΔBDE and ΔREB. The calculated free energy differences and barriers are provided for the CBS-QB3 and B3LYP methods with unrestricted and restricted open shell wave functions in Table S1 (Supporting Information).

3. RESULTS AND DISCUSSION

3.1. Method Selection and Basis Set Dependence.

Table 1 shows a comparison of methods for the relative stabilization between 1A, 1B and 1C using ΔBDE approach. The B3LYP functional shows an excellent agreement with open-shell spin restricted post-HF methods like CCSD(T) and composite methods such as CBS-QB3. If unrestricted formalism is utilized, the HF based methodologies suffer from significant spin contamination. For example, S² expectation value for UHF calculations was observed to be 1.58 for 1C instead of 0.75. In fact, Hrovat and Borden indicated such spin contaminated calculations would suffice for geometry opti-

mizations while the quantitative energetics would be negatively impacted.⁴⁵ Additionally, Houk et al. and others show that minimal methodological dependence was observed for studies involving the rotation barriers of benzyl cation, anion and radical.^{41,45,54} It is clear from Table 1 that unrestricted HF based techniques are not the most suitable methods to investigate the relative energetics of the aforementioned systems, and that the hybrid density functionals represent a good compromise between low spin contamination and good accuracy. Table 1 also shows that double hybrid methods such as B2PLYP, which rely on MP2 extrapolation of hybrid DFT calculations also suffered from spin contamination and predicted higher relative stabilization of **1A** vs **1B**. On the other hand, B3LYP results at the restricted open-shell and unrestricted levels had similar relative energetics when compared to CBS-QB3 methodology, and increasing the basis set to the triple- ζ , CBSB7 (6-311G(2d,d,p)) basis set also resulted in minimal (0.1 kcal/mol) differences in the relative energetics obtained. Unrestricted calculations utilizing composite methods and perturbation theory were typically 0.7–1.3 kcal/mol greater than the corresponding restricted open-shell calculations. As a result, all of the subsequent calculations were performed using the B3LYP functional using unrestricted wave functions.

Following our selection of the B3LYP functional, calculations were performed to evaluate the effect of implicit solvation on our system. As these are fairly nonpolar molecules with no net charge, the effect of solvation was expected to be minimal. Implicit solvents of varying dielectric constant were tested, including *n,n*-dimethylformamide, toluene, water, chloroform, carbon tetrachloride, and methanol. The choice of implicit solvent was shown to have no significant effect on the relative energetics between **1A** and **1B**, with fluctuations of no more than 0.2 kcal/mol. Solvent effects were also explored on rotational transition state structures as it has been previously noted in the literature that solvation effects can have significant implications in the rotational energy barrier for benzyl and allyl cations and anions.⁴¹ However, relative transition state barriers between solvents were within ~ 0.1 kcal/mol for our system (see Supporting Information, Tables S2 and S3).

On the basis of these results, we selected the B3LYP functional with 6-31+G(d,p) basis set without any implicit solvation. The diffuse function, although unnecessary for our radical species, may provide better comparison with literature results for cationic and anionic systems. Calculations with this level of the theory (Table 1) showed excellent agreement with spin-restricted CBS-QB3 and CCSD(T) methods, experimental results,^{55,92} previous multiconfigurational calculations by Hrovat and Borden,⁴⁵ and recently published G4 and W1BD calculations⁵⁴ (see Supporting Information, Table S4).

3.2. Relative Stabilization of Allyl and Benzyl Radicals.

Calculated relative stabilization of radicals **1A**, **1B** and **1C** using both Δ BDE and Δ REB approaches are shown in Table 2. The Δ BDE approach suggests that the allyl radical (**1A**) is more stable than the benzyl radical (**1B**) by 2.9 kcal/mol while the Δ REB method shows a difference of 3.0 kcal/mol. This observation is in good agreement with previous studies showing that propene radicals are more stable than toluene radicals.^{45,48,54} Previous work by Hrovat and Borden, who utilized similar methods to determine the relative stability between toluene and propene, shows insignificant (~ 0.5 – 1.0 kcal/mol) differences compared to our results. A more recent computational study by Borden et al. utilizing composite, high-

Table 2. Rotational Barrier Energies for **1A, **1B** and **1C** Calculated at B3LYP/6-31+G(d,p) Level of Theory, and Comparison of Δ REB and Δ BDE Methods^a**

structure (bond)	ΔH^\ddagger		(–) $\Delta\Delta H^\ddagger$	Δ BDE
1A	16.1	1A–1B	–3.0	–2.9
1B	13.2	1A–1C(a)	–4.7	11.1 (1A–1C)
1C(a)	11.4	1A–1C(b)	–8.3	–
1C(b)	7.9	1B–1C(a)	–1.7	14.0 (1B–1C)
		1B–1C(b)	–5.3	–

^a“a” and “b” in site **1C** indicates the corresponding bond for the rotation (see Scheme 1). Values are in kcal/mol.

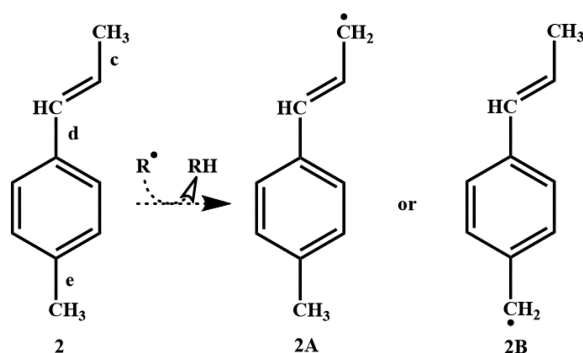
accuracy W1BD and G4 methods predicted lower rotational barriers when compared to our results (Table 2).⁵⁴ Nevertheless, the experimentally calculated allyl rotational barrier of 15.7 ± 1.0 kcal/mol by Korth, Trill and Sustmann using EPR is in exceptional agreement with our computed value for the allyl radical rotational barrier, 16.1 kcal/mol.⁵⁵ Though the experimental work was in an acidic media, we expect minimal solvent effects as previously discussed.

A comparison of the relative stabilization of **1A**, **1B** and **1C** shows that **1C** is by far the most stable radical. Considering that the unpaired electron in **1C** can be stabilized by both allylic as well as benzylic functionalities, these results are not surprising. Using the Δ BDE approach, the **1C** radical is 11.1 kcal/mol more stable than **1A** and 14.0 kcal/mol more stable than **1B**. The rotational barriers of the benzyl and allyl subparts of radical **1C** show trends in the rotational barriers which are mirrored by **1A** and **1B** Δ REB. The barriers for rotation of the benzyl unit along bond “b” and the allyl unit along bond “a” (Scheme 1) in **1C** are 4–5 kcal/mol lower than the rotational barriers calculated for **1A** and **1B** respectively. This suggests that either the conjugation from both directions decreases the rotational barriers or additional interactions introduced from the rotated groups decrease the rotational energy barriers for **1C**. Determining the relative magnitude of these effects is difficult using the Δ REB method, as rotation induces σ -MO hyperconjugation in the transition state but not in the planar structures. Comparisons between these two methods provide further insight into the interactions which contribute to the relative stability of these radical sites, especially in the case of derivatization, explored in the subsequent text.

The trends in Table 2 indicate that more stable radical conformations (e.g., **1A** vs **1B**) have greater barrier energies for methylene rotation, in agreement with previous studies.⁴¹ In the case of **1C**, if the rotational barriers are added, a resonance stabilization energy for **1C** is calculated to be 19.3 kcal/mol. On the other hand, the relative difference of the two barriers for **1C** is 3.6 kcal/mol, which is in good agreement with the relative rotation barriers of **1A** and **1B** (3.0 kcal/mol). We posit the 0.6 kcal/mol difference is the result of **1C** being a secondary carbon radical center while **1A** and **1B** are primary carbon radical centers, and/or the degree of hyperconjugation in the minimal and rotated structures around bond “a” and “b” are not the same. These calculations indicate that the comparison of rotational barriers and Δ BDE can explain the behavior of resonance in these three sites. For the sake of brevity, further energetic analysis of **1C** will be omitted; however, a population analysis of **1C** will be provided in the subsequent sections.

3.3. Effect of π -Conjugation in Systems with Benzyl-Allyl Functionalities. The methylene unit where radical **1C** originates effectively cuts off the π -conjugation between the

Scheme 3. Allyl (2A) and Benzyl (2B) Functionality Containing Molecules Derived from a Parent Molecule, 2^a



^aBonds c, d and e are labeled for defining the rotational energy barriers.

Table 3. Relative Stabilization of 2A and 2B Using the Δ REB and Δ BDE Methods^a

	ΔH^\ddagger		(-) $\Delta\Delta H^\ddagger$	Δ BDE
2A(c)	20.8	2A(c) – 2B(e)	-6.0	-5.8
2A(d)	7.9	2A(d) – 2B(d)	-3.0	-
2B(e)	14.7			
2B(d)	4.9			

^aValues given in kcal/mol. Letters in brackets indicate the bond about which the rotation has taken place.

benzyl and allyl functionalities in compound 1. If that methylene group is eliminated (compound 2, Scheme 3), the unpaired electron originating from compound 2 on the allyl (2A) or benzyl (2B) units should be stabilized by five contributing resonance structures. Considering previous discussion, one would anticipate 2A to be more stable than 2B but not by more than 2.9 kcal/mol, as was observed in the case of 1A and 1B. For both 2A and 2B radicals, there are two possible ways to calculate rotational transition state barriers, which are shown in Scheme 3. For example, rotating the methylene unit in radical 2A along bond “c” disjoins the radical site from the rest of the molecule, while rotating along bond “d” would result in an allyl radical disjoined from the rest of the molecule. Similarly, for radical 2B, rotation along bond “e” would isolate this doubly stabilized radical site while rotation about bond “d” would make a benzyl radical. By effectively removing the π -conjugation via the rotations about bond “d” in 2, it allows us to compare the relative stability of the benzyl and allyl radical from another perspective.

As summarized in Table 3, 2A was found to be 6.0 and 5.8 kcal/mol more stable than 2B via the Δ REB and Δ BDE

methods, respectively. Surprisingly, the degree of stabilization in the allyl versus the benzyl radical is nearly double the amount of relative stability observed between 1A and 1B, indicating that increased π -conjugation via the deletion of the $-\text{CH}_2$ functionality in 1 increases the stability of the allyl radical to a much greater extent than seen by the benzyl radical.

The rotational barriers for 2A(d) and 2B(d) were calculated to be 7.9 and 4.9 kcal/mol respectively. These barrier energies are significantly less than the rotational barriers derived from the $-\text{CH}_2$ rotations in radical daughter products of 1, presumably as no radical sites are located on the atoms connecting two functionalities. Furthermore, the difference between these rotations is 3.0 kcal/mol, which is similar as was seen in the case of relative rotational barriers of 1C(a) and 1C(b). This shows the presence of error cancellation in our utilized methods. However, our earlier postulate that a 0.6 kcal/mol difference for site C was due to the position being a secondary carbon radical is not verified with the Δ REB results for compound 2.

The results provided in Table 3 demonstrate radical 2A is significantly more stable than radical 2B; this is reflected in the rotational transition state barriers for these radicals compared to their partners originating from precursor 1. If conjugation of an allylic radical is extended through a phenyl functionality (2A), the rotational barrier increases by 4.6 kcal/mol compared to the case where the conjugation is broken by the $-\text{CH}_2$ unit in 1A. Similarly, if a benzyl radical experiences an extension of π -conjugation through the allylic functionality at the *para* position (2B), the rotational barrier increases by only 1.6 kcal/mol compared to the case with broken conjugation, 1B. This differential enhancement in the rotational energy barriers implies that the allyl radical is able to utilize the π -conjugation more effectively for radical delocalization, in turn increasing the rotational barrier by 4.6 kcal/mol. This result is similar to the findings of Sui et al., who investigated the spin distributions of benzannulated benzyl radicals.⁶⁰ On the contrary, the benzyl radical is not able to utilize the extended conjugation effectively. The overall extent of electron delocalization and stability in the aforementioned systems is further discussed in the subsequent section with the aid of population analyses.

3.4. Spin Density and Molecular Orbital Analysis.

Population analyses including Mulliken population analysis, NBO and QTAIM (or AIM) were performed to gain a deeper understanding of the nature of radical stabilization by allyl and benzyl functionalities. The NBO and QTAIM results for the atomic spin density for 1A and 1B are summarized in Figure 1, which demonstrates that the spin is delocalized in both systems; however, the extent of delocalization is starkly different. Mulliken spin density derived plots (Figure 2) showed qualitative agreement with the NBO and AIM analyses.

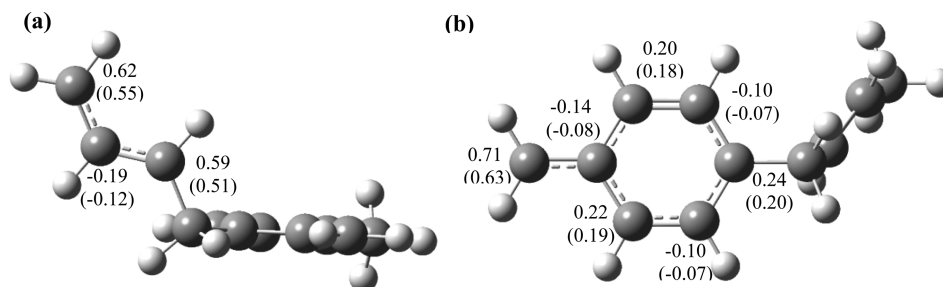


Figure 1. NBO and QTAIM atomic spin densities on carbons of interest in (a) 1A and (b) 1B.

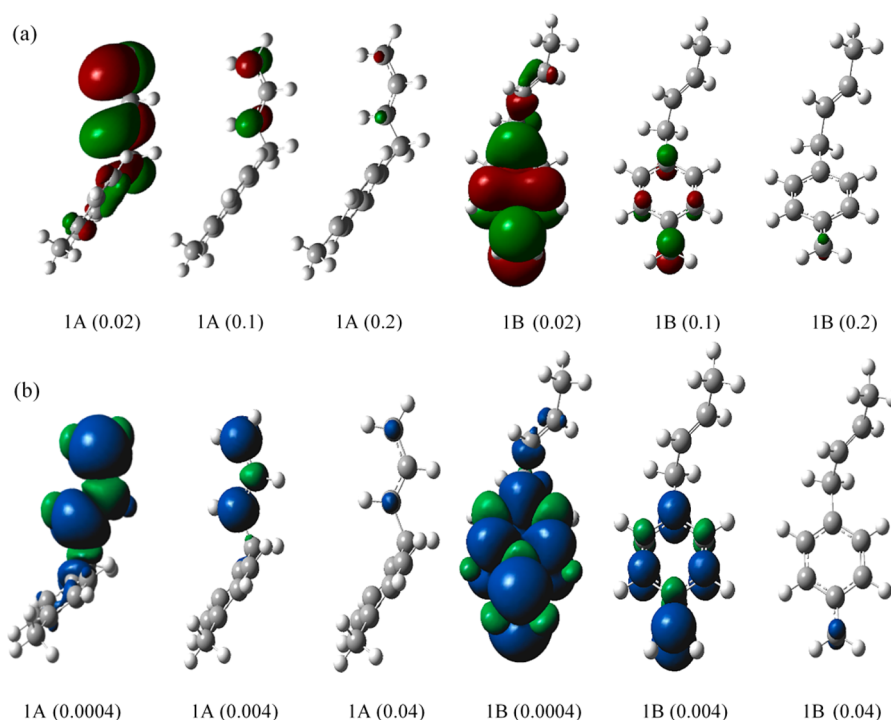


Figure 2. (a) SOMO electron density isosurfaces of **1A** and **1B** at three different isocontour values. (b) SCF atomic spin density isosurfaces of **1A** and **1B** at three different isocontour values.

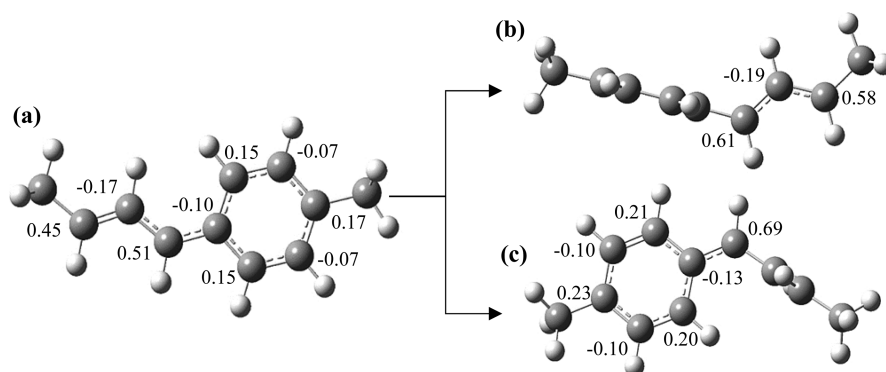


Figure 3. NBO atomic spin densities for carbon centers in (a) **1C**, (b) rotated **1C(a)**, and (c) rotated **1C(b)**.

The values obtained from the three population analyses for all atomic centers in structures **1A** and **1B** are presented in the Supporting Information (Table S6).

Figures 1 and 2 indicate the degree of radical delocalization for the benzyl radical is less than that of allyl radical. In the case of **1A**, the radical character is almost equally shared between the two alternate carbons of the allyl unit, with a small excess of β -spin density in the carbon joining these two. On the contrary, the majority of the spin density is located on the benzylic carbon center in **1B** with small sharing of alternating excess α and β atomic spin density on phenyl carbons, which is unexpected from a traditional view of resonance structures. This observation may also corroborate the notion that breaking the aromaticity would not allow for proper sharing of an unpaired electron by an aromatic unit.

Singly occupied molecular orbitals (SOMOs) and atomic spin densities for **1A** and **1B** are shown at three different isocontour values in Figure 2. Inspection of these plots for the same isocontour values (± 0.04 au for spin density and ± 0.2 au for the SOMO) clearly shows that the electron is more

delocalized in the allyl structure than the benzyl structure. Although the benzyl radical has three possible contributing resonance structures through the phenyl group, these analyses indicate that they contribute less significantly to the stabilization of the benzyl radical center. In the allyl radical case, the opposite is true, as the excess α atomic spin density is observed to be spread between two different carbon sites. This observation can also be linked to the results provided in Table 2, which shows that allylic radicals have a slightly higher barrier to rotation than benzyl radicals. The reason for the extra energy needed for an allylic rotation may indicate that the more delocalized spin contributes to the increased energy needed to rotate the methylene carbon 90° out of plane. This means that understanding the degree of delocalization through population analyses and SOMO isosurfaces could be a useful factor to estimate the rotational barriers of a variety of conjugated radicals.

Analysis of structure **1C** through NBO calculations confirms that **1C** benefits from both allylic and benzyl delocalization, Figure 3(a). This population analysis is consistent with the

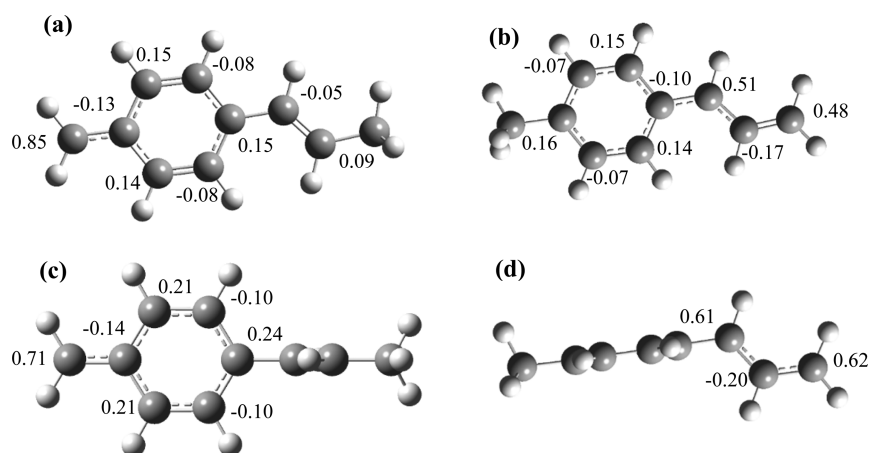
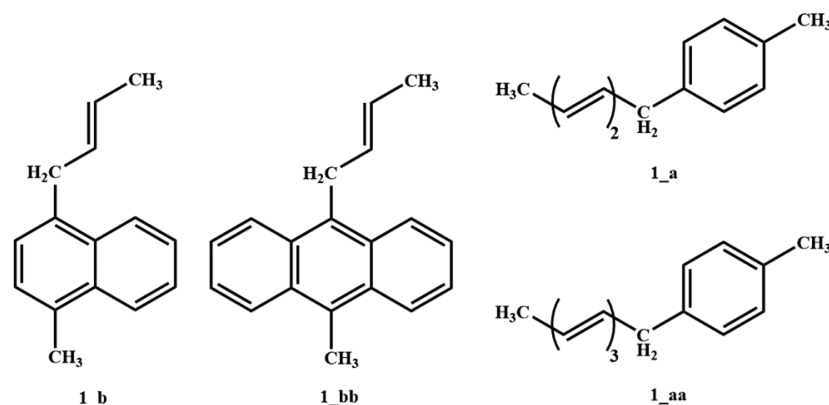


Figure 4. NBO atomic spin densities for carbon centers in (a) **2B**, (b) **2A**, (c) rotated **2B(d)**, and (d) rotated **2A(d)**.

Scheme 4. Extending Conjugation of Structure 1 Using Fused Benzene Rings and Linear Conjugated Double Bonds



results shown in Table 2, which shows greater rotational barriers for bond “a” versus bond “b”. Figures 3(b) and 3(c) corroborate the previous population results found in Figure 1, as the transition state structure associated with the rotation of the allyl or benzyl functionality reproduces the spin populations within 5% for all pertinent carbon centers compared to the minimum structures. Furthermore, Figure 3(a) shows that both the allylic and benzylic functionalities in **1C** are sharing a nearly equal amount of excess α spin density, 0.45 au for allyl functionality and 0.47 au (0.15 + 0.15 + 0.17) for the phenyl functionality. In the case of carbons with excess β spin, the difference between the two radicals increases to 34.1%, with the allyl functionality having -0.17 au excess β spin and the phenyl group having -0.24 au ($-0.07 - 0.07 - 0.10$) excess β spin. The relative difference of the excess β spin in both functionalities in compound **1C** correlates well to the relative barriers of the rotations about bonds “a” and “b”. The relative difference between the barriers of **2C(a)** and **2C(b)**, Table 2, is 35.2%, in near agreement with the difference in excess β spin for the benzyl and allyl functionalities in **1C**. The degree of substitution for the carbon center (primary or secondary) and the type of substituent (allyl, benzyl or methyl) did not significantly change the observed total partial atomic spin densities in all cases investigated.

Figure 4 displays the NBO results for **2A** and **2B** and associated transition state structures rotated about bond “d”. The population analysis for **2B** insinuates the benzyl radical does not share a significant amount of spin density with the adjacent allyl unit. Through comparison of Figures 4(a) and

4(c), one can see that **2B** contains less spin delocalization, as the spin density is mostly associated with the benzyl carbon when compared to the rotated structure **2B(d)**. When the conjugation is broken through rotation about bond “d”, the spin density is more delocalized for **2B**. It is clear for the benzyl radical that utilization of the phenyl and allyl units is minimal, highlighting our original claim that benzyl carbons are much less likely to benefit from conjugation from an energetic or rotational barrier perspective. This perspective on radical delocalization is shared by Sui et al., who suggested that spin density distributions onto annulated arenes is avoided as much as possible.⁶⁰ Interestingly, the degree of spin delocalization on the benzene ring in **2A** is in quantitative agreement with the populations in **2B**, further indication that benzyl radicals do not utilize the aromatic unit to a greater extent than with compound **2A**. This mirrors the results of Table 3, which showed a differential enhancement in the computed barrier heights (+1.6 kcal/mol for benzyl radicals and +4.7 kcal/mol for allyl radicals) for similar methylene rotations in compounds **1** and **2**.

3.5. Effect of Increasing π -Conjugation. In order to understand the impact of additional π -conjugation on the relative stabilization of the radical, one and two additional functionalities were incorporated in molecule **1** (see Scheme 4). To this end, the phenyl unit was replaced with naphthyl and anthryl units, while the allylic unit was extended by introducing one and two more double bonds. The precursor molecules with additional benzene units are named **1_b** and **1_bb**, while precursors with additional allylic units are named **1_a** and **1_aa**.

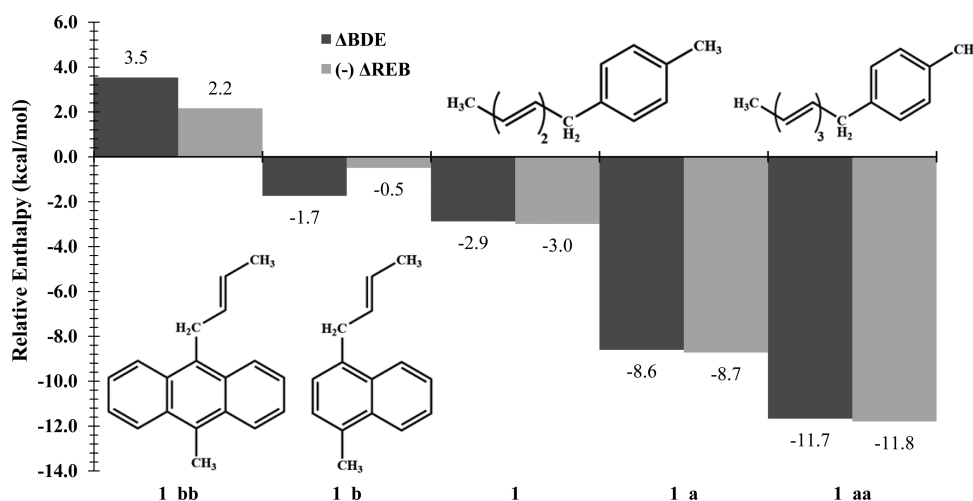


Figure 5. Relative stability of allyl and benzyl radicals via increasing π -conjugation as calculated using Δ BDE and Δ REB methods. Parent structures shown for each case. Numbers are in kcal/mol.

The corresponding radicals are named in the same manner as the previously; for example, allyl and benzyl radicals from **1_a** are named as **1A_a** and **1B_a** respectively. The Δ BDE and Δ REB approaches were utilized to evaluate the impact of these additional units on the radical stabilization. For example, to compare the relative stability of our butadiene-modified structure, the Δ BDE method calculates the stability via $\Delta H = H_{1A_a} - H_{1B_a}$. Likewise, the Δ REB method compares the rotational transition state associated with the radical with extended conjugation and the benzyl or allyl rotation (obtained from rotating **1A** and **1B**), as the functionalization of one side of compound **1** will not affect the barrier associated with the other side due to the break in conjugation. For example, the difference in rotational barriers of radicals derived from **1_a** was calculated from the rotation of **1A_a** and **1B**, denoted as $\Delta\Delta H^\ddagger = \Delta H^\ddagger_{1A_a} - \Delta H^\ddagger_{1B}$.

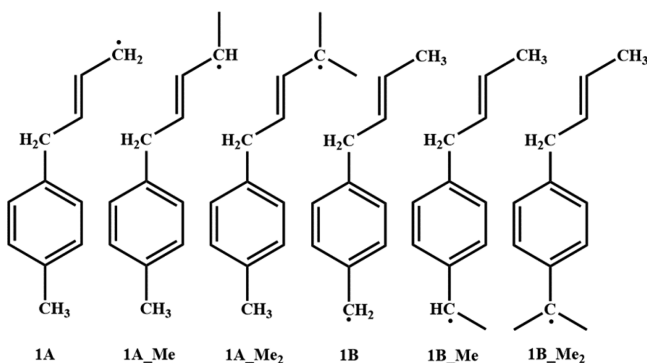
Figure 5 shows the difference between allyl and benzyl type radicals for all the molecules shown in Scheme 4 formed from precursor **1**. We note that even naphthylmethyl radical is less stable than an allyl radical by about 0.5–1.7 kcal/mol. However, when the conjugation is extended to produce an anthrylmethyl radical, this radical is observed to be more stable than the allyl radical (Figure 5). Furthermore, when double bonds are added to the allylic unit, both the Δ REB and Δ BDE approaches show similar results. However, disagreement between the two methods is observed in anthracene and naphthalene functionalized compounds, indicating that more complicated molecular interactions may be present in these molecules. In the case of **1_b**, the resonance stabilization of the allyl radical and the naphthylmethyl radical differs by over 1.2 kcal/mol when calculated via the two methods. The rotational barriers fail to account for the stability of allyl radical relative to naphthylmethyl radical. For anthrylmethyl radical, the Δ BDE shows that the allyl radical is 1.3 kcal/mol less stable compared to the rotational approach, which is a similar difference observed in the case of naphthylmethyl system (1.2 kcal/mol). The radical position in these ring structures could elucidate why the allyl radical is more stable than a naphthylmethyl radical.

The increasing π -density of the naphthalene and anthracene rings may be altering the degree to which the barrier energy is representing the overall stabilization of the molecule. It is

possible that increased aromaticity could alter the electron density in the benzene where the two groups are positioned, perhaps due to aromatic C–H interactions with the rotated methylene SOMO or effects which may depend on the radical position in these ring structures. These effects may lead to hyperconjugation effects in the transition state, which would explain the difference between the Δ REB and Δ BDE approaches. In our structures, this difference between allyl and naphthyl/anthryl radicals derived from **1_b** and **1_bb** is most likely due to the position of the naphthyl and anthryl carbon. In **1B_bb**, the anthryl radical carbon is adjacent to two hydrogens in similar chemical environments, while in **1B_b** the naphthyl radical is not adjacent to hydrogens in similar chemical environments. Previous work has shown that the position of the benzyl radicals in polycyclic aromatic hydrocarbons has a significant effect on the stabilization of the radical site.^{27,93,94} Hemelsoet et al. showed that C–H bond strength corresponding to the methyl group attached to a central ring is much smaller than that of the C–H involving a methyl group that is on the border of a linear acene.⁹³ They argued that the π -character of the radical contributes the most to the stability of that particular radical site, as these radicals are intrinsically stabilized by resonance effects. However, the relief of steric hindrance of a methyl carbon at the central positions of linear acenes with the introduction of the radical is also a large contributor to radical stabilization, indicating the structure of the parent molecule is an important factor when considering stabilized radicals via aromatic groups. Our results also suggest that the position of the methyl group and the corresponding —CH₂—CH=CH—CH₃ functionality play a large role in determining the relative stabilization of these benzyl radicals vs the allyl radicals.

3.6. Effect of Increasing Hyperconjugation. The rotation of methylene radical carbons adjacent to π -conjugation completely diminishes any p-orbital overlap from the carbon radical with the nearby conjugation. Additionally, as the π -conjugation or resonance effects are diminished, the transition state associated with the 90° methylene rotation is dominated by σ -hyperconjugation effects from the rotated hydrogens. This section attempts to quantify the effect of increasing hyperconjugation at either of the radical sites through the addition of methyl groups in **1** as shown in Scheme 5. Allyl and benzyl

Scheme 5. Derivatives of Radicals 1A and 1B Used to Evaluate the Effect of Hyperconjugation on Allyl and Benzyl Radical Stability



radicals with one and two additional methyl groups are named with the suffix of *_Me* and *_Me2* respectively. As before, ΔREB and ΔBDE provide a method to quantitatively compare these radical centers. First, ΔREB and ΔBDE were used to compare the relative stability of methylated and dimethylated radical centers as shown in Table 4. For instance, the relative barriers

Table 4. Rotational Transition State Barriers and Relative Stability of Methylated Allyl and Benzyl Radicals along with the Parent Radicals^a

parent structure	ΔH^\ddagger (1A)	ΔH^\ddagger (1B)	(-) ΔREB	ΔBDE
1	16.1	13.2	-3.0	-2.9
1_Me	15.8	11.8	-4.0	-4.5
1_Me2	14.7	9.6	-5.2	-6.0

^aValues given in kcal/mol.

or ΔREB for methylated allyl and benzyl radicals, e.g., $1A_Me - 1B_Me$ could be calculated as $= \Delta H^\ddagger_{1A_Me} - \Delta H^\ddagger_{1B_Me}$, while the ΔBDE is calculated in a similar fashion via the minimum enthalpies $= H_{1A_Me} - H_{1B_Me}$.

Next, ΔREB and a modified ΔBDE method were used to compare the differences between the radicals shown in Scheme 5 within the allyl or the benzyl family and the results are shown in Table S5. In this case, ΔREB can be calculated in the same way as discussed above. However, the ΔBDE approach must be modified because this approach relies on the difference between the energies of the two radicals. Consequently, a comparison 1A with 1A_Me is not possible due to the presence of an extra methyl unit and the same is true for other comparisons. As a result, four additional isodesmic reactions were constructed to conserve the stoichiometry of the differing radical containing molecules, shown in Figure S1 (Supporting Information). For example, to compare the relative energetics of 1A_Me and 1A via the ΔBDE approach, structure 1A was modified with one methyl at the benzyl carbon, to conserve the number of methyl groups in the reaction. It should be noted that the ΔBDE and ΔREB approaches do not necessarily capture the same contributions to the overall relative energy differences. In the case of the ΔBDE method, the relative energy difference will encompass π -conjugation effects, σ -conjugation effects, steric effects (minimum structures) and the change in the order of the carbon radical (e.g., 1°, 2°, or 3° center). In the case of ΔREB , the relative barrier energies will be affected by the differences in π -conjugation, σ -conjugation, and steric effects (in TS and minimum structures). These differences are

minimalized in Table 4, as the nature of the carbon radical and the relative steric factors are kept constant when mono- and disubstituted radical centers are compared. The same cannot be said for Table S5, where the order of the carbon radical changes, and the relative steric affects between the mono- and disubstituted radical centers will not be conserved as in Table 4. For this reason, the comparison of ΔREB and ΔBDE in Table S5 will not yield comparable results, e.g., the ΔBDE method predicts that the stability increases with the increasing methyl substitution, however the ΔREB method implies that stability should decrease as the barrier energies are shown to decrease.

In the case of methyl derivatized allyl radicals, Table 4 shows one additional methyl group does not significantly impact the value of the transition state barriers, however adding a second methyl group lowers the transition state barrier by 1.4 kcal/mol. This decreasing stability is also noted for one and two methyl substituted benzyl radicals, where the barrier decreases with each additional methyl unit, however; the decrease in the barrier is much more pronounced in the case of derivatized benzyl radicals. As with our previous systems, both ΔREB and ΔBDE methods agree with each other when comparing methylated allyl radicals to the corresponding benzyl radicals. The difference between the ΔREB and ΔBDE methods increases with the amount of methyl substituents; 0.5 and 0.8 kcal/mol for one and two methyl substituents, respectively. As previously stated, the larger barrier energy corresponds to a more stable conjugated radical, therefore the addition of methyl units to an allyl or benzyl radical has an overall destabilizing effect compared to the control case, where for allyl radicals, the addition of methyl groups to allyl radical sites does not significantly impact radical stability until the second methyl unit is added. These results could have significant implications in understanding the reactivity of derivatized benzyl radicals, as the more methyl groups would lead to a more reactive radical site decreasing the residence times of such radical species, subsequently limiting their detection. Paradoxically, methyl derivatized benzyl radicals are useful to use in experimental studies due to their nonsymmetrical nature vs a nonsubstituted radical position. As with the previous sections, NBO calculations were undertaken to understand the degree of spin delocalization in hyperconjugated allyl and benzyl radicals.

Table 5 shows the atomic spin density for the radical site in each structure. Upon introduction of methyl groups, both allyl and benzyl radicals are shown to become less localized on the methylene unit in both the minimum energy structures and the transition states. In the minimum energy structures, the spin densities decrease by approximately 0.03 au for each consecutive methyl group added, regardless of the type of

Table 5. NBO Spin Densities on the Radical Site in Hyperconjugated Structures in Both the Minimum and the Transition State^a

	MIN	TS
1A	0.62	1.03
1A_Me	0.59	0.96
1A_Me2	0.56	0.90
1B	0.71	1.04
1B_Me	0.68	0.97
1B_Me2	0.66	0.91

^aSpin densities provided for 1A and 1B for comparison purposes.

radical. In the transition state structures, the change is much more significant, the spin density decreases by ~ 0.06 au for each methyl group adding to the radical site. Our NBO results do not show a significant difference between the two radical sites from the standpoint of hyperconjugation; however, it appears that the change in the spin density for the allyl radical structures is greater moving from the minimum to the transition state for allyl radicals, which would substantiate our previous results. It appears that the spin densities on the radical sites for allyl and benzyl radicals could be a marker for the energetic values shown for the rotational barriers in Table 4; however, there are other interactions such as sterics which must be playing a significant role in the differences between the hyperconjugated allyl and benzyl radicals.

4. CONCLUSIONS

Using probe molecules, it was established that benzyl radicals are ~ 3.0 kcal/mol less stable than allyl radicals. Through population analyses, namely NBO calculations, this relative stability was understood via the differences in the radical delocalization in these two species. NBO calculations clearly showed that benzyl radicals are much less delocalized than their allyl radical counterparts. This extent of delocalization, probed via NBO spin densities, was corroborated by Δ REB results, which showed that rotating the methylene group in benzyl radical requires less energy since it is less delocalized. When radical sites are stabilized by both phenyl and allyl functionalities, allyl sites were calculated to be at least twice as stable as the benzyl sites, which was also evident by the NBO analysis.

When the impact of increased conjugation was evaluated, naphthylmethyl radicals were shown to be less stable than allyl radicals while the anthrylmethyl radicals were more stable. The number and type of neighboring hydrogen atoms for naphthylmethyl and anthrylmethyl radicals was posited to play a significant role in the stabilization energy calculated by Δ REB and Δ BDE. The Δ REB method was sensitive to the position of the radical site in naphthylmethyl and anthrylmethyl radicals. On the contrary, when conjugation was extended with double bonds in the case of allyl radicals, no differences in the computed energetics were noted. Overall, an extension of π -conjugation affected the stability of allyl radicals more than benzyl radicals.

Upon increasing the σ -conjugation by addition of methyl groups, it was concluded that the first methyl group has a higher impact on the radical stability when compared to the introduction of the second methyl group presumably due to the sterics. Differences in the calculated results from Δ BDE and Δ REB approaches were noted. The Δ REB method showed that a decreasing trend in rotational transition state barriers was observed for benzyl radicals, however allyl radicals did not show this trend. These differences were attributed to steric factors and C–H interactions with the neighboring π -density. Furthermore, decreasing trends in total atomic spin densities at the radical site was observed for increasing σ -conjugation for both radical sites, with greater decreases observed for transition state structures. The correlation between the relative spin densities at two radical sites and the relative stability of those sites may provide useful insight into the amount of contribution σ -conjugation and π -conjugation and other factors to the overall relative stability of these radicals.

Overall, these calculations highlight the general misconception that more resonance structures lead to more stable

chemical species, which is not always true. The relative stability of allyl and benzyl radicals computed through energetic differences derived from two separate methods were understood in terms of the relative degree of spin delocalization between these radicals. This work provides chemical insight useful to many scientific disciplines, including polymers, atmospheric research, and organic chemistry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00549.

Tables of free energy and enthalpic comparisons, implicit solvation affects, comparisons to literature values, population analyses and a list of optimized molecular coordinates and their associated HF energy (PDF)

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Notes

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