

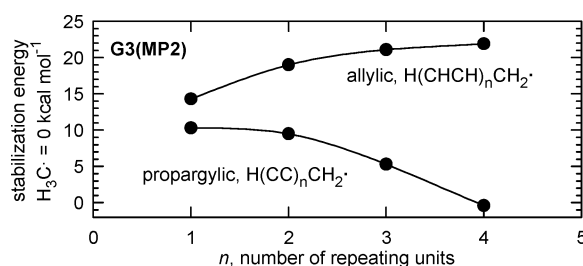
Stabilization Energies of Extensively Conjugated Propargylic Radicals

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G3(MP2) and other model chemistry calculations indicate that stabilization energies of extensively conjugated allylic radicals $H_2(C=C)_nCH_2^*$, $n = 1-4$, increase monotonically as the number of repeating C=C units increase. In contrast, stabilization energies of the analogous propargylic radicals, $H(C\equiv C)_nCH_2^*$, decrease beyond $n = 2$. Breaking up the number of contiguous conjugated C≡C units in conjugation with the odd electron enhances rather than diminishes stability. These results complement previous findings of significant differences in the stabilization of conjugated ground-state polyenes vs polyynes.

Introduction

Hydrogenation of one double bond of 1,3-butadiene releases -26.2 ± 0.3 kcal mol⁻¹ and hydrogenation of the second double bond releases -29.9 ± 0.3 kcal mol⁻¹. The difference of 3.7 kcal mol⁻¹ was interpreted by Kistiakowsky in 1936 as being due to conjugative stabilization of the alternating double–single–double bonds in 1,3-butadiene.¹ This definition of stabilization, sometimes called delocalization energy or resonance energy, has been used widely and is incorporated in most textbooks of organic chemistry.² This is an operational definition in the sense that all enthalpies have been or can, in principle,

be measured experimentally. Recently we reported³ the surprising result that the enthalpy of hydrogenation, ΔH_{hyd} at 298 K, of one of the triple bonds of 1,3-butadiyne to yield 1-butyne (-69.6 kcal mol⁻¹) is equal to the enthalpy of hydrogenation of the second triple bond in 1-butyne to yield *n*-butane (-69.6 kcal mol⁻¹). These are G3(MP2) computed values⁴ and they contrast with both experimental and computed results for 1,3-butadiene. By the widely accepted operational definition, the conjugative stabilization of 1,3-butadiyne is zero.

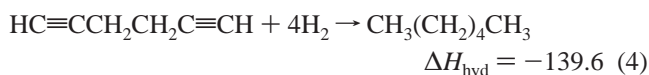
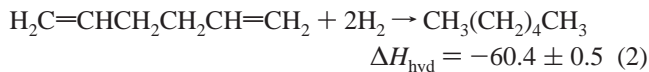
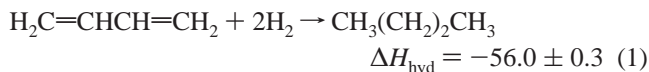
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Subsequently we reported results for larger sets of diynes and polyynes,⁵ which confirmed that an alternating arrangement of triple–single–triple bonds produces a very small difference between ΔH_{hyd} of the first and of the second triple bond, indicating minor thermochemically measurable stabilization, not only in 1,3-butadiyne but in conjugated or unconjugated terminal triple bonds and in conjugated or unconjugated nonterminal triple bonds. The unexpected contrast between the behavior of conjugated double and triple bonds upon hydrogenation is illustrated by the examples of reactions 1–4.



The difference of $4.4 \pm 0.6 \text{ kcal mol}^{-1}$ between experimental⁶ enthalpies of hydrogenation for reactions 1 and 2 is attributable to conjugative stabilization in 1,3-butadiene, which is absent in 1,5-hexadiene. The difference computed by G3(MP2) calculations is $3.7 \text{ kcal mol}^{-1}$. For the corresponding reactions 3 and 4 of diynes, the computed difference is only $0.5 \text{ kcal mol}^{-1}$. Currently, theoretical calculations provide the best estimates that can be made regarding enthalpies of formation, of hydrogenation, etc. of simple conjugated polyacetylenes, because conventional calorimetric experimentation is hampered by their tendency to explode even at low temperature and in the absence of air.⁷

Evidently because of the unexpected nature of our results Jarowski, Wodrich, Wannere, Schleyer, and Houk repeated some of our calculations for diynes and confirmed our reported values.⁸ They interpreted our results differently. On the basis of hyperconjugation arguments and comparisons of hypothetical “virtual states”, they concluded that conjugative stabilization is $8.5 \text{ kcal mol}^{-1}$ in 1,3-butadiene and $9.8 \text{ kcal mol}^{-1}$ in 1,3-butadiyne.

The results we obtained for the thermochemistry of polyacetylenes prompted us to investigate properties of radicals conjugated to extended series of double and of triple bonds and,

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again, we find surprising differences between allylic, $\text{H}(\text{CH}=\text{CH})_n\text{CH}_2^\bullet$, and propargylic, $\text{H}(\text{C}\equiv\text{C})_n\text{CH}_2^\bullet$, radicals ($n = 1$ to 4).

Computational Methods

Bond dissociation energies (BDE) and enthalpies of formation, $\Delta_f H^{298}$, of conjugated allylic and propargylic radicals and of their hydrocarbon precursors ($\text{R}-\text{CH}_3$) were calculated by the G3(MP2) method.⁹ Enthalpies of formation were calculated by the standard atomization method^{5b,9a} and utilizing enthalpies of formation of the elements in their standard states.^{9a} Calculations of radicals using the unrestricted Hartree–Fock (UHF) based method can give spin-contaminated wave functions. It has been suggested¹⁰ that Density Functional Theory (DFT) methods, such as the B3LYP-based model chemistry, give better geometries and energies with less spin contamination in some cases. Accordingly, we also used the G3-(MP2)-B3LYP method, replacing the UHF/6-31G(d) zero-point energy and subsequent MP2/6-31G(d) geometry optimization with the geometry and zero-point energy obtained with the B3LYP/6-31G(d) method. In addition to G3(MP2) and G3(MP2)-B3LYP, the CBS-QB3 method¹¹ was also used to examine the effect of the complete basis set (CBS) extrapolation on the model chemistry. The CBS-QB3 method attempts to explicitly take into account possible spin contamination by incorporating the absolute overlap between α and β orbitals in adjustable parameters.

All methods mentioned utilize an unrestricted wave function and, thus, can be spin-contaminated. The expectation values of the square of the total spin, $\langle S^2 \rangle$, of the various methods were also obtained. The $\langle S^2 \rangle$ values of the UHF wave functions at the full electron MP2/6-31G(d) geometry for the G3(MP2), of the UB3LYP wave functions at the B3LYP/6-31G(d) geometry for G3(MP2)-B3LYP, and of the UHF wave function at the geometry of MP2/CBSB3 for CBS-QB3 are compared.

The energy localized molecular orbitals (LMO) of Edmiston and Ruedenberg¹² were constructed to obtain information about interactions between orbitals. The energy localized molecular orbital is constructed by maximizing the sum of the self-repulsion molecular orbital integrals, $\sum[\psi_i\psi_i|\psi_i\psi_i]$. The energy localized orbitals constructed over the complete active space (CAS) of the multi-configuration self-consistent field (MCSCF) wave functions yield “atomic orbital-like molecular orbitals (AO-like MO)”.¹³ These MOs are dominantly localized on each of the atomic centers that the active space spans. We used full π orbital CAS and constructed all electron configurations generated by including all π electrons in all the π orbitals. The first-order density matrix of CAS-MCSCF was diagonalized to obtain the natural orbitals and their eigenvalues which are called natural orbital occupation numbers (NOON). Subsequently, the localized orbitals were constructed and, as a consequence of maximizing the self-repulsion integrals, the density matrix is no longer diagonal, but the diagonal elements or electron populations of each AO-like MO are close to one. The off-diagonal elements of the density matrix, here called bond orders, can give useful information on the strength of bonding between particular AO-like MOs. All calculations of the MCSCF used the 6-31G-

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TABLE 1. Enthalpies of Formation of Allylic and Propargylic Radicals (R•) and of Their Hydrocarbon Precursors (R-CH₃)^a

R-CH ₃ and R•	$\Delta_f H^{298}$ (lit.)	$\Delta_f H^{298}$ (theo) G3(MP2)	BDE[R-CH ₃] ^b G3(MP2)	BDE[R-CH ₃] ^c CBS-QB3	BDE[R-CH ₃] ^c B3LYP ^d	BDE[R-CH ₃] lit.
H ₃ C-CH ₃	-20.1 ± 0.1 ^e	-20.1	88.5	90.7	88.7	89.7
H ₃ C•	34.8 ± 0.2 ^e	34.2				
H ₂ C=CHCH ₂ -CH ₃	-0.2 ± 0.2 ^e	-0.4	74.2	75.0		75.9
H ₂ C=CHCH ₂ • (allyl)	40.9 ± 0.7 ^e	39.6				
(E)-H(CH=CH) ₂ CH ₂ -CH ₃	13.0 ± 0.4 ^f	13.0	69.5	68.7		71.6, ^g 70.8 ^h
(E)-H(CH=CH) ₂ CH ₂ •	49.8, ^g 49 ^h	48.3				
(E,E)-H(CH=CH) ₃ CH ₂ -CH ₃		25.8	67.4	65.2		
(E,E)-H(CH=CH) ₃ CH ₂ •		59.0				
(E,E,E)-H(CH=CH) ₄ CH ₂ -CH ₃		38.4	66.6	(62.8)		
(E,E,E)-H(CH=CH) ₄ CH ₂ •		70.8				
HC≡CCH ₂ -CH ₃	39.5 ± 0.2 ^e	39.4	78.2	78.9	78.1	77.6, ⁱ 76.3 ^e
HC≡CCH ₂ • (propargyl)	82.3, ⁱ 81 ± 1 ^e	83.4				
H(C≡C) ₂ CH ₂ -CH ₃		93.6	79.0	75.8	78.0	
H(C≡C) ₂ CH ₂ •		138.4				
H(C≡C) ₃ CH ₂ -CH ₃		147.5	83.2	(75.1)	81.3	
H(C≡C) ₃ CH ₂ •		196.5				
H(C≡C) ₄ CH ₂ -CH ₃		201.7	88.9	(76.4)	85.5	
H(C≡C) ₄ CH ₂ •		256.4				
H(C≡C) ₂ CH-CH ₃		101.2	70.0			
H(C≡C) ₂ CH•		137.0				
(HC≡CC≡C) ₂ CH-CH ₃		210.1	73.1			
(HC≡CC≡C) ₂ CH•		249.0				
H ₂ C=CH-CH ₃	4.9 ± 0.1 ^e	4.3	100.2			100.9
H ₂ C=CH•	71 ± 1 ^e	70.3				
HC≡C-CH ₃	44.3 ± 0.2 ^e	43.9	126.1			125.8/ ^j 122.2 ^e
HC≡C•	135.3, ^j 133 ^e	135.8				
CH ₃ C≡C-CH ₃	34.7 ± 0.2 ^e	34.9	125.1			
CH ₃ C≡C•		125.8				

^a Energy values are in kcal mol⁻¹ at 298 K. Values in parentheses may be questionable, see text. ^b Calculated as BDE[R-CH₃] = $\Delta_f H^{298}[R^\bullet] + \Delta_f H^{298}[CH_3^\bullet] - \Delta_f H^{298}[RCH_3]$. ^c BDE values were obtained directly from enthalpies in hartrees as BDE[R-CH₃] = $H^{298}[CH_3^\bullet] - H^{298}[CH_3CH_3] - H^{298}[R^\bullet] + H^{298}[RCH_3]$. ^d Denotes G3(MP2)-B3LYP. ^e Reference 6. ^f Reference 15. ^g Reference 16. ^h Reference 17. ⁱ Reference 18. ^j Reference 19.

(d,p) atomic basis set, and these calculations were performed with the GAMESS quantum chemistry package.¹⁴

Results and Discussion

Table 1 lists experimental and theoretical enthalpies of formation, $\Delta_f H^{298}$, of multiply conjugated allylic and propargylic radicals (R•), and of their hydrocarbon precursors (R-CH₃). The term “conjugated” is used here to indicate alternation of single and multiple bonds and does not imply thermodynamically measurable stabilization.

Calculated values were obtained by the G3(MP2) method, following the methodology described previously.⁵ The calculated enthalpies of formation of the radicals, $\Delta_f H^{298}$ (theo) values from G3(MP2), are in good agreement with experimental values in the few cases where the latter exist. Bond dissociation energies BDE[R-CH₃] are also given in Table 1, as calculated by the G3(MP2) and CBS-QB3 methods, the latter being a DFT method extrapolating to the complete basis set limit at the B3LYP geometries. Both methods yield BDE values in good agreement with existing literature values.

Concerns about spin contamination with the UMP2 method have been reviewed and DFT methods (such as B3LYP) have been recommended for free radical species.¹⁰ Radom's group

has examined the performance of various methods of calculation of enthalpies of formation of free radical species, compared to experimental values.²⁰ Their results with 29 open shell species indicate that, despite large spin-squared expectation values ($\langle S^2 \rangle$ greater than 1, rather than 0.75), heats of formation calculated by the G3(MP2) method for conjugated radicals such as allyl and benzyl are in good agreement with experiment and so are values for vinyl and ethynyl radicals.^{20b} A method specifically proposed for open shell species is G3-RAD. Among other modifications of the G3 method, it uses B3LYP geometries and energies. G3-RAD showed some improvement over G3(MP2) results; mean absolute deviations from experiment were 0.5 and 1.0 kcal mol⁻¹, respectively.^{20b} Enthalpy of formation results with a slightly different set of 29 open shell systems and an optimized set of high level correction (HLC) parameters, using G3X-RAD,^{20a} showed mean absolute deviations of 0.60 kcal

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TABLE 2. Spin-Squared Expectation Values for Selected Radical Species of Table 1, before and after Spin Annihilation^a

Radical	G3(MP2)		CBS-QB3		G3(MP2)-B3LYP	
	before	after	before	after	before	after
CH ₃ •	0.762	0.750	0.762	0.750	0.762	0.750
H(CH=CH)CH ₂ •	0.945	0.757	0.951	0.757		
H(CH=CH) ₂ CH ₂ •	1.135	0.843	1.164	0.857		
H(CH=CH) ₃ CH ₂ •	1.348	1.065	1.414	1.145		
H(CH=CH) ₄ CH ₂ •	1.583	1.511	1.690	1.747		
HC≡CCH ₂ •	1.013	0.794	0.959	0.779	0.973	0.783
H(C≡C) ₂ CH ₂ •	1.106	0.870	1.441	1.270	1.106	0.870
H(C≡C) ₃ CH ₂ •	1.275	1.067	2.017	3.018	2.069	3.228
H(C≡C) ₄ CH ₂ •	1.402	1.305	2.596	5.967	2.662	6.319

^a The $\langle S^2 \rangle$ values before and after spin annihilation are calculated at the Method 1 level at the geometry of Method 2, denoted as Method 1//Method 2. For G3(MP2), UHF/6-31G(d)//MP2/6-31G(d); for CBS-QB3,¹¹ UHF/6-311+G(3d2f,2d2f2p)//B3LYP/6-31G†; and for G3(MP2)-B3LYP, UHF/6-31G(d)//B3LYP/6-31G(d).

mol⁻¹. This value compares with 0.84 kcal mol⁻¹ with standard G3 and 0.76 kcal mol⁻¹ with G3//B3LYP. Overall it appears that all methods mentioned above gave reliable heats of formation with mean average deviations of 1 kcal mol⁻¹ or less for the set of radical species for which experimental values are available.

Concerns about spin contamination led us to perform calculations with both the G3(MP2) method and the DFT modification of CBS-QB3, the latter using B3LYP geometries and extrapolating the pair correlation energies to the complete basis set limit. Our calculations leading to the results of Table 1 show spin contamination with the larger species we examined. $\langle S^2 \rangle$ values for the various species with both methods are shown in Table 2, which also gives the $\langle S^2 \rangle$ values before and after spin annihilation.

Radom reported an enthalpy of formation of 53.5 kcal mol⁻¹ at 0 K for the benzyl radical, a seven carbon conjugated system, in good agreement with the experimentally based value of 54.0 kcal mol⁻¹. The UMP2(full)/6-31G(d) level value of $\langle S^2 \rangle$ was 1.305. Similarly, $\Delta_f H^\circ[\text{C}_6\text{H}_5\text{CH}_2\text{B}_1]$ and $\Delta_f H^\circ[\text{NH}(3\Sigma^-)]$ with the G3(MP2) method were within ± 1 kcal mol⁻¹ of experimental values despite $\langle S^2 \rangle$ values of 2.015 and 2.014, respectively. In trying to establish the reliability of calculated enthalpies of formation of radicals as affected by the value of $\langle S^2 \rangle$, we calculated BDE[C₆H₅CH₂-CH₃], which is known, by the G3(MP2) and CBS-QB3 methods. The G3(MP2) result was 79.3 kcal mol⁻¹ ($\langle S^2 \rangle[\text{C}_6\text{H}_5\text{CH}_2\text{•}] = 1.272$ before and 0.926 after spin annihilation) and the CBS-QB3 result was 78.9 kcal mol⁻¹ ($\langle S^2 \rangle[\text{C}_6\text{H}_5\text{CH}_2\text{•}] = 1.335$ before and 1.063 after annihilation). Experimental values are 77.2⁶ and 79.3¹⁹ kcal mol⁻¹ and values calculated by both methods are in acceptable agreement with experiment. On this basis and the results of Radom we conclude that $\langle S^2 \rangle$ values up to about 1.5 are unlikely to lead to large errors in the enthalpies of formation. A peculiarity is evident with three of the $\langle S^2 \rangle$ values of Table 2, using the CBS-QB3 method, which show a greater value after spin annihilation than before. In addition, these three $\langle S^2 \rangle$ values are considerably greater than 1.5. We consider such values questionable and they are shown in parentheses in Table 1. For the larger species we examined, the CBS-QB3 method appears more problematic in terms of spin-squared expectation values.

BDE[R-CH₃] values of Table 1 were used to determine the stabilization energies (SE) of the allylic and propargylic radicals studied relative to SE[CH₃•] = 0.0. Relative stabilization energy of carbon radicals, R₁• and R₂•, has long been estimated from

relative bond dissociation energies of R₁-H and R₂-H. We have shown that this is a poor approximation, which leads to substantial errors and inconsistencies because it disregards the variability of the electronegativity of hydrogen and the effects of electronegativity differences between various R and H.^{18,21} Theoretical support for this appeared subsequently.²² SE[R•] is more appropriately evaluated as the difference BDE[H₃C-CH₃] - BDE[R-CH₃], where effects of differences in electronegativity are smaller.¹⁸ The results of Table 1 with G3(MP2) indicate that the strength of the bond to methyl, BDE[H(CH=CH)_nCH₂-CH₃], decreases monotonically for allylic radicals as the number of conjugated CH=CH units increases. For $n = 1, 2, 3,$ and 4 , stabilization energies for the conjugated allylic radicals relative to SE[CH₃•] = 0.0 are 14.3, 19.0, 21.1, and 21.9 kcal mol⁻¹, respectively. Each additional CH=CH unit in conjugation makes allylic radicals *more stable*. The G3(MP2) results are consistent with previous theoretical and experimental values for the allylic systems. Luo and Holmes^{23a} have found a similar trend and estimated the limit, as n increases, of stabilization enthalpies at 25 kcal mol⁻¹, while Doering et al.^{23b,c} extrapolated their experimental data to 23.8 kcal mol⁻¹. The corresponding CBS-QB3 results for $n = 1-4$ are 15.7, 22.0, 25.5, and 27.9 kcal mol⁻¹, the last value being questionable. The CBS-QB3 results are not consistent with those in the literature.¹⁸

For the conjugated alkynes, BDE[H(C≡C)_nCH₂-CH₃] *increases* monotonically with G3(MP2) as the number of conjugated C≡C units increases, in contrast with the conjugated alkenes. For $n = 1, 2, 3,$ and 4 , stabilization energies of the propargylic radicals are 10.3, 9.5, 5.3, and -0.4 kcal mol⁻¹, respectively, where the negative value denotes less stable than the methyl radical. Each additional C≡C unit in a conjugative arrangement makes propargylic radicals thermodynamically *less stable*. The CBS-QB3 method shows stabilization energies of 11.8, 14.9, 15.6, and 14.3 kcal mol⁻¹, the last two values being questionable on the basis of $\langle S^2 \rangle$ behavior. Because of the differences between G3(MP2) and CBS-QB3 results, we performed additional calculations for the propargylic radicals by the G3(MP2)-B3LYP method and obtained values of SE = 10.6, 10.7, 7.4, and 3.1 kcal mol⁻¹ for $n = 1, 2, 3,$ and 4 , respectively. The trend of decreasing stabilization past $n = 2$ is also shown by this DFT method, but B3LYP geometries and frequencies lead to questionable results in terms of $\langle S^2 \rangle$ behavior for $n = 3$ and 4 (see Table 2).

There is the possibility that small errors in atomization energies may be propagated in the larger species, leading to erroneous enthalpies of formation. For this reason we also calculated stabilization energies of the propargylic radicals with B3LYP geometries and energies and obtained SE values from H^{298} in hartrees by enthalpies of reaction, without utilizing atomization and gaseous atomic enthalpies of formation.²⁴ In this fashion, total enthalpies of formation H^{298} of C(g) and H(g) and the corresponding enthalpy of formation from the corre-

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(22) Coote, M. L.; Pross, A.; Radom, L. *Org. Lett.* **2003**, *5*, 4689-4692.

(23) (a) Luo, Y. R.; Holmes, J. L. *Chem. Phys. Lett.* **1994**, *228*, 329-332. (b) Doering, W. von E.; Kitagawa, T. *J. Am. Chem. Soc.* **1991**, *113*, 4288-4297. (c) Doering, W. von E.; Sarma, K. *J. Am. Chem. Soc.* **1992**, *114*, 6027-6043.

(24) SE[R•] = 627.51{H²⁹⁸[CH₃•] - H²⁹⁸[CH₃CH₃] - H²⁹⁸[R•] + H²⁹⁸.[RCH₃]}, where 627.51 converts hartrees to kcal mol⁻¹.

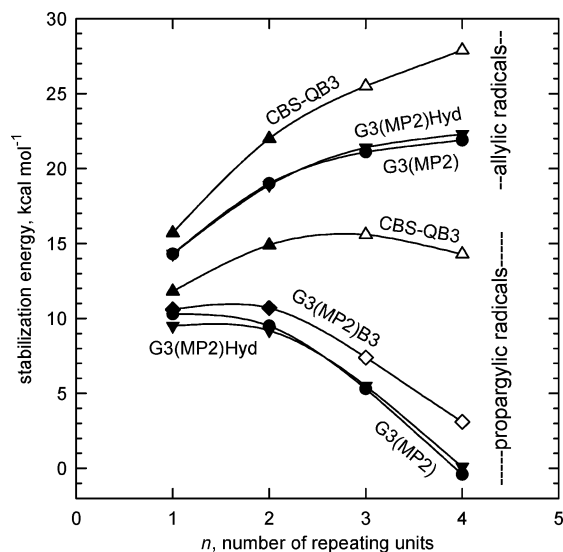


FIGURE 1. Plot of stabilization energies (relative to $SE[CH_3^*] = 0.0$) of allylic and propargylic radicals vs contiguous repeating units conjugated to the unpaired electron. Open symbols indicate values that are questionable on the basis of spin-squared expectation values. G3-(MP2)Hyd indicates SE by differences in enthalpies of hydrogenation (see text).

sponding standard states cancel in calculating BDE and SE. This is because there are equal numbers of C and of H atoms in reactants and products. The $SE[R^*]$ values obtained in this fashion are the same as those obtained from heats of formation. As expected, possible errors in enthalpies of formation cancel out and do not lead to errors in BDE and the SE values derived from them. These results are shown graphically in Figure 1, where results questionable on the basis of the behavior of spin-squared expectation values are represented by open symbols. In summary, only the G3(MP2) values show acceptable $\langle S^2 \rangle$ behavior for $n = 1-4$ for both allylic and propargylic radicals.

Finally, stabilization of allylic radicals by conjugation with repeating $-CH=CH-$ units may be estimated by comparing enthalpies of hydrogenation of $H(CH=CH)_nCH_3$ to $H(CH=CH)_nCH_2^*$. The difference is the stabilization of the unpaired electron imparted by the repeating $-CH=CH-$ units. Similarly comparisons of $H(C\equiv C)_nCH_3$ to $H(C\equiv C)_nCH_2^*$ indicate unpaired electron stabilization imparted by repeating $-C\equiv C-$ units. G3-(MP2) calculations in this fashion showed stabilization energies for the conjugated allylic radicals as 14.3, 18.9, 21.4, and 22.3 $kcal\ mol^{-1}$ for $n = 1, 2, 3,$ and $4,$ respectively. Stabilization energies of the propargylic radicals are 9.5, 9.0, 5.5, and 0.1 $kcal\ mol^{-1}$ for $n = 1, 2, 3,$ and $4,$ respectively. These values and their trends are quite similar to those obtained by the more formally correct procedure of obtaining stabilization energies from the BDE values of Table 1 by G3(MP2) and are denoted by G3(MP2)Hyd in Figure 1.

Solely on the basis of p orbital overlap with the odd electron, one might have expected about equal stabilization of allyl and propargyl, because the additional p orbitals of the latter are orthogonal to the pair that delocalizes the odd electron. However, resonance Lewis structures that can be written for allyl are degenerate ($CH_2=CHCH_2^* \leftrightarrow ^*CH_2CH=CH_2$), while those for propargyl are not ($CH\equiv C-CH_2^* \leftrightarrow ^*CH=C=CH_2$). Consistent with this, the carbon-carbon bond lengths in allyl are equal, but in propargyl they are 1.20 and 1.39 Å (UMP2/6-31G(d)).

SCHEME 1. Off-Diagonal Elements of the First-Order Density Matrices of CAS-MCSCF/LMO of Allyl and Propargyl^a

Elements		NOON		
1		0.100		
2	0.700	2	1.000	
3	0.003	3	1.900	

1		0.064		
2	0.882	2	0.065	
3	0.002	3	1.002	
4	0.000	4	1.933	
5	0.000	5	1.936	

^a The matrices are constructed from the localized orbitals (AO-like MO) of the MCSCF/6-31G(d,p) wave functions. The numbering and the phase of the orbitals are given pictorially in the inset. The natural orbital occupation number (NOON) is from the canonical MCSCF/6-31G(d,p) wave functions

All methods of calculation described above indicate quite different behavior in the stabilities of extensively conjugated linear allylic and propargylic radicals. This is consistent with our findings of different behavior of the thermodynamic stabilization of the corresponding hydrocarbons.^{3,5}

A qualitative picture of the spin distribution in the propargyl radical can be obtained by using the energy localized molecular orbitals (LMO) of Edmiston and Ruedenberg.¹² They are shown in Scheme 1, which gives the off-diagonal elements of the density matrix from the localization procedure performed on the CAS-MCSCF wave functions for allyl and propargyl radicals, along with the orbital numbering, orbital phase, and the NOON of the unlocalized CAS-MCSCF orbitals. When two orbitals are in phase, a positive element is interpreted as bonding and a negative element as antibonding. When two orbitals are out of phase, the reverse applies. Hence the density matrix of this type is also known as the bond order matrix. The off-diagonal elements in Scheme 1 are normalized to the π interaction elements found in ethylene (0.909) and for one π bond in acetylene (0.936), for allyl and propargyl, respectively.

No antibonding is found in any π orbital interactions of the two radicals in Scheme 1. As expected, the π bonding between orbitals 1-2 and 2-3 in the allyl radical is equal. However, the π bonding between the parallel orbitals 1-2 and 2-3 in propargyl is not equal, being 0.882 and 0.466, respectively. This indicates that some resonance is important but that it is not as pronounced as in the allyl radical. Bonding interactions in propargyl between orbital 3 and orbitals 4 or 5 is zero, the orbitals being orthogonal. This is consistent with 1.000 for bonding between orbitals 4 and 5, indicating that they are not interacting with the orthogonal orbitals. The π bonding between orbitals 2 and 3 in allyl is 70% of a π bond and that in propargyl is only 47%.

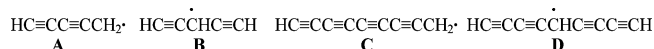
The qualitative LMO results are consistent with the results of an electron spin resonance (ESR) study that were interpreted as indicating the spin densities on the sp and sp² carbons of propargyl radical to be 0.53 and 0.75, respectively.^{25a} A detailed

(25) (a) Kasai, P. H. *J. Am. Chem. Soc.* **1972**, *94*, 5950-5956. (b) Jochowitz, E. B.; Zhang, X.; Nimlos, M. R.; Verner, M. E.; Stanton, J. F.; Ellison, G. B. *J. Phys. Chem. A* **2005**, *109*, 3812-3821. (c) Fantasier, R. M.; Poutsma, M. L. *J. Am. Chem. Soc.* **1968**, *90*, 5490-5498.

infrared study of the propargyl radical has also shown unequal distribution of spin densities and reported CCSD(T)/ANO calculations that show the partitioning of the spin as 35% on the sp and 65% on the sp² carbons.^{25b} Product analysis of reactions of propargyl radicals has also supported greater spin density at the sp² carbon relative to the sp carbon, with a ratio of 1.7:1.0.^{25c}

We also examined a Lowdin population analysis of the electron densities of the singly occupied molecular orbitals (SOMO) of allyl and propargyl radicals. The analysis gave densities of 0.476 for the CH₂ carbon of the allyl radical vs 0.823 for that of propargyl, again indicating greater localization of the odd electron on the methylene carbon of the propargyl (CH≡C–CH₂• ↔ •CH=C=CH₂) and consistent with the results of Scheme 1.

When conjugation of multiple contiguous triple bonds is broken in isomeric polyynes, there is a small *loss* of about 0.9 kcal mol⁻¹ in thermodynamic stability.⁵ The reverse is true in the radicals, where there is a substantial *gain* in stability when contiguous conjugation is broken. This is demonstrated by examining the G3(MP2) enthalpies of formation of radicals **A–D** from Table 1.



Radical **B**, with a bent carbon skeleton, is 1.4 kcal mol⁻¹ more stable than the linear **A**, even though the Lewis structure of **B** has two terminal, unconjugated triple bonds vs one terminal and one internal conjugated bonds in **A**. On the basis of both the type and placement of the triple bonds, **A** might have been expected to be more stable. The effect is more pronounced in comparing the two nine-carbon radicals, where **D** is more stable than **C** by 7.4 kcal mol⁻¹. The energetics may be skewed by the fact that **B** and **D** have two strong terminal C–H bonds, whereas **A** and **C** have only one. However, any effect of the number of terminal C–H bonds is the same for **B** and **D**, but the energetic difference of the two pairs **A, B** and **C, D** is quite different and much more pronounced in the tetraynes. Analogous comparisons of the corresponding allylic radicals are not

meaningful because H₂C=CHCH=CHCH₂• and (H₂C=CH)₂–CH• are simply resonance structures of the same species (share the same stationary point on the potential energy surface). The same holds true for the alkene analogues of **C** and **D**.

The last two pairs of entries in Table 1 allow estimation of the effect of methyl substitution on the stabilization energy of ethynyl radicals. SE[HC≡C•] = –35.0 kcal mol⁻¹ vs SE[CH₃C≡C•] = –34.0 kcal mol⁻¹ (the negative value shows destabilization relative to methyl),²⁶ indicating a small stabilizing effect of methyl on ethynyl, similar to the small stabilization of alkyl radicals by methyl substitution at a β carbon. We note that the G3(MP2) calculation yields a reasonable value for the bond dissociation energy of the C(sp²)–C(sp³) bond of H₂C=CH–CH₃, 100.8 kcal mol⁻¹ in Table 1 vs the experimental value of 100.9 ± 1.0 kcal mol⁻¹.⁶ The same is true for the C(sp)–C(sp³) bond of HC≡C–CH₃, 126.7 kcal mol⁻¹ vs experimental 123.5 ± 2⁶ and 125.8 ± 2 kcal mol⁻¹.¹⁹

Conclusions

Stabilization energies of highly conjugated allylic and propargylic radicals behave quite differently, as the number of CH=CH or C≡C units in conjugation with the unpaired electron increases. These results supplement our previously reported differences in the thermochemistry of conjugated polyenes vs conjugated polyynes.^{3,5} Breaking up the contiguous number of C≡C units conjugating to the odd electron increases stabilization of propargylic radicals.

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Supporting Information Available: G3(MP2) and CBS-QB3 files and energies and geometries of alkynes, alkenes, and radicals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(26) In calculating SE values for HC≡C• and CH₃C≡C• the BDE values of Table 1 were decreased by 2.0 ± 1.0 kcal mol⁻¹, which is the bond strengthening due to electronegativity differences between such radicals and methyl. This correction is required¹⁸ for obtaining SE values when there is a difference in electronegativity, as is the case for RC≡C• and CH₃•.