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On the Lack of Conjugation Stabilization in Polyynes (Polyacetylenes)

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Received April 12, 2004

By analogy to conjugated polyenes, conjugative stabilization of polyynes with the −C≡C−C≡C− group might be expected to be substantial. On the contrary, consistent with our recent report of a surprising lack of conjugative stabilization in butadiyne, we find by G3(MP2) calculations and by comparisons with available experimental data from these and other laboratories that the ground-state stabilization of conjugated polyynes is in fact quite small, amounting to <1 kcal mol^{-1}. By similar calculations, the 2,4-pentadiyn-1-yl radical shows no enhanced stabilization relative to 2-propyn-1-yl radical, despite the potential stabilization of the odd electron by two conjugated triple bonds and unlike the behavior of 2,4-pentadien-1-yl radical. The thermochemistry of straight-chain alkynes and polyynes is very self-consistent. Enthalpies of hydrogenation, leading to enthalpies of formation, are predictable with a high degree of accuracy (absolute mean deviation = ±0.39 kcal mol^{-1} vs theoretical values and ±0.52 vs experimental) from three molecular structure enthalpies and one conjugation stabilization parameter.

Introduction

In a recent letter,[1] we pointed out that the conjugation stabilization enthalpy of 1,3-butadiyne, which might reasonably, if naively, be supposed to be equal to or greater than the 3.9 kcal mol^{-1} ascribed to 1,3-butadiene, is zero by G3(MP2) calculation. In the same letter, we report the conjugation stabilization of 1,3-pentadiyne as 1.4 kcal mol^{-1}. There is a possibility that the 1,3-butadiyne case is a small-molecule anomaly and, despite preliminary results to the contrary, that triple bonds in conjugation to one another in larger molecules may begin to show a more “normal” stabilization as judged from their diene counterparts. Therefore we felt that examination of conjugation stabilization in relatively long chain straight chain diynes and polyynes was justified and we report the results here. Despite the importance of polyynes (sometimes called polyacetylenes) in general[2] and their potential applications in nanotechnology,[3] thermochemical studies of polyynes are sparse and give no systematic picture of their relative stabilities.[4] There are sound reasons for this and the experimental difficulties and dangers involved have been described.[1] In the case of polyynes, high-level theoretical calculations are probably more reliable than experiment.

In addition to our finding that conjugative stabilization remains at a remarkably consistent 0.9 kcal mol^{-1} from 1,3-pentadiyne to 1,3,5,7-octatetrayne, we find that the thermochemistry of isolated terminal or isolated internal triple bonds is remarkably self-consistent. We also find a consistent 3.9 kcal mol^{-1} destabilization when two triple bonds are separated by a methylene. Carbon radicals formed by loss of a propargylic hydrogen atom, when a second triple bond is in conjugation on the same side, do not show increased stabilization relative to the propargyl radical itself. This contrasts with the behavior of allylic radicals derived from similarly conjugated dienes.

Theory

The G3(MP2) method of Curtiss et al.,[5] part of the GAUSSIAN03 suite of programs,[6] was used throughout. Both theory[7] and methodology[8,9] have been discussed. G3(MP2) calculations have proven in past studies[1,5] to be especially well adapted to hydrocarbons, having mean absolute deviations from experiment of <1.0 kcal mol^{-1} for a large data set.

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10.1021/jo049390o CCC: $27.50

The G3(MP2) method uses three calculated points in a basis set-correlation level space to extrapolate to a fourth point, the QCISD(T)/G3MP2Large result, which is inaccessible for the molecule of interest because of limitations on computer time and storage. The extrapolation is made in two steps. First the MP2/6-31G(d) calculation is "corrected" for basis set truncation error by carrying out a more rigorous calculation with the MP2/G3MP2Large basis set, taking note of the difference in energy, $\Delta E_{MP2} = [E(\mathrm{MP2/G3MP2Large})] - [E(\mathrm{MP2/6\text{-}31G(d)})]$, brought about by the calculation at the higher level basis set relative to the lower one. A similar decrement in energy, $[E(\mathrm{QCISD(T)/6\text{-}31G(d)})] - [E(\mathrm{MP2/6\text{-}31G(d)})]$, is found upon imposing the post-Hartree–Fock treatment QCISD(T), using the 6-31G(d) basis set, relative to the MP2 energy obtained from the same basis set. Subject to the assumption that the two energy differences are additive, the first correction plus E(QCISD(T)/6-31G(d)) gives the desired energy at the QCISD(T)/G3(MP2)Large level of approximation.

The primary difference between the G2(MP2)[7c] and G3(MP2) methods[5] for hydrocarbons is the substitution of a new basis set, called *G3MP2Large*, for the 6-311G(3d,2p) set previously used. Details of the new basis set are given in the original publications[5,7f] and it is available on the web.[5] Once having made the change in basis set, the computational strategy is similar to that of the G2(MP2) method.

A second difference between G2(MP2) and G3(MP2) calculations is inclusion of atomic spin–orbit coupling energies (E(SO)) in the G3(MP2) sequence. Only atomic ΔE(SO) corrections (C, 0.14 mhartrees; H, 0.0 mhartrees) in the atomization calculation are included in G3(MP2).[7g] A "higher level correction" (HLC) and a zero-point energy (E(ZPE)) are used as in G2(MP2). The HLC (9.279 mh per pair of valence electrons) is a purely empirical factor, reparametrized in the newer method so as to give the minimum discrepancy between the G2/97 test set of experimental energies[7d] and calculated energies. The sum of these five energies is E_0[G3(MP2)].

$$E_0[\mathrm{G3(MP2)}] = E(\mathrm{QCISD(T)/6{-}31G(d)}) + \Delta E_{\mathrm{MP2}} + \Delta E(\mathrm{SO}) + E(\mathrm{HLC}) + E(\mathrm{ZPE}) \quad (1)$$

The geometry is at the MP2(full)/6-31G(d) level and the zero-point energy is from the scaled (0.8929) HF/6-31G(d) harmonic oscillator frequencies.[10] Other calculations are carried out on valence electrons only (the "frozen core" approximation).

E_0[G3(MP2)] is the energy of the molecule in the gas phase at 0 K relative to isolated nuclei and electrons. This energy is converted to the ground-state enthalpy (H°) at 298 K, by adding a thermal correction to the enthalpy (TCH) over the temperature range from 0 to 298 K. The TCH is a composite of classical statistical thermodynamic enthalpy changes with a quantum harmonic oscillator term for vibrational energy.[7d,9] Once having obtained E_0[G3(MP2)] and H°, there are several ways of converting either to the thermodynamically desired $\Delta_f H°$. All are in some degree empirical.

We have used the "atomization method", in which E_0[G3(MP2)] of each atom in the molecule is calculated (C, −37.78934 hartrees; H, −0.50184 hartrees).[7d] The *experimental* enthalpy of atomization of each element in the standard state (C, 169.73 kcal mol^{-1} at 298 K; H, 50.62 kcal mol^{-1} at 298 K) is subtracted from E_0[G3(MP2)] of the elements to find H° of the elements in the standard state to obtain $\Delta_f H°$ (hydrocarbon at 298 K) from H° (hydrocarbon) via the reaction

$$\mathrm{C}_m(\mathrm{s,gr}) + \frac{n}{2}\mathrm{H}_2(\mathrm{g}) = \mathrm{C}_m\mathrm{H}_n(\mathrm{g}) \quad (2)$$

where all components are in the standard state. An analogous treatment with use of energies of atomization at 0 K and E_0[G3(MP2)] leads to $\Delta_f E_0$, the energy of formation in the standard state at 0 K.

Computations

In the actual calculation, we used the gui of PCMODEL 8.0[11] to draw the desired structure that was then minimized by using MM3. The minimized geometry was checked visually for obvious flaws. Where close-lying conformers existed or were suspected to exist, the GMMX random search option of PCMODEL was used to select the low-energy conformer. The structure was saved in G3(MP2) Cartesian format and sub-

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sequently sent to the National Center for Supercomputing Applications IBM P690 supercomputing cluster. The G3(MP2) calculation was run with 2 gb swap memory, 4−8 processors, and stipulating 4−6 h wall time. In a few cases convergence was not achieved on the first run or was achieved but with an imaginary frequency. These flaws can often be removed simply by making a random change of 0.01−0.10 Å in the input geometry near the center of a symmetrical molecule. For the more difficult case of free radicals, imaginary frequencies were removed by displacing atoms according to the imaginary normal mode vector. No geometries reported here have an imaginary frequency.

Thermochemistry

The theoretical and experimental results of Table 1 exhibit consistent patterns that can be used to estimate quite accurately the enthalpies of formation of polyynes from the enthalpy of formation of the corresponding alkane: (a) The enthalpy of hydrogenation of a terminal, unconjugated triple bond can be taken as −69.7 kcal mol^{-1}. (b) The enthalpy of hydrogenation of an internal, unconjugated triple bond can be taken as −65.2 kcal mol^{-1}. (c) The presence of a methylene between two triple bonds ($-C{\equiv}CCH_2C{\equiv}C-$) destabilizes the molecule by 3.9 kcal mol^{-1}. (d) Conjugation of two triple bonds stabilizes both terminal and internal triple bonds by 0.9 kcal mol^{-1}. Conjugation of a triple bond with triple bonds on both sides stabilizes it by twice 0.9 kcal mol^{-1}. This empirical procedure yields total enthalpies of hydrogenation that are independent of the order in which the triple bonds are taken as being hydrogenated.

These patterns can be used to estimate enthalpies of hydrogenation of various types of triple bonds and to predict enthalpies of formation of straight chain alkynes and polyynes from the enthalpy of formation of the corresponding alkane. The calculation is demonstrated by four examples below, where ΔH_{hyd} stands for the enthalpy of hydrogenation.

For 1,3-pentadiyne

$$HC{\equiv}CC{\equiv}CCH_3 \rightarrow HC{\equiv}CCH_2CH_2CH_3$$

$$\Delta H_{\mathrm{hyd}} = -65.2 + 0.9 = -64.3 \text{ (internal conjugated)}$$

$$HC{\equiv}CCH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_2CH_3$$

$$\Delta H_{\mathrm{hyd}} = -69.7 \text{ (terminal unconjugated)}$$

$$\Delta_f H°[\text{1,3-pentadiyne}] = \Delta_f H°[\text{pentane}] + 64.3 + 69.7 = -35.22 + 134.00 = 98.78 \text{ kcal mol}^{-1}$$

For 1,4-pentadiyne

$$HC{\equiv}CCH_2C{\equiv}CH \rightarrow CH_3CH_2CH_2C{\equiv}CH$$

$$\Delta H_{\mathrm{hyd}} = -3.9 - 69.7 = -73.6 \text{ } (-C{\equiv}CCH_2C{\equiv}C- \text{ and terminal unconjugated)}$$

$$CH_3CH_2CH_2C{\equiv}CH \rightarrow CH_3CH_2CH_2CH_2CH_3$$

$$\Delta H_{\mathrm{hyd}} = -69.7 \text{ (terminal unconjugated)}$$

$$\Delta_f H°[\text{1,5-pentadiyne}] = \Delta_f H°[\text{pentane}] + 73.6 + 69.7 = -35.22 + 143.3 = 108.08$$

For 1,3,5-hexatriyne

$$HC{\equiv}CC{\equiv}CC{\equiv}CH \rightarrow HC{\equiv}CCH_2CH_2C{\equiv}CH$$

$$\Delta H_{\mathrm{hyd}} = -65.2 + 0.9 + 0.9 \text{ (internal doubly conjugated)}$$

$$HC{\equiv}CCH_2CH_2C{\equiv}CH \rightarrow CH_3CH_2CH_2CH_2C{\equiv}CH$$

$$\Delta H_{\mathrm{hyd}} = -69.7 \text{ (terminal unconjugated)}$$

$$CH_3CH_2CH_2CH_2C{\equiv}CH \rightarrow CH_3CH_2CH_2CH_2CH_2CH_3$$

$$\Delta H_{\mathrm{hyd}} = -69.7 \text{ (terminal unconjugated)}$$

$$\Delta_f H°[\text{1,3,5-hexatriyne}] = \Delta_f H°[\text{hexane}] + 63.4 + 69.7 + 69.7 = -40.29 + 202.8 = 162.51$$

For 1,3,6-heptatriyne

$$HC{\equiv}CC{\equiv}CCH_2C{\equiv}CH \rightarrow HC{\equiv}CC{\equiv}CCH_2CH_2CH_3$$

$$\Delta H_{\mathrm{hyd}} = -3.9 - 69.7 = -73.6 \text{ } (-C{\equiv}CCH_2C{\equiv}C- \text{ and terminal unconjugated)}$$

$$HC{\equiv}CC{\equiv}CCH_2CH_2CH_3 \rightarrow CH_3CH_2C{\equiv}CCH_2CH_2CH_3$$

$$\Delta H_{\mathrm{hyd}} = -69.7 + 0.9 = -68.8 \text{ (terminal conjugated)}$$

$$CH_3CH_2C{\equiv}CCH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_2CH_2CH_2CH_3$$

$$\Delta H_{\mathrm{hyd}} = -65.2 \text{ (internal unconjugated)}$$

$$\Delta_f H°[\text{1,3,6-heptatriyne}] = \Delta_f H°[\text{heptane}] + 73.6 + 68.8 + 65.2 = -45.36 + 207.6 = 162.24$$

Results

Results of this approach of adding increments a−d for obtaining $\Delta_f H°$ for all straight chain alkynes studied in this work and $\Delta_f H°$ of their corresponding alkanes are given in Table 1, where all values pertain to ground states at 298 K. Acetylene (ethyne) is unique in that its triple bond is terminal twice. Terminal triple bonds are 4.5 kcal mol^{-1} more unstable than corresponding internal ones. Assuming that the triple bond of acetylene, being terminal twice, will be 4.5 kcal mol^{-1} more unstable than a singly terminal one, we obtain $\Delta_f H°$(ethyne) = $\Delta_f H°$(ethane) + 69.7 + 4.5 = −20.09 + 74.2 = 54.11 vs an experimental value of 54.19 ± 0.19,[12] in excellent agreement.

In Table 1 the average absolute deviation between values of enthalpies of formation by increments as above from those calculated at the G3(MP2) level of theory is 0.39 kcal mol^{-1}. The largest such individual deviation is with 2,4-hexadiyne (+1.19 and is the only one greater than 1 kcal mol^{-1}), where the value obtained by adding enthalpies of hydrogenation lies between the experimental and theoretical values. Compared to available experi-

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TABLE 1. Enthalpies of Formation of Alkynes and Corresponding Alkanes (kcal mol^{-1}) at 298 K: Experimental, Theoretical G3(MP2), Increments a−d, and Deviation

hydrocarbon	$\Delta_f H°$(exp)	$\Delta_f H°$(theo)	$\Delta_f H°$(incr)	dev[h]
propyne	44.32 ± 0.21[a]	43.92	44.63	+0.71
propane	−25.02 ± 0.12[b]	−25.07		
1-butyne	39.48 ± 0.21[c]	39.43	39.55	+0.12
2-butyne	34.68 ± 0.24[c]	34.89	35.05	+0.16
1,3-butadiyne	111[c]	109.00	108.35	−0.65
butane	−30.03 ± 0.16[b]	−30.15		
1-pentyne	34.50 ± 0.50[a]	34.22	34.48	+0.26
2-pentyne	30.80 ± 0.50[a]	30.29	29.98	−0.31
1,3-pentadiyne		98.28	98.78	+0.50
1,4-pentadiyne		107.81	108.08	+0.27
pentane	−35.08 ± 0.14[b]	−35.22		
1-hexyne	29.23 ± 0.29[e]	29.14	29.41	+0.27
2-hexyne	25.73 ± 0.58[e]	25.02	24.91	−0.11
3-hexyne	25.19 ± 0.46[e]	25.66	24.91	−0.75
1,3-hexadiyne		93.58	93.71	+0.13
1,4-hexadiyne		98.12	98.51	+0.39
1,5-hexadiyne	99.44 ± 1.1[b]	99.31	99.11	−0.20
2,4-hexadiyne	90.20[f]	88.02	89.21	+1.19
1,3,5-hexatriyne		163.39	162.51	−0.78
hexane	−39.96 ± 0.19[b]	−40.29		
1-heptyne	24.80 ± 0.61[e]	24.03	24.34	+0.31
2-heptyne	20.26 ± 0.53[e]	19.97	19.84	−0.13
3-heptyne	19.78 ± 0.58[e]	20.41	19.84	−0.57
1,3-heptadiyne		88.29	88.64	+0.35
1,4-heptadiyne		93.47	93.44	−0.03
1,5-heptadiyne		89.81	89.54	−0.27
1,6-heptadiyne		94.08	94.04	−0.04
2,4-heptadiyne		83.33	84.14	+0.81
2,5-heptadiyne		88.62	88.94	+0.32
1,3,5-heptatriyne		152.31	152.94	+0.63
1,3,6-heptatriyne		162.40	162.24	−0.16
heptane	−44.89 ± 0.19[b]	−45.36		
1-octyne	19.29 ± 0.87[e]	18.95	19.22	+0.27
2-octyne	15.24 ± 0.36[e]	14.88	14.72	−0.16
3-octyne	14.94 ± 0.44[e]	15.34	14.72	−0.62
4-octyne	14.36 ± 0.51[e]	15.14	14.72	−0.42
1,7-octadiyne	89.88 ± 1.2[g]	88.65	88.92	+0.27
1,3,5,7-octatetrayne		217.52	216.62	−0.90
octane	−49.82 ± 0.16[b]	−50.48		
1-nonyne	14.88 ± 0.71[e]	13.86	14.14	0.28
2-nonyne	10.42 ± 0.72[e]	9.78	9.64	−0.14
3-nonyne	10.03 ± 0.59[e]	10.22	9.64	−0.58
4-nonyne	10.03 ± 0.68[e]	10.03	9.64	−0.39
nonane		−55.56		
1-decyne	10.01 ± 0.82[e]	8.76	9.05	0.29
2-decyne	5.63 ± 0.82[e]	4.70	4.55	−0.15
3-decyne	5.22 ± 0.78[e]	5.12	4.55	−0.57
4-decyne	4.75 ± 0.72[e]	4.95	4.55	−0.40
5-decyne	4.46 ± 0.78[e]	4.99	4.55	−0.44
decane	−59.67 ± 0.26[b]	−60.65		

[a] Reference 13. [b] Reference 12. [c] Reference 14. [d] Reference 15. [e] Reference 16a. [f] Reference 17. [g] Reference 18. [h] Column 4 − column 3.

mental values in Table 1, the enthalpies of formation obtained by the G3(MP2) calculation show an average absolute deviation of 0.59 kcal mol^{-1}; the corresponding value for those calculated by increments a−d is 0.52 kcal mol^{-1}. These results increase one's confidence in calculations on molecules for which there are no experimental results.

Discussion

The proposed empirical procedure for estimating $\Delta_f H°$ and ΔH_{hyd} uses equal conjugative stabilizations of terminal and internal triple bonds conjugated with one triple bond, 0.9 kcal mol^{-1}. This equality, in fact, is a mathematical requirement imposed by thermodynamics. The total ΔH_{hyd} for complete hydrogenation must be independent of the order in which the bonds are hydrogenated. For example, there are two routes for hydrogenating 1,3-penradiyne to pentane: route A, $HC{\equiv}CC{\equiv}CCH_3 \rightarrow CH_3CH_2C{\equiv}CCH_3 \rightarrow CH_3(CH_2)_3CH_3$, and route B, $HC{\equiv}CC{\equiv}CCH_3 \rightarrow HC{\equiv}CCH_2CH_2CH_3 \rightarrow CH_3(CH_2)_3CH_3$. Denote by a and b the conjugative stabilization energies of the terminal and internal bonds, respectively. By route A, total $\Delta H_{\mathrm{hyd}} = (-69.7 + a) + (-65.2) = -134.9 + a$; by route B, total $\Delta H_{\mathrm{hyd}} = (-65.2 + b) + (-69.7) = -134.9 + b$. Therefore $a = b$. Implicit in the procedure is that extended conjugation, e.g., three or more triple bonds, does not impart any additional stability to the terminal triple bonds of such a system. If a triple bond conjugated on both sides is stabilized by twice the amount of single conjugation, as is found, then the lack of additional stabilization by extended conjugation is also a thermodynamic requirement as shown for hydrogenation of 1,3,5-heptatriyne, as an example. Two of the routes for complete hydrogenation are: route C, $HC{\equiv}CC{\equiv}CC{\equiv}CCH_3 \rightarrow CH_3CH_2C{\equiv}CC{\equiv}CCH_3 \rightarrow CH_3CH_2CH_2CH_2C{\equiv}CCH_3 \rightarrow CH_3(CH_2)_5CH_3$; and route D, $HC{\equiv}CC{\equiv}CC{\equiv}CCH_3 \rightarrow HC{\equiv}CCH_2CH_2C{\equiv}CCH_3 \rightarrow CH_3CH_2CH_2CH_2C{\equiv}CCH_3 \rightarrow CH_3(CH_2)_5CH_3$. Then, by route C, total $\Delta H_{\mathrm{hyd}} = (-69.7 + 0.9 + c) + (-65.2 + 0.9) + (-69.7) = -202.8 + c$; by route D, total $\Delta H_{\mathrm{hyd}} = (-65.2 + 1.8) + (-69.7) + (-69.7) = -202.8$. Therefore, $c = 0.0$.

In addition to the lack of stabilization in conjugated polyynes, we found a consistent destabilizing effect of triple bonds in a 1,4-relationship to one another leading to a parameter value of 3.9 kcal mol^{-1}. We found no evidence of 1,4-destabilization in polyenes. Because of the difference between the 180° sp bond angle and the 120° sp^2 bond angle, the geometry of the 1,4-diyne is quite different from that of the 1,3-diene as shown in Figure 1 where pentadiyne and pentadiene were chosen as the simplest examples. It is possible that the source of the destabilization is repulsion between the cylindrically symmetrical orbitals of the triple bonds which are forced into overlap near the sp^3 carbon atom in 1,4-pentadiyne. Figure 1 shows that this orbital crowding may be substantially reduced in the equilibrium geometry of 1,4-pentadiene.

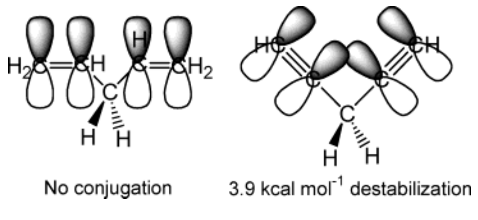

FIGURE 1. Possible p orbital arrangements in 1,4-pentadiene and 1,4-pentadiyne for rationalizing the destabilization of $-C{\equiv}CCH_2C{\equiv}C-$ structures. Only four of the eight p orbitals are shown for the diyne.

To investigate this destabilization further, we carried out G3(MP2) calculations on 1,4-pentadiyne substituted by methyl groups at the central carbon atom in Figure 1. Results for 1,4-pentadiyne, 3-methyl-1,4-pentadiyne, and 3,3-dimethyl-1,4-pentadiyne were $\Delta H_{\mathrm{hyd}} = -143.0$, -142.3, and -141.1 kcal mol^{-1}. These values lead to destabilization energies that decrease in the order 3.6, 2.9, and 1.7 kcal mol^{-1} as compared to the expected 2(−69.7) = −139.4 kcal mol^{-1} for two terminal unconjugated triple bonds. The 2,3,4 C−C−C bond angle for these three compounds closes slightly in the sequence 113.1°, 112.6°, and 111.0°.

These types of destabilization indicated by the theoretical calculations are supported by actual measurements on highly methyl-substituted polyynes, all containing repeating $-C{\equiv}CC(CH_3)_2C{\equiv}C-$ structures.[17b] For the sequence $n = 2, 3, 4, 5$ in $(CH_3)_3C[C{\equiv}CC(CH_3)_2]_nCH_3$, experimental enthalpies of hydrogenation are more negative than the values of $-65.2n$ kcal mol^{-1} that would result from internal triple bonds of straight chain, unconjugated alkynes. Such destabilizations are 0.6 ± 1.0 kcal mol^{-1} for $n = 2$, 5.4 ± 1.0 for $n = 3$, 10.2 ± 1.0 for $n = 4$, and 13.0 ± 2.0 for $n = 5$ from the hydrogenation measurements. The amount of destabilization per triple bond is less than the value of 3.9 kcal mol^{-1} obtained with straight chain polyynes, but theoretical calculations indicate that the stability of triple bonds is enhanced somewhat by methyl substitutions at their propargylic position, and this effect partially offsets the destabilization of two triple bonds separated by one sp^3 carbon.

We examined the effect of extended triple bond conjugation of propargylic radicals and compared them to those of extended double bond conjugation of allylic radicals, i.e., $HC{\equiv}CC{\equiv}CCH_2^{\bullet}$ vs $H_2C{=}CHCH{=}CHCH_2^{\bullet}$. Stabilization energies of such carbon radicals relative to SE[methyl] = 0.0 can be approximated well by $SE[R^{\bullet}] = BDE[H_3C\text{-}CH_3] - BDE[CH_3\text{-}R]$,[19] because the electronegativity differences of methyl, propargyl, and allyl are minor and have a negligible effect on BDE. $BDE[H_3C\text{-}R] = \Delta_fH°[H_3C^{\bullet}] + \Delta_fH°[R^{\bullet}] - \Delta_fH°[H_3C\text{-}R]$. With experimental $\Delta_fH°[H_3C^{\bullet}] = 34.8$ and $BDE[H_3C\text{-}CH_3] = 89.7$,[12] and G3(MP2) results for the other needed values from Tables 1 and 2, we obtain $SE[H_2C{=}CHCH_2^{\bullet}] = 89.7 - [34.8 + 39.4 - (-0.4)] = 14.9$ kcal mol^{-1}, where the odd electron is conjugated to one double bond in the allyl radical.

TABLE 2. Enthalpies of Formation of Allylic and Propargylic Radicals and of Relevant Alkenes (kcal mol^{-1}) at 298 K[e]

species	$\Delta_fH°$(lit.)	$\Delta_fH°$(theo)
$H_2C{=}CHCH_2^{\bullet}$ (allyl)	40.9 ± 0.7[b]	39.6
$H_2C{=}CHCH_2CH_3$	−0.2 ± 0.2[b]	−0.4
$H_2C{=}CHCH{=}CHCH_2^{\bullet}$	49.8[c]	48.3
(*E*)-$H_2C{=}CHCH{=}CHCH_2CH_3$	13.0 ± 0.4[d]	13.0
$HC{\equiv}CCH_2^{\bullet}$ (propargyl)	82.3,[e] 81 ± 1[b]	83.4
$HC{\equiv}CC{\equiv}CCH_2^{\bullet}$		138.4
$(HC{\equiv}C)_2CH^{\bullet}$		137.0

[a] Values from the literature and from theoretical G3(MP2) calculations of this work. [b] Reference 12. [c] Reference 20; The same (lit.) and (theo) values pertain to $(H_2C{=}CH)_2CH_2^{\bullet}$, which is just another resonance structure depiction of $H_2C{=}CHCH{=}CHCH_2^{\bullet}$. [d] Reference 21. [e] Reference 13b.

Similarly, we obtain $SE[H_2C{=}CHCH{=}CHCH_2^{\bullet}] = 19.6$ for the doubly conjugated 2,4-pentadien-1-yl radical, where the more extended conjugation of the odd electron increases SE by 4.7 kcal mol^{-1} over the singly conjugated allyl radical. By contrast, we obtain $SE[HC{\equiv}CCH_2^{\bullet}] = 10.9$ kcal mol^{-1}, where the odd electron is conjugated with one triple bond in the propargyl radical, and $SE[HC{\equiv}CC{\equiv}CCH_2^{\bullet}] = 10.1$, where there is no additional stabilization by the second conjugated triple bond. In fact, there is a small decline in SE. We also examined a propargylic radical flanked by two triple bonds, one on either side. We find that the enthalpies of formation of the two isomeric radicals $HC{\equiv}CC{\equiv}CCH_2^{\bullet}$ and $(HC{\equiv}C)_2CH^{\bullet}$ are quite similar, the latter being only 1.4 kcal mol^{-1} more stable (Table 2). This contrasts with a 4.7 kcal mol^{-1} increase in SE for the doubly conjugated allylic radical over the singly conjugated species. The behavior of these extended propargyl radicals is consistent with the lack of additional stability in the extended triple bond conjugations discussed above. Unlike double bonds, such extended conjugation arrangements of triple bonds do not lead to increased thermodynamic stability of propargyl radicals. These results address the issue of thermodynamic stabilities, not to be confused with possible electron delocalization per se.

Conclusion

We find that stabilization energies of straight chain conjugated alkynes are almost negligible and that stabilization analogous to that found in conjugated alkenes is small or nonexistent. The same is the case for extended conjugated propargylic compared to extended conjugated allylic radicals.

Acknowledgment. We acknowledge grants of computer time from the National Science Foundation and the National Center for Supercomputing Applications http://ncsa.uiuc.edu.

Supporting Information Available: Input files, energies, and geometries of the alkanes and alkynes. This material is available free of charge via the Internet at http://pubs.acs.org.

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