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The Conjugation Stabilization of 1,3-Butadiyne Is Zero

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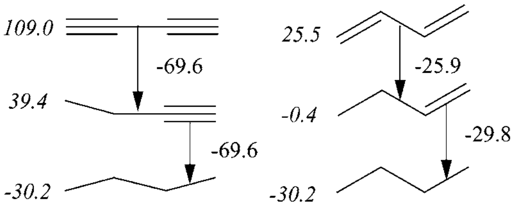
ABSTRACT



In contrast to 1,3-butadiene, the textbook example of "conjugation stabilization", G3(MP2) calculations yielding the enthalpy of hydrogenation $\Delta_{hyd}H^{298}$ of 1,3-butadiyne indicate that it is not stabilized by the conjugated configuration of its triple bonds. Differences between ethylenic and acetylenic π bonds are examined in the light of CAS-MCSCF calculations on 1,3-butadiene and 1,3-butadiyne.

Every chemistry sophomore knows that the enthalpy (heat) of hydrogenation of 1-butene is −30 kcal/mol but the enthalpy of hydrogenation of 1,3-butadiene falls short of twice this amount by about 3.8 kcal/mol, a discrepancy ascribed to "conjugation stabilization". Whatever the ensuing quantum mechanical argument may be to explain conjugation stabilization, the stability of conjugated double bonds relative to isolated double bonds is a thermochemical fact.

But what of triple bonds? Naively supposing a triple bond to be two superimposed π bonds on an inert σ bond, one might think that the stabilization energy of 1,3-butadiyne (diacetylene) would be twice that of the π bond in 1,3-butadiene or about 8 kcal/mol. In fact this is wrong. We show here that the stabilization in diacetylene is at or near zero.

Even after spirited debate and many alternative proposals, it is difficult to stray very far from the original view expressed in G. B. Kistiakowsky's papers[1] that conjugation stabilization in polyunsaturated molecules is the difference in energy (enthalpy) between those molecules in which single and double bonds alternate and analogous molecules in which they do not. Several other physical properties have been found to correlate well with conjugation, but they do not define it. Stabilization is a *thermochemical property*.

Moreover, following Kistiakowsky, it is, in principle, a simple matter to measure this "conjugation energy" by finding the difference in enthalpies of reaction upon converting a molecule in which single and double bonds are conjugated and a standard, in which they are not conjugated, to the same product (thermodynamic state). Traditionally, the reaction of choice has been that of hydrogenation leading to $\Delta_{hyd}H$, which is then compared to the $\Delta_{hyd}H$ expected from a real or hypothetical unconjugated molecule.

When this is done, an enthalpy diagram results such as the one shown on the right of Figure 1. For 1,3-butadiene, the only differences between Kistiakowsky's work and the diagram on the right of Figure 1 are the temperature, 355 K in the original work and 298 K in the present work, and the methods, direct hydrogenation in Kistiakowsky's classical paper and the results of G3(MP2) calculations shown here. The point of this communication is not to show that

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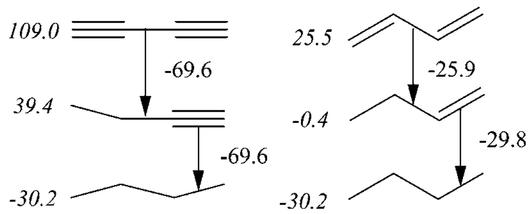

Figure 1. Comparison of the G3(MP2) calculated enthalpies of formation $\Delta_f H^{298}$ (italic) and hydrogenation $\Delta_{hyd}H$ (arrows) of butenes and butynes. The conjugation energy of 1,3-butadiene (right) is 3.9 ± 0.1 kcal/mol, but for 1,3-butadiyne (left), it is zero.

Kistiakowsky's work can be duplicated by computer but to show that a replica of the G3(MP2) procedure, differing only in the substitution of 1,3-butadiyne for 1,3-butadiene, *shows no conjugation energy at all*, as seen on the left of Figure 1.

A similar diagram results from calculations on 1,3-pentadiyne. In this case, the conjugation stabilization is not zero, but it is quite small, 1.4 kcal/mol, not much outside of the combined uncertainties of the computational and experimental methods. Preliminary calculations on larger alkynes show the same result; the conjugation stabilization energy, if any, is not significantly different from zero.

Given the importance of polyynes in general[2] and their potential applications in nanotechnology,[3] one wonders why Kistiakowsky's experimental method of $\Delta_{hyd}H$ determination has not been extended to 1,3-butadiyne. Thermochemical studies of polyacetylenes in general are scattered and give no systematic picture of their relative stabilities.[4] There are sound reasons for this: many acetylenes polymerize under laboratory conditions,[5] burn incompletely,[5] or may even detonate.[6] Thermochemical studies that might normally have been carried out have been avoided as dangerous or unlikely to produce useful information due to an ill-defined reactant or product state.

Combustion thermochemistry carried out on larger, more stable acetylenes, which might normally be the method of choice, has the drawback that it produces large energies of combustion $\Delta_c E$. The energy or enthalpy deficit sought, due to conjugation stabilization, can be distorted or obscured by quite small *relative* errors in $\Delta_c E$. Conversely, small conjugated diynes, especially 1,3-butadiyne and 1,3-pentadiyne, which would provide the best comparisons with 1,3-butadiene and 1,3-pentadiene, are unstable to polymerization and raise doubts as to sample purity. In such cases, high-level theoretical calculations are probably more reliable than experiment.

Accordingly, we have carried out G3(MP2) calculations[7,8] of the enthalpies of formation of 16 hydrocarbons related to 1,3-butadiyne and 1,3-pentadiyne (see Table 1 and Supporting Information). Some of the compounds have been thoroughly studied, both experimentally and computationally, and some have not. Agreement between values calculated in this work and experimental values, where the latter are available, is remarkably good (±0.33 kcal/mol), lending credence to our calculated values for the diynes that are not experimentally accessible.

Table 1. G3(MP2) Calculated and Experimental Values for $\Delta_f H^{298}$Alkynes and Related Compounds of Four-Carbon Atoms

compd	$\Delta_f H^{298}$ calcd[a]	$\Delta_f H^{298}$ exp[b]	(exp − calcd)
1,3-butadiyne	108.95[c]		
1-butyne	39.44	39.48 ± 0.21	0.04
2-butyne	34.86	34.82 ± 0.29	−0.04
1,3-butadiene	25.54	26.29 ± 0.26	0.75
1-butene	−0.42	0.02 ± 0.24	0.44
(*E*)-2-butene	−2.94	−2.72 ± 0.24	0.22
butane	−30.15	−30.12 ± 0.17	0.03
		MAD = 0.24[d]	

[a] References 6g,h. [b] Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1986. [c] Present work. [d] Mean absolute difference, (exp − comp).

The four-carbon compounds in Table 1 have a mean absolute difference from experimental results of 0.24 kcal/mol. (The calculated $\Delta_f H^{298}$(propyne) = 43.92 kcal/mol and the experimental value is 44.19 ± 0.19 kcal/mol, a difference of 0.27 kcal/mol.) Suppose that we double 0.24 kcal/mol to estimate the difference between the calculated $\Delta_f H^{298}$(diacetylene) = 108.95 kcal/mol and the unknown experimental enthalpy of formation to get ±0.50 kcal/mol. The root-mean-

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square uncertainty for the hydrogenation reaction is

$$\begin{array}{ccccc} \text{1,3-butadiyne} & + & 2\text{H}_2 & \rightarrow & \text{1-butyne} \\ 0.48 & & 0.0 & & 0.04 \end{array}$$

$$\text{rms uncertainty} = 0.5\ \text{kcal/mol}$$

Note that H_2 does not contribute to the uncertainty in $\Delta_{\text{hyd}}H^{298}$ because it has $\Delta_{\text{f}}H^{298} = 0.0$ *by definition*. If we take 0.48 kcal/mol as the uncertainty of *both* the reactant and the product, the rms uncertainty for $\Delta_{\text{hyd}}H^{298}$ is 0.7 kcal/mol, which is probably an upper limit on the computational error for this reaction. Computed values for larger molecules may suffer larger errors. A similar estimate of the upper limit on the computational error of C5 hydrocarbons (Supporting Information) is 1.2 kcal/mol. The experimental data on these compounds are quite precise. The rms estimate of the error of Kistiakowsky's value for the stabilization enthalpy in Table 1 is 0.12 kcal/mol. The grand arithmetic mean of the absolute deviations from the sample means in Table 1 is 0.24 kcal/mol, the same as the mean absolute difference (MAD) between experimental and calculated values.

A few thermochemical results and estimates exist in the literature that relate to these calculated enthalpies. In particular, Luk'yanova et al.[5a] determined the enthalpies of formation from $\Delta_{\text{c}}E$ of 2,4-hexadiyne, 1-cyclopropyl-1,3-pentadiyne, and 1,4-dicyclopropyl-1,3-dibutadiyne. Using Benson's group additivity numbers[9] for all groups except $C_t{-}C_t$, for the triple bonds, they found values for $C_t{-}C_t$ by comparison with the experimental $\Delta_{\text{f}}H^{298}$. In the first two cases, they obtained a $C_t{-}C_t$ close to Benson's value for a *nonconjugated* triple bond,[4a] concluding that triple bond conjugation is "not explicitly manifest" in these compounds. In 1,4-dicyclopropyl-1,3-butadiyne, however, they found a conjugation energy of 3.9 kcal/mol by the same method. Using a $C_t{-}C_t$ group value of 27.5 kcal/mol (as compared to Benson's 27.6 kcal/mol for the *nonconjugated* $C_t{-}C_t$), Luk′yanova et al. arrived at $\Delta_{\text{f}}H^{298}$(1,3-butadiyne) = 108.8 kcal/mol as compared to our G3(MP2) value of 109.0 kcal/mol.

Flitcroft, Skinner, and Whiting[10] obtained a conjugation stabilization of 3.9 ± 0.9 kcal/mol for dodeca-5,7-diyne by comparing its $\Delta_{\text{hyd}}H^{298}$ measured on the liquid sample in a glacial acetic acid medium by comparison to that of dodeca-3,9-diyne. Correction for the enthalpy of solution was made.

Complete active space multiconfigurational self-consistent field[11] (CAS-MCSCF) calculations were carried out[12] on 1,3-butadiene and 1,3-butadiyne. The active space used included all π electrons distributed over all π orbital space, for 1,3-butadiene, a 4-electron/4-orbital space, and for 1,3-butadiyne, an 8-electron/8 orbital space. The natural orbital occupation number for the first π^* orbitals are 0.1248 and 0.0853 for the diene and diyne, respectively, indicating that the lowest π^* orbital of the diene is more accessible than it is in the diyne. Energetically, the barrier to electron delocalization is lower in the diene than it is in the diyne, suggesting a mechanism involving electron transfer across the central bond that favors conjugation stabilization in the former case but not in the latter case.

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Supporting Information Available: Calculated and experimental values of enthalpies of formation of C5 alkanes, alkenes, alkynes, dienes, and diynes. This material is available free of charge via the Internet at http://pubs.acs.org.

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