Communication

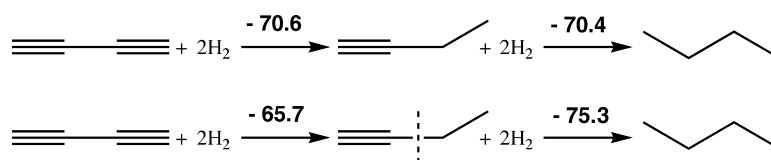# How Large Is the Conjugative Stabilization of Diynes?

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How Large Is the Conjugative Stabilization of Diynes?

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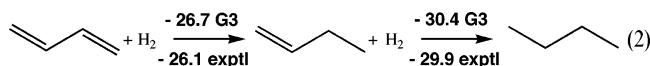
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A recent paper by Rogers et al. reported, "The Conjugation Stabilization of 1,3-Butadiyne is Zero."[1] This conclusion was based upon unmodified energetic comparisons of conjugated species with nonconjugated analogues; a method first applied by Kistiakowsky in 1936 to assess the energetic consequences of conjugation in butadiene.[2a] Following this approach, Rogers et al.[1] computed the stepwise hydrogenation of 1,3-butadiyne first to 1-butyne and then to butane (eq 1) at the G3(MP2)[3] level. Both these steps were calculated to be equally exothermic, indicating an absence of conjugation energy for 1,3-butadiyne according to the Kistiakowsky method. Our higher-level G3[4] results (eq 1, in kcal/mol) confirm the hydrogenation data of ref 1, but we disagree with the interpretation.

$$\text{(equation 1): } -70.6\ \text{G3} \quad + 2H_2 \quad -70.4\ \text{G3} \quad -69.5\ \text{exptl} \quad (1)$$
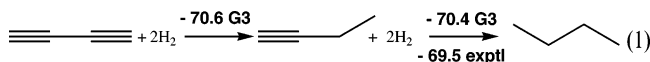
The analogous stepwise hydrogenation of 1,3-butadiene[2a] (eq 2) reproduces the widely accepted empirical value of 3.7 kcal/mol,[5] typically ascribed to conjugative stabilization, derived from the difference between the first and second hydrogenation step.

$$\text{(equation 2): } + H_2 \quad -26.7\ \text{G3} \quad -26.1\ \text{exptl} \quad + H_2 \quad -30.4\ \text{G3} \quad -29.9\ \text{exptl} \quad (2)$$
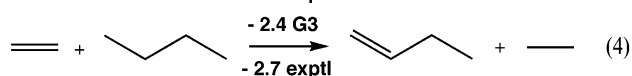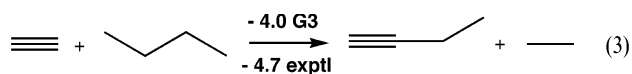
Rogers et al.'s evaluation led them to conclude that diyne conjugation is less stabilizing than diene conjugation.[1] All accepted theoretical models for conjugation would predict the opposite to be true.[5] Pauling,[5b−d] Dewar,[5e−f] Conn,[2c] and others[5g−k] have invoked resonance, hybridization, and nonbonded repulsion effects, respectively, to interpret the thermodynamically favorable consequences of conjugation. Kollmar[6] computed the resonance stabilization of 1,3-butadiyne (19 kcal/mol) to be nearly double that of 1,3-butadiene (9.7 kcal/mol), based upon comparison to hypothetical systems with nonresonating acetylene and ethylene units. In addition, the greater s-character of the central single bond and the lower coordination of the interacting carbon atoms would favor the conjugation of acetylene units over ethylene units. All these effects are manifested in the remarkably short (1.38 Å)[5a,d] carbon−carbon single bond of 1,3-butadiyne.[5a]

Conjugative stabilization, like many well-accepted constructs in chemistry, is a virtual thermodynamic quantity that depends on the choice of model systems and method of evaluation. The true conjugative stabilization is not a measurable quantity: it is the difference in energy between a conjugated molecule and its hypothetical energy (virtual state) if the entire contribution stemming from conjugation could be accounted for and excised. Kistiakowsky's hydrogenation evaluation gives only a rough

approximation of this conjugation energy: comparisons of heats of hydrogenation evaluate not only conjugation effects but also other structural and electronic differences between the conjugated molecule and its hydrogenated products. More refined conjugative stabilization evaluations should eliminate or minimize these differences as much as possible. Specifically, 1-butyne, the reference compound for 1,3-butadiyne, is stabilized significantly by hyperconjugation,[7] which is not present in 1,3-butadiyne. Hyperconjugation also complicates the evaluation of the conjugative stabilization of 1,3-butadiene but was not considered in Kistiakowsky's[2] original work. We now propose modifications of the Kistiakowsky scheme, which take hyperconjugative interactions into account. Determined by this modified method, the conjugative stabilization of butadiyne and butadiene are both quite large, in accord with the well-based theoretical expectations.[5,6]

We have calculated the energies of hyperconjugation of substituted acetylenes and ethylenes using computational and experimental data. These quantities are applied to refine the evaluation of diyne and diene conjugation energies, not only using Kistiakowsky's method, but also isomerization reactions of diynes and dienes. Using the Gaussian 98 program,[8,9] we employed G3,[4] a well-established method for computing accurate thermochemical data. We also used G3(MP2),[3] which is a less computer intensive, but comparably accurate variation, for the larger systems employed for isomerization reactions. Data obtained from both theoretical methods agree very well with the experimentally available heats of formation and hydrogenation.[2,10−12] Data and their analyses are given in Supporting Information, Tables 1−4.

When evaluated by the conventional method, hyperconjugation involving alkynes is twice as large as alkenes; the stabilization of ethylene (in kcal/mol) by an ethyl substituent (2.4 G3; 2.2 G3-(MP2); 2.7 expt) is based on the difference between the heats of hydrogenation of ethylene and 1-butene. Likewise, the hyperconjugative stabilization of acetylene by an ethyl group (4.9 G3; 4.8 G3(MP2); 4.7 expt)[14] is the difference between the heat of hydrogenation of acetylene and 1-butyne. Equivalently, the hyperconjugative stabilization can also be described by isodesmic reactions 3 and 4 that produce data consistent with the above evaluation:

$$\text{(equation 3): } + \quad -4.0\ \text{G3} \quad -4.7\ \text{exptl} \quad + \quad (3)$$

$$\text{(equation 4): } + \quad -2.4\ \text{G3} \quad -2.7\ \text{exptl} \quad + \quad (4)$$

Deleting the hyperconjugative interactions evaluated conventionally gives the virtual states shown below. These states have energies that are 4.9 and 2.4 kcal/mol higher than those of 1-butyne and 1-butene, respectively.

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Employing these virtual states in a Kistiakowsky scheme (eq 5) results in a 9.8 (9.2 G3(MP2)) kcal/mol conjugative stabilization for 1,3-butadiyne. This is 1.3 (1.0 G3(MP2)) kcal/mol *more* than the 8.5 (8.2 G3MP2) kcal/mol stabilization obtained for 1,3-butadiene (eq 6).
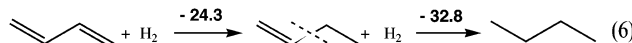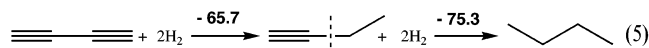
Isomerization reactions also yield conjugative stabilization energies. The directly computed G3(MP2)[3] heats of isomerization of 1,3-hexadiyne (4.0 kcal/mol)[15] and of 1,3-hexadiene (4.3 kcal/mol) to their respective 1,4-unsaturated isomers are nearly the same (note they are not zero). However, these equations are not hyperconjugation-balanced: the products are stabilized more than the reactants. When the hyperconjugation stabilization of each species is taken into account (Supporting Information, Table 4), the isomerization energies are 9.2 kcal/mol for the isomerization of 1,3-hexadiyne (eq 7) and 8.2 kcal/mol for the isomerization of 1,3-hexadiene (eq 8).
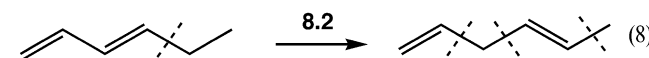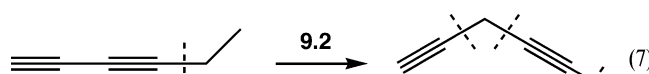
These agree with the directly computed energies of isomerization of species that are more nearly hyperconjugation-balanced: 11.3 kcal/mol for 2,4-hexadiyne and 8.6 kcal/mol for 2,4-hexadiene. After minor adjustments for subtle changes in hyperconjugation (Supporting Information, Table 4), the isomerization energies of eqs 9 and 10 are in near perfect agreement with our other conjugation stabilization evaluations, eqs 5 and 7, as well as eqs 6 and 8.
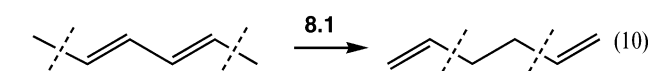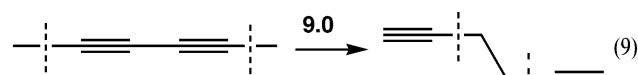
The conjugative stabilization for butadiene and butadiyne, as given by Kistiakowsky's scheme, is counterbalanced by the hyperconjugative stabilization by the ethyl groups in 1-butene and 1-butyne, respectively. These hyperconjugative interactions[7] are large enough to fully obscure the conjugative stabilization in 1,3-butadiyne and considerably diminish the analogous 1,3-butadiene value.

The results of Rogers et al.[1a] bring to light the limitations in Kistiakowsky's method. For 1,3-butadiene, the method gave results that seemed reasonable at the time, but for 1,3-butadiyne, the results defy well-founded theoretical models,[5] as well as the simple expectation (confirmed by the hyperconjugation evaluations) that the two double bonds in an alkyne should conjugate better than the single double bond in an alkene. In our view, Kistiakowsky's method substantially underestimates conjugative stabilization of dienes and of diynes to an even greater extent. Consideration of hyperconjugative interactions provides a more refined measure of

conjugative stabilization. All the conjugation energies of the isomerization and hydrogenation reactions considered here agree superbly, 9.3 ± 0.5 kcal/mol for diynes and 8.2 ± 0.1 kcal/mol for dienes, only when this is done.

Supporting Information Available: Tables 1−4 of computed and experimental thermodynamic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) These magnitudes are close to the experimental isomerization energies of 1-butene to *trans*-2-butene, 2.4 kcal/mol (see ref 11), and 1-butyne to 2-butyne, 4.8 kcal/mol (see ref 10), which involve an increase of one hyperconjugative interaction.

(15) A 3.8 kcal mol^{-1} experimental isomerization energy of the conjugated 5,7-dodecadiyne to the nonconjugated 3,9-dodecadiyne has been reported (Benson, S. W.; Garland, L. J. *J. Phys. Chem.* **1991**, *95*, 4915).

JA046432H