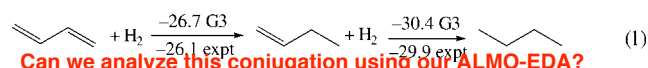


Direct Estimate of the Conjugative and Hyperconjugative Stabilization in Diynes, Dienes, and Related Compounds**

Daniel Cappel, Sandor Tüllmann, Andreas Krapp, and Gernot Frenking*

Compounds with conjugated double bonds such as 1,3-butadiene are energetically stabilized through π interactions. Kistiakowsky et al. suggested in 1936 that the energetic consequences can be assessed by stepwise hydrogenation first to 1-butene and then to butane [Eq. (1)].^[1] The first step is

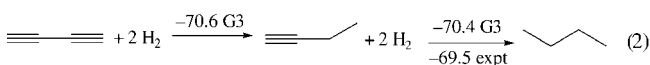


Can we analyze this conjugation using our ALMO-EDA?

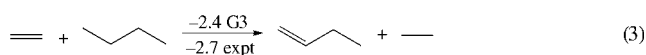
Is this the simplest pseudo-diagonalization?

Really, how to separate the H12 and S12 contributions to 2-orbital mixing?

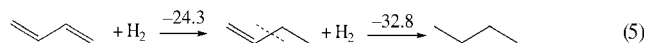
3.8 kcal mol⁻¹ less exothermic (calculated value at G3 level 3.7 kcal mol⁻¹)^[2] than the second step, which according to Kistiakowsky et al. indicates the strength of the π conjugation in 1,3-butadiene. 1,3-Butadiyne has two pairs of conjugating double bonds and should have stronger conjugative stabilization than 1,3-butadiene, which has only one pair. A recent publication by Rogers et al. reported that the conjugation in the former compound is zero, because the stepwise hydrogenation of 1,3-butadiyne yields nearly equally exothermic values [Eq. (2)].^[3]



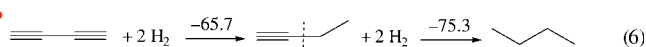
The results of Rogers et al.^[3] have been confirmed in a recent publication of Jarowski et al.^[4] But their divergent interpretation sparked renewed discussion.^[5] Jarowski et al. pointed out that hyperconjugation plays an important role in the thermodynamics of the hydrogenation reactions, which was not considered by Rogers et al. Hyperconjugation has recently been suggested to be the driving force for the staggered equilibrium conformation of ethane, but the claim was not undisputed.^[6] Jarowski et al.^[4] estimated the strength of the hyperconjugation by comparing the calculated and experimental heats of hydrogenation of ethylene and 1-butene with the values for acetylene and 1-butyne. This shows that the hyperconjugative stabilization of acetylene by an ethyl group is 2.5–3.0 kcal mol⁻¹ higher than the stabilization of ethylene by an ethyl substituent. A similar result was obtained using isodesmic reactions [Eqs. (3), (4)], which



suggest that hyperconjugative stabilization of a triple bond is roughly twice as high as the stabilization of a double bond. The calculated energies for the reactions in Equations (5) and



(6), which employ virtual intermediates in which hyperconjugation is eliminated, indicate that the conjugation in 1,3-butadiyne is now even slightly stronger (9.6 kcal mol⁻¹)^[7] than



in 1,3-butadiene (8.5 kcal mol⁻¹). This is in agreement with previous theoretical investigations.^[8,9]

The studies by Rogers et al.^[3] and by Jarowski et al.^[4] are based on the suggestion of Kistiakowsky^[1] to correlate reaction energies with conjugative stabilization, and the latter work modified the original proposal by considering hyperconjugation. Jarowski et al.^[4] pointed out that comparisons of heats of hydrogenation evaluate not only conjugative effects but also other structural and electronic differences between the conjugated molecule and its hydrogenated products. We note that the absolute values of the conjugative stabilization given by Equations (5) and (6) are very different from the data of Equations (1) and (2). It would be helpful if a direct estimate of the intrinsic conjugative stabilization in 1,3-butadiene and 1,3-butadiyne could be made based on a well-defined quantum chemical partitioning of the interaction energy. An attempt was published in 1979 by Kollmar, who calculated the resonance stabilization of 1,3-butadiyne (19 kcal mol⁻¹) to be nearly twice that of 1,3-butadiene (9.7 kcal mol⁻¹); this is in agreement with the chemical intuition that two conjugative π systems should be twice as strong as one system.^[9] Kollmar's values come from calculations of the two molecules with hypothetical reference systems having nonresonating acetylene and ethylene units. It would be more useful if the actual $\cdot\text{C}\equiv\text{CH}$ and $\cdot\text{HC}=\text{CH}_2$ fragments would be used for an estimate of the conjugative stabilization.

Here we report on an energy decomposition analysis (EDA)^[10] of the C–C interactions in 1,3-butadiene, 1,3-butadiyne, and related systems which allows a direct estimate of the intrinsic conjugative and hyperconjugative stabilization that arises from the mixing between the occupied and vacant orbitals of the conjugating fragments. EDA has proven to give important information about the nature of the bonding in main-group^[11] and transition-metal compounds.^[12] Since the method has been described in detail previously^[10–12] we shall

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describe the concept only briefly. In EDA, bond formation between the interacting fragments is divided into three steps, which can be interpreted in a plausible way. In the first step the fragments, which are calculated with the frozen geometry of the entire molecule, are superimposed without electronic relaxation; this yields the quasiclassical electrostatic attraction ΔE_{elstat} . In the second step the product wave function becomes antisymmetrized and renormalized, which gives the repulsive term ΔE_{Pauli} , termed Pauli repulsion. In the third step the molecular orbitals relax to their final form to yield the stabilizing orbital interaction ΔE_{orb} . The latter term can be divided into contributions of orbitals having different symmetry which is crucial for this study. The sum of the three terms $\Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}$ gives the total interaction energy ΔE_{int} . Note that the latter is not the same as the bond dissociation energy, because the relaxation of the fragments is not considered in ΔE_{int} .

Table 1 gives the EDA results^[13] of the calculated molecules. In all cases a central C–C single bond connects the interacting fragments, which are calculated in the electronic doublet state with the unpaired electron in a σ orbital. As expected, the C–C bond in 1,3-butadiyne has a much larger interaction energy ($\Delta E_{\text{int}} = -176.0 \text{ kcal mol}^{-1}$) than in 1,3-butadiene ($\Delta E_{\text{int}} = -128.5 \text{ kcal mol}^{-1}$). The electrostatic character^[14] of the former bond is smaller (33.9%) than that of the latter (42.8%). The largest contribution to the C–C attraction in both molecules comes from the orbital term ΔE_{orb} . The partitioning of the C–C orbital interactions in σ and π bonding shows that σ bonding is stronger. We note that the strength of σ bonding in 1,3-butadiene ($\Delta E_{\sigma} = -207.5 \text{ kcal mol}^{-1}$) is greater than in 1,3-butadiyne ($\Delta E_{\sigma} = -178.3 \text{ kcal mol}^{-1}$). This is because σ bonding in 1,3-butadiyne involves only the C–C σ bond, while σ bonding in 1,3-

butadiene has additional contributions from the hyperconjugative interactions of the C–H and terminal C–C bonds. Thus, σ bonding in 1,3-butadiyne comes from only the C–C mixing of the 2s and 2p(σ) atomic orbitals (AOs) of carbon, while the σ bonding in 1,3-butadiene comes not only from the 2s and 2p(σ) orbitals but also from the in-plane 2p(π) AO of carbon and the 1s AO of hydrogen. Consequently, the total value of the attractive orbital interactions in 1,3-butadiene is slightly larger ($\Delta E_{\text{orb}} = -227.0 \text{ kcal mol}^{-1}$) than in 1,3-butadiyne ($\Delta E_{\text{orb}} = -223.3 \text{ kcal mol}^{-1}$). The electrostatic attraction in 1,3-butadiene ($\Delta E_{\text{elstat}} = -169.9 \text{ kcal mol}^{-1}$) is also larger than in 1,3-butadiyne ($\Delta E_{\text{elstat}} = -114.6 \text{ kcal mol}^{-1}$), although the central C–C bond in the former is longer (1.453 Å) than in the latter (1.361 Å). This is because the unpaired electron in the $\cdot\text{HC}=\text{CH}_2$ fragment is in a (formally) sp^2 -hybridized orbital, which is more diffuse and thus has a higher density at the carbon nucleus of the other fragment than the unpaired electron in the more compact sp orbital of $\cdot\text{C}\equiv\text{CH}$.

The most important results of our analysis are the calculated values for ΔE_{π} , which are a direct measure of the π conjugation in 1,3-butadiyne and 1,3-butadiene. Table 1 shows that the conjugative stabilization in the former molecule ($\Delta E_{\pi} = -45.0 \text{ kcal mol}^{-1}$) is more than twice that calculated for the latter species ($\Delta E_{\pi} = -19.5 \text{ kcal mol}^{-1}$). This is a reasonable result because the conjugation of the two π systems in 1,3-butadiyne takes place at a shorter C–C distance than in 1,3-butadiene.

How strong is the hyperconjugation in 1-butyne and 1-butene? The hyperconjugation of the multiple bonds in these molecules with the p(π) orbitals of the adjacent carbon atoms involve C–H and C–C bonds. To address the question whether C–H or C–C bonds are better hyperconjugative donors or acceptors, we first analyzed the C–C bonding

How are sigma and pi contributions are computed?

Table 1: Results of the energy decomposition analysis at the BP86/TZ2P level. Energy values in kcal mol^{-1} .

	HCC-CCH	H ₂ CCH-CHCH ₂	HCC-CH ₃	HCC-C(CH ₃) ₃	H ₂ CCH-CH ₃	H ₂ CCH-C(CH ₃) ₃	HCC-CHCH ₂	(CH ₃) ₃ C-C(CH ₃) ₃	CH ₃ -CH ₃
Symmetry	$D_{\infty h}$	C_{2h}	C_{3v}	C_{3v}	C_s	C_s	C_s	D_{3d}	D_{3d}
ΔE_{int}	-176.0	-128.5	-143.6	-133.1	-119.4	-108.8	-150.2	-93.2	-114.8
ΔE_{Pauli}	161.8	268.4	176.5	219.1	228.9	267.9	209.4	253.6	200.8
$\Delta E_{\text{elstat}}^{[a]}$	-114.6 (33.9%)	-169.9 (42.8%)	-125.5 (39.2%)	-151.8 (43.1%)	-147.5 (42.4%)	-171.8 (45.6%)	-143.1 (39.8%)	-163.5 (47.2%)	-131.3 (41.6%)
$\Delta E_{\text{orb}}^{[a]}$	-223.3 (66.1%)	-227.0 (57.2%)	-194.6 (60.8%)	-200.4 (56.9%)	-200.7 (57.6%)	-204.9 (54.4%)	-216.4 (60.2%)	-183.2 (52.8%)	-184.2 (58.4%)
$\Delta E_{\sigma}^{[b]}$	-178.3 (79.8%)	-207.5 (91.4%)	-174.6 (89.7%)	-179.8 (89.7%)	-191.5 (95.4%)	-195.4 (95.4%)	-195.9 (90.5%)	-171.0 ^[d] (93.3%)	-174.3 (94.6%)
$\Delta E_{\pi}^{[b]}$	-45.0 (20.2%)	-19.5 (8.8%)	-20.1 (10.3%)	-20.6 (10.3%)	-9.3 (4.6%)	-9.5 (4.6%)	-20.5 (9.5%)	-11.6 ^[d] (6.4%)	-10.0 (5.4%)
ΔE_{prep}	5.4	13.0	13.1	14.5	17.2	18.8	23.8	30.2	21.8
$\Delta E^{[c]} (= -D_e)$	-170.6	-115.5	-130.5	-118.6	-102.2	-90.0	-126.4	-63.0	-93.0
$r(\text{C}-\text{C})$ [Å]	1.361	1.453	1.456	1.469	1.500	1.516	1.419	1.591	1.532

[a] The percentages in parentheses give the contribution to the total attractive interactions $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$. [b] The percentages in parentheses give the contribution to the orbital interactions ΔE_{orb} . [c] $\Delta E = \Delta E_{\text{int}} + \Delta E_{\text{prep}}$. [d] There is a small contribution of 0.6 kcal mol^{-1} from orbitals having δ symmetry.

situations in propyne $\text{HC}\equiv\text{CCH}_3$ and its trimethyl-substituted derivative 3,3-dimethyl-1-butyne $\text{HC}\equiv\text{CCMe}_3$. Table 1 shows that hyperconjugation of the C–H bonds in the former molecule is rather strong ($\Delta E_\pi = -20.1 \text{ kcal mol}^{-1}$). The hyperconjugative stabilization in $\text{HC}\equiv\text{CCMe}_3$ is even slightly larger ($\Delta E_\pi = -20.6 \text{ kcal mol}^{-1}$), although the C–C bond is a bit longer than in propyne. This means that C–C bonds stabilize multiple bonds through hyperconjugation better than C–H bonds. It is interesting to note that the hyperconjugative stabilization of the degenerate π systems in $\text{HC}\equiv\text{CCH}_3$ and $\text{HC}\equiv\text{CCMe}_3$ is even slightly stronger than the conjugative stabilization in 1,3-butadiene ($-19.5 \text{ kcal mol}^{-1}$), which has nearly the same central C–C bond length (1.453 \AA) as the former species (1.456 \AA and 1.469 \AA).

We also calculated the hyperconjugation in propene $\text{H}_2\text{C}=\text{CHCH}_3$ and its trimethyl-substituted derivative $\text{H}_2\text{C}=\text{CHCMe}_3$. The calculated ΔE_π values (Table 1) for the former molecule ($\Delta E_\pi = -9.3 \text{ kcal mol}^{-1}$) and the latter species ($\Delta E_\pi = -9.5 \text{ kcal mol}^{-1}$) suggest that the hyperconjugative stabilization of C–H and C–C bonds with olefinic double bonds is half as strong as that of $\text{C}\equiv\text{C}$ triple bonds. This is reasonable because alkynes have two π components but alkenes have only one π component. The stabilization of the C–C bonds are again slightly larger than that of the C–H bonds.

Hyperconjugation involves donation from the occupied π orbitals of the multiple bonds into the vacant π^* orbitals of the CH_3 or CMe_3 groups and backdonation from occupied π orbitals of CH_3 or CMe_3 into π^* orbitals of the multiple bonds. Which of the two contributions is stronger? We estimated the strength of the $\pi \rightarrow \pi^*$ donation and backdonation separately by carrying out EDA calculations on propene and propyne where the vacant π^* orbitals of either fragment were deleted. The results show that both contributions are important for the hyperconjugation but that the backdonation from the π orbitals of CH_3 into the π^* orbitals of the multiple bonds is stronger than the donation. In propene the calculated value for the π -orbital donation $\pi(\text{H}_2\text{C}=\text{CH}) \rightarrow \pi^*(\text{CH}_3)$ becomes $\Delta E_\pi = -4.0 \text{ kcal mol}^{-1}$ when the virtual π orbitals in the $\text{H}_2\text{C}=\text{CH}^+$ fragment are deleted, while the $\pi^*(\text{H}_2\text{C}=\text{CH}) \leftarrow \pi(\text{CH}_3)$ backdonation becomes $\Delta E_\pi = -6.0 \text{ kcal mol}^{-1}$ after deletion of the virtual π orbitals in the CH_3^+ fragment. In the same fashion we found that the π -orbital donation $\pi(\text{HC}\equiv\text{CH}) \rightarrow \pi^*(\text{CH}_3)$ becomes $\Delta E_\pi = -9.3 \text{ kcal mol}^{-1}$ after deletion of the π^* orbitals of $\text{HC}\equiv\text{CH}^+$, while the $\pi^*(\text{HC}\equiv\text{CH}) \leftarrow \pi(\text{CH}_3)$ backdonation becomes $\Delta E_\pi = -12.8 \text{ kcal mol}^{-1}$ when the π^* orbitals of CH_3^+ are deleted.

We also calculated the conjugative stabilization between a triple and a double bond in but-1-en-3-yne $\text{H}_2\text{C}=\text{CH}-\text{C}\equiv\text{CH}$. Table 1 shows that the π -bonding contribution to the central C–C bonding ($\Delta E_\pi = -20.5 \text{ kcal mol}^{-1}$), which involves only one π component of the triple bond, is slightly stronger than the π conjugation in 1,3-butadiene ($\Delta E_\pi = -19.5 \text{ kcal mol}^{-1}$); this can be explained by the shorter C–C distance in the former compound. We finally calculated the strength of the hyperconjugation in ethane and 2,2,3,3-tetramethylbutane. The doubly degenerate C–C hyperconjugation in the latter compound ($\Delta E_\pi = -11.6 \text{ kcal mol}^{-1}$) is slightly stronger than the degenerate C–H hyperconjugation in the former species ($\Delta E_\pi = -10.0 \text{ kcal mol}^{-1}$).

In summary, EDA calculations show that the intrinsic conjugative stabilization arising from the $\pi-\pi^*$ interactions in 1,3-butadiene is approximately twice as strong as that in 1,3-butadiene. Hyperconjugation of C–H and C–C bonds with multiple bonds is quite strong. The hyperconjugation is roughly half as strong as π conjugation between two multiple bonds. The hyperconjugation of C–C bonds is slightly stronger than hyperconjugation of C–H bonds.

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