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Intramolecular multi-bond strain: the unrecognized side of the dichotomy of conjugated systems

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Electron conjugation stabilizes unsaturated systems and diminishes the differences among bond distances. Experimentally, Kistiakowsky and coworkers first measured and noticed the difference between the hydrogenation heats of carbon–carbon double bonds in conjugated systems. For instance, the hydrogenation heat of butadiene is 57.1 kcal mol^{−1}, which is less than two times that of the hydrogenation heat of 1-butene (30.3 kcal mol^{−1}), and the difference (3.5 kcal mol^{−1}) is the extra stabilization due to the resonance between two double bonds in the former, and is referred to as the experimental resonance energy. Following Kistiakowsky's definition, Rogers *et al.* studied the stepwise hydrogenation of 1,3-butadiyne and concluded that there is no conjugation stabilization in this molecule. This claim received objections instantly, but Rogers and coworkers further showed the destabilizing conjugation in 2,3-butanedione and cyanogen. Within resonance theory, the conjugation energy is derived "by subtracting the actual energy of the molecule in question from that of the most stable contributing structure." The notable difference between the experimental and theoretical resonance energies lies in that the former needs other real reference molecules while the latter does not. Here we propose and validate a new concept, intramolecular multi-bond strain, which refers to the repulsion among π bonds. The π – π repulsion, which is contributed to by both Pauli exchange and electrostatic interaction, is quantified with the B₄H₂ model system (16.9 kcal mol^{−1}), and is compared with the σ – σ repulsion in B₂H₄ (7.7 kcal mol^{−1}). The significance of the π – π repulsion can be demonstrated by the much longer carbon–nitrogen bond in nitrobenzene (1.486 Å) than in aniline (1.407 Å), the very long and weak nitrogen–nitrogen bond (1.756 Å) in dinitrogen tetroxide, and the instability of long polyynes. This new concept successfully reconciles the discrepancy between experimental and theoretical conjugation energies. However, we maintain that by definition, electron conjugation must be stabilizing.

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1. Introduction

Ever since the proposal of strain theory by Baeyer in 1885,¹ the concept of molecular strain has been well accepted as one of the key factors influencing the preference of molecular conformations and reactivity.^{2–10} Strain energy is often derived as the difference between the experimental heat of formation for a strained molecule and the expected heat of formation for a hypothetical strain-free molecule with the same number of atoms which is derived from group contributions of additivity

methods^{11,12} or *ab initio* computations.^{13,14} Strain is also addressed in terms of bond length, bond angle, torsional angle and noncovalent interactions. In general, molecular strain can be classified as either ring strain, such as in cyclopropane,^{14–19} or steric strain, such as in eclipsed ethane.^{20–25}

Different from destabilizing molecular strains, electron delocalization refers to the electron transfer from one moiety to another, and includes hyperconjugation and conjugation based on the symmetry of the orbitals involved. A notable example in this regard is conjugated linear molecules.²⁶ By definition, electron delocalization must be a stabilizing factor, otherwise nature would choose an electron localized structure. This effect has been well recognized in conjugated systems such as graphene and conductive polymers and many organic pigments which are widely used in organo-luminescent devices and dye-sensitized solar cells. A conjugated system cannot be well described with a single Lewis structure where each bonding pair of electrons is localized on no more than two atoms and thus a resonance theory is needed.^{27,28} Theoretically, conjugation (resonance) energy can be derived "by subtracting the actual

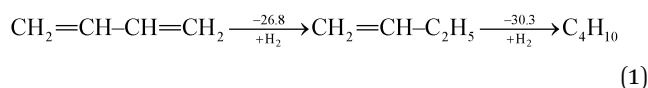
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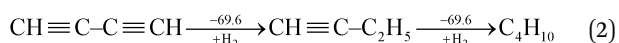
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energy of the molecule in question from that of the most stable contributing structure²⁸ using *ab initio* valence bond (VB) theory.^{29–32} The popular molecular orbital (MO) theory, however, has difficulties in defining electron-localized states for references in the way VB theory does,³³ though approximate approaches have been developed particularly in the study of electron transfer processes.^{34–38} Alternatively, other reference molecules have to be chosen and various isodesmic and homodesmotic model reactions need to be designed to estimate resonance energies,³⁹ but the intrusion of other effects in the reference systems, such as strain, hyperconjugation, Coulomb repulsion imbalance, and uncompensated van der Waals (dispersion) attractions, has been recognized.^{40,41} Experimentally, Kistiakowsky and coworkers first measured and noticed the differences between the hydrogenation heats of the carbon–carbon double bonds in substituted and/or conjugated systems.^{42,43} For instance, the hydrogenation heat of butadiene is 57.1 kcal mol^{−1}, which is less than two times the hydrogenation heat of 1-butene (30.3 kcal mol^{−1}), and the difference (3.5 kcal mol^{−1}) is the extra stabilization due to the resonance between two double bonds in the former, and is referred to as the Kistiakowsky resonance energy. The process can be expressed as the sequential hydrogenation in the following steps (in kcal mol^{−1})⁴³



If we take ethylene instead of 1-butene as the reference, however, the difference would be 8.5 kcal mol^{−1}.

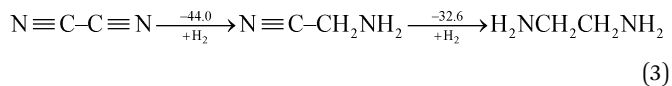
Following Kistiakowsky's definition,⁴² Rogers *et al.* computationally studied the stepwise hydrogenation of 1,3-butadiyne as



and concluded that there is no conjugation stabilization in this molecule.^{44,45} Even if we use acetylene as a reference, the difference is 10.0 kcal mol^{−1}, which is close to, rather than twice, the value for butadiene with reference to ethylene (8.5 kcal mol^{−1}). Based on resonance theory, we would expect that the thermodynamic conjugation stabilization in 1,3-butadiyne with two Π_4^4 (4-electron-4-center) bonds to be two times that of the quantity in 1,3-butadiene with only one Π_4^4 bond, as demonstrated first by Kollmar who derived the resonance stabilization energies in 1,3-butadiene and 1,3-butadiyne as 9.7 and 19.1 kcal mol^{−1}, respectively, by replacing their π MOs with the π MOs of ethylene and ethyne.⁴⁶

Rogers' claim that the conjugation stabilization in 1,3-butadiyne is zero received objections instantly.^{47–49} Jarowski *et al.* pointed out that there is significant hyperconjugation from the ethyl group to the triple bond (*i.e.*, $\sigma \rightarrow \pi^*$) in 1-butyne.⁴⁸ This stabilizing force leads to an underestimation of the conjugation with Kistiakowsky's definition. Jarowski *et al.* predicted conjugation energies of 9.3 kcal mol^{−1} for diynes and

8.2 kcal mol^{−1} for dienes. Based on the energy decomposition analysis between two fragments ($\text{C}\equiv\text{CH}$ and $\text{CH}=\text{CH}_2$), Cappel *et al.* estimated the conjugative stabilization in 1,3-butadiyne (45.0 kcal mol^{−1}) to be about twice the value of that in 1,3-butadiene (19.5 kcal mol^{−1}).⁴⁷ Nevertheless, Rogers *et al.* continued their work and showed the cases of 2,3-butanedione and cyanogen where the conjugation is even destabilizing, *e.g.*



Rogers surmised that the lack of overall thermodynamic stabilization in polyynes is due to the repulsions among the six electrons of each triple bond.⁵⁰ But this kind of interaction exists in ethyne as well and the extra stabilization in 1,3-butadiyne with reference to ethyne is still only 10.0 kcal mol^{−1}.

A molecular structure results from a balance of repulsive and attractive forces. Electron delocalization is an electronic effect and concerns charge transfer from an occupied bond orbital to vicinal unoccupied anti-bond orbitals, while a steric effect reflects the interaction between neighbouring occupied bond orbitals, and generally comprises the classical electrostatic (*e.g.*, local dipole–dipole interaction) term and quantum mechanical Pauli exchange repulsion. Thus, by definition, conjugation must be stabilizing. The seeming lack of stabilization or even destabilization found by Rogers *et al.* must result from a certain unrecognized repulsion. Here we propose and demonstrate a new concept, intramolecular multi-bond strain, as the source of significant repulsion among π bonds, which has not been well appreciated.

2. Synopsis

Multi-bond strain refers to the repulsion among conjugated π bonds or hyperconjugated σ – π bonds that, up until now, has not been identified with only the stabilizing conjugative or hyperconjugative interactions being generally recognized. The coexistence of the stabilizing and destabilizing forces can be better described by the following orbital interaction diagrams (Fig. 1). We consider two neighbouring π bonds on fragments A and B. The conjugation occurs between an occupied orbital (π_A or π_B) and the other moiety's virtual orbital (π_B^* or π_A^*) as shown in Fig. 1a. This has been the focal point for π conjugation, and *ab initio* valence

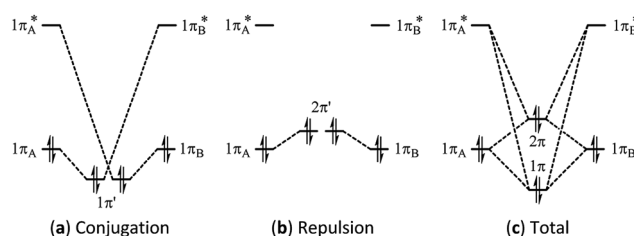


Fig. 1 Orbital interaction diagrams showing (a) conjugation, (b) repulsion and (c) the sum of conjugation and repulsion in two symmetrical conjugated π bonds.



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Fig. 3 Correlations of (a) ΔE_{orb} , (b) ΔE_s and (c) overlap integral S_{12} with the central BB bond distance in the B_4H_2 model system.

Fig. 3 shows the excellent exponential correlation of the energy terms with the bond distance. Considering that the energy terms are implicated by both the Pauli exchange and electrostatic interaction and the consensus that the Pauli repulsion increases exponentially as atomic wavefunctions decay exponentially,⁶⁸ we speculate that in B_4H_2 the π - π repulsion is largely contributed to by the Pauli exchange repulsion. In addition, Fig. 3 indicates a linear relationship between the orbital energy difference (ΔE_{orb}) and the steric energy (ΔE_s). As expected, the overlap integral between the two π orbitals in the parallel orientation ($1\pi_A$ and $1\pi_B$ in Fig. 1) is a good indicator of the steric repulsion in this case as a similar exponential correlation with the distance can be found (Fig. 3c).

5. Conjugation and repulsion in butadiene (1), butadiyne (2), cyanogen (3) and α -dicarbonyl (4)

We first compare the resonance in the two most typical conjugated systems, butadiene and butadiyne. A comparison of the DFT and BLW optimizations shows that the localization of π electrons on their respective multiple bonds considerably stretches the central CC bonds by 0.071 and 0.101 Å, respectively for 1 and 2, and the optimal distances reflect the intrinsically shorter Csp-Csp (1.465 Å) *versus* Csp²-Csp² (1.528 Å) single σ bonds. In the meantime, the deactivation of resonance modestly shortens the double and triple bond lengths which are essentially the same as the bond distances in ethylene (1.329 Å) and acetylene (1.199 Å) at the same B3LYP/6-311+G(d,p) level. Theoretically, there are two types of resonance energies, namely vertical resonance energy (VRE) and adiabatic resonance energy (ARE). The former is the energy difference between DFT and BLW computations of the same structure, while the latter is the energy difference between the optimal delocalized state (*i.e.*, DFT optimization) and the optimal localized state (*i.e.*, BLW optimization). Fig. 4 shows the change in VRE along the central CC bond distance in the conjugated systems studied in this work. Much like in Fig. 3, there is an excellent exponential correlation between VRE and the central bond distance in each molecule.

In the DFT optimized geometries, the VRE of butadiyne (32.9 kcal mol⁻¹) is a little more than two times that of the value in butadiene (14.5 kcal mol⁻¹). This is in agreement with the



Fig. 4 The exponential correlation of vertical resonance energy (VRE) with the central CC bond distance (R_2) in butadiene (1), butadiyne (2), cyanogen (3) and α -dicarbonyl (4).

studies by Kollmar,⁴⁶ and Cappel *et al.*,⁴⁷ and consistent with the facts that the central bond in butadiyne is shorter than in butadiene and there are two Π_4^4 bonds in the former but only one in the latter. The ARE is supposed to be comparable to experimental resonance energies with reference to individual multiple bonds such as ethylene and acetylene. However, isodesmic reactions show that the experimental resonance energies (EREs) for butadiene (8.5 kcal mol⁻¹) and butadiyne (10.0 kcal mol⁻¹) are not only similar but also considerably lower than the theoretical AREs (12.6 and 27.0 kcal mol⁻¹ for 1 and 2, respectively). If we take the difference between ARE and ERE as the steric contribution, the steric repulsion in butadiene and butadiyne are 4.1 and 18.8 kcal mol⁻¹ respectively. The latter is much more than two times the former, due to the much shortened central CC bond distance, and the repulsive force increases exponentially along the distance (Fig. 3). It should be noted that our AREs are very close to the evaluations of conjugation stabilization (14.8 and 27.1 kcal mol⁻¹) in butadiene and butadiyne by Wodrich *et al.* who reinterpreted the differences in the hydrogenations of the first and second multi-bond in eqn (1) and (2) after introducing the “protobranching” concept.⁶⁹

One way to estimate the intramolecular steric repulsion ΔE_s is the compression energy,²⁸ which is the difference between the VRE of the optimal DFT structure and the ARE and reflects the energy cost for the structural change (dominated by the central CC single bond variation ΔR_2) when conjugation is deactivated. Here we propose a force constant k to evaluate and compare the magnitude of the intramolecular steric repulsion

$$k = \frac{\Delta E_s}{[\Delta R_2]^2} = \frac{\text{VRE} - \text{ARE}}{[R_2(\text{BLW}) - R_2(\text{DFT})]^2} \quad (4)$$

Table 1 shows that butadiyne has a much higher k value than butadiene. Of course, k measures the change of repulsion with the distance, *i.e.*, the repulsive force, rather than the absolute energetic value of the steric repulsion. While the π - π repulsion considerably offsets the theoretical resonance energy (ARE) and leads to the experimental resonance energy (ERE), the repulsion



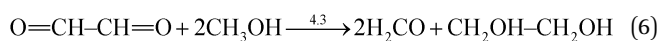
Table 1 Major optimal bond distances (Å) in delocalized (DFT) and localized (BLW) states and the computed resonance energies (VRE and ARE, in kcal mol⁻¹) compared with experimental resonance energies (ERE, in kcal mol⁻¹) and the force constant (kcal Å⁻²)

Molecule	State	<i>R</i> ₁	<i>R</i> ₂	VRE	ARE	ERE	<i>k</i>
Butadiene	DFT	1.338	1.457	14.5	12.6	8.5	382
	BLW	1.326	1.528	10.9			
Butadiyne	DFT	1.207	1.364	32.9	27.0	10.0	589
	BLW	1.194	1.465	22.2			
Cyanogen	DFT	1.155	1.376	27.2	22.7	-4.3 ^a	576
	BLW	1.145	1.467	18.9			
α-Dicarbonyl	DFT	1.203	1.529	6.3	5.6	4.3 ^a	380
	BLW	1.196	1.583	4.9			

^a Reaction enthalpy at 298 K.

in butadiyne is much stronger than in butadiene. In the end, both molecules exhibit comparable EREs, and interestingly, as found by Rogers *et al.*,^{44,45} there is zero thermodynamic conjugation stabilization in butadiyne.

We further look at the cases of cyanogen (3) and α-dicarbonyl (4) where Rogers *et al.* showed even thermodynamic destabilization.⁷⁰ Indeed, we confirmed a reduced conjugation stabilization in both systems, compared with butadiyne and butadiene, respectively. The central CC bond in cyanogen is 0.012 Å longer than that in butadiyne. But when π electrons are localized, the optimal central bond lengths are quite similar (1.465 *versus* 1.467 Å) and correspond to the Csp-Csp single σ bond. This suggests a stronger repulsion between the triple bonds in cyanogen than in butadiyne, most likely due to the polarity of the CO π bonds which lead to dipole-dipole electrostatic repulsion. In fact, if we use the isodesmic reaction eqn (5) to measure the experimental resonance energy, we find that the ERE is even negative at the G3 theoretical level. This is consistent with eqn (3) where the hydrogenation of the first cyano group is more exothermic than the hydrogenation of the second cyano group. The stretched central C-C bond in α-dicarbonyl is an example where the π-π electrostatic repulsion plays a big role.



Electron density difference (EDD) maps can be used to directly visualize the resonance, as the electron density difference between the electron-localized state (BLW) and the electron-delocalized state (DFT) reflects the movement of electron density. Fig. 5 plots the EDD maps of the four conjugated systems studied here. The orange color means a gain of electron density while the cyan color shows a loss of electron density. Following the conventional view, resonance moves the π electron density from multiple bonds to the linking single



Fig. 5 Electron density difference (EDD) maps showing the resonance in butadiene (1), butadiyne (2), cyanogen (3) and α-dicarbonyl (4).

bonds, leading to the significant shortening of the central bonds.

6. Conclusion

Conjugation has been associated with high stability, planarity, small bond length alternation and many other physicochemical properties such as the bathochromic shift and lifetime of excited states. However, this is only one side of the story and concomitantly there is significant repulsion between π bonds which has not been well-recognized. In other words, while conjugation results in the stabilization of a conjugated system, the stability of the system is not solely determined by the conjugation, and there is intramolecular π-π repulsion which counteracts the stabilizing forces. This unrecognized repulsion is the culprit for the findings that conjugation has no stability or even is destabilizing. Considering that “strain, in a general sense, represents a cornerstone of the 150 year old field of conformational analysis”,⁷¹ here we propose the concept of intramolecular multi-bond strain to recognize the π-π repulsion. The magnitude of the π-π repulsion can be quantitatively assessed with the linear B₄H₂ (16.9 kcal mol⁻¹), in comparison with the σ-σ repulsion in B₂H₄ (7.7 kcal mol⁻¹). This new concept thus elucidates the difference between experimental and theoretical conjugation energies, although by definition, conjugation or resonance must be stabilizing.

Although quantum Pauli exchange repulsion is the primary cause for the π-π repulsion when the π bonds are nonpolar, local dipole-dipole repulsion can contribute and sometimes even dominate the π-π repulsion in cases with polarized π electron densities. The strong π-π repulsion is also implicated in numerous experimental findings. One notable example is the much longer carbon-nitrogen bond in nitrobenzene (1.486 Å) than in aniline (1.407 Å). Due to the resonance of the lone nitrogen pair to more electronegative oxygen atoms in the nitro group, there is a significant π dipole, which repels the π electron density in the benzene ring *via* both Pauli exchange and electrostatic interactions, leading to a long carbon-nitrogen bond in nitrobenzene.⁷² In fact, the strong π-π electrostatic repulsion, as shown by the much longer central C-C bond distance in α-dicarbonyl than in



butadiene when conjugation is quenched (Table 1), is the major culprit for the remarkably stretched nitrogen–nitrogen bond in the weakly bound dinitrogen tetroxide (1.756 Å) compared with the single bond in hydrazine (1.47 Å).⁷³ With both the electrostatic and Pauli repulsion deactivated, the nitrogen–nitrogen bond in dinitrogen tetroxide can be dramatically shortened to 1.471 Å as optimized by the BLW method at the B3LYP/6-311+G(d,p) level.⁷² The well-recognized instability of long polynes should be contributed to by the strong intramolecular multi-bond strain as well.^{74–77}

7. Methodology

The block-localized wavefunction (BLW) method originates from *ab initio* valence bond (VB) theory as it simplifies the original Heitler–London–Slater–Pauling (HLSP) function to a BLW of only one Slater determinant form with block-localized MOs. Orbitals in the same subspace are subject to the orthogonality constraint, but orbitals belonging to different subspaces are nonorthogonal. Thus, the BLW method combines the advantages or features of both MO and VB theories. In general, for an electron-localized state which is usually the most stable resonance structure, we partition the system to k blocks and define its wavefunction with a BLW (here we assume that the number of electrons in each block is even (equal to $2n_i$) and thus orbitals are doubly occupied) as

$$\psi^{\text{BLW}} = \det[\varphi_{11}^2 \varphi_{12}^2 \dots \varphi_{1n_1}^2 \dots \varphi_{i1}^2 \dots \varphi_{in_i}^2 \dots \varphi_{kn_k}^2] = \hat{A}[\Phi_1 \dots \Phi_i \dots \Phi_k] \quad (7)$$

where

$$\Phi_i = \hat{A}[\varphi_{i1}^2 \varphi_{i2}^2 \dots \varphi_{in_i}^2] \quad (8)$$

is defined for the block i . For the cases studied in this work, apart from the σ frame which forms one block, each block is composed of two π electrons on two atoms. The resonance energy (RE) is defined as

$$\text{RE} = E(\psi^{\text{BLW}}) - E(\psi^{\text{DFT}}) \quad (9)$$

Geometry optimizations and calculations for adiabatic states with the regular DFT and diabatic states with the BLW method were performed with our in-house version of the quantum mechanical software GAMESS.⁷⁸

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