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Interference Effect and the Nature of the π -Bonding in 1,3-Butadiene[†]

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The nature of the chemical bond in 1,3-butadiene is analyzed by applying the recently developed generalized product function energy partitioning (GPF-EP) scheme, which allows the calculation of the quantum mechanical interference contribution to the energy in a meaningful and intuitive fashion. The method is applied to investigate the breakage of the middle C–C bond, and the rotation along the torsional angle defined by the carbon atoms. A comparison between bonding in ethylene and butadiene is also performed. It is shown that bond delocalization plays no role in the properties of a conjugated molecule and that existing alternative explanations should be revisited.

Introduction

Compounds with alternating single and double bonds present a number of chemical and physical characteristics which have attracted the attention of several investigators and have been the subject of much theoretical speculation.¹ These characteristics range from geometric properties, like the shortening of single bonds and the tendency for planar geometries,^{2,3} to spectroscopic behavior, like the bathochromic shift,⁴ in addition to presenting a greater evaluated thermodynamic stability than the corresponding nonconjugated isomers.^{5,6}

The most widespread explanation for both the geometric and thermodynamic properties of compounds makes use of the “delocalized bonding” concept,^{5,7} which states that part of the electron density of two conjugated bonds is displaced to the region between the two adjacent nuclei, each associated with one of the bonds. This “bond delocalization” is then said to be responsible for both the planarity and bond shortening verified in conjugated molecules, as well as for increasing the molecule’s thermodynamic stability. This view is not without its critics, however.^{8–11} As pointed out in a number of works, the single bond shortening observed in conjugated compounds can be explained without recourse to delocalization, by invoking the difference in electronegativity between the sp^3 -hybridized carbon atoms of C–C bonds in saturated compounds, and the sp^2 -hybridized carbon atoms of the single bond in molecules like 1,3-butadiene, for instance.^{10,11} Other important questions have been raised regarding the importance of delocalization in 1,3-butadiene, especially the fact that the excited structure corresponding to singlet coupling of the atomic π orbitals in the 2 and 3 positions is too high in energy, which would make its contribution to the ground state unimportant.⁸ In this case, the properties of butadiene have been attributed to simple polarization of the π electron density.^{8,9}

There are, also, some fundamental issues with the delocalization concept that are critical to the discussion of bonding (and bond conjugation), which, although well-known, have not been previously discussed in this context.

Chemical bonds are not strict physicochemical entities, being rather a manifestation of the quantum mechanical nature of

electron densities, which are constructed by squaring the sum of electron eigenstates, instead of simply summing the density from each eigenstate. This manner of constructing electron densities leads to the appearance of interference terms in the total expression of the density. When interference between quasi-atomic eigenstates is constructive, electron density is displaced toward the middle of the bond region (i.e., delocalizes), an effect known to be the main factor for the bonding of atoms.^{12–19}

Now, rigorously, there are no interference components in electron densities obtained from wave functions constituted of doubly occupied strongly orthogonal orbital products (such as RHF or qualitative MO wave functions), since interference between equal eigenstates is identically zero. However, when MOs are constructed by linear combinations of atomic orbitals (LCAO) or, more importantly, by a variational procedure involving a number of orbital-like functions, one is implicitly approximating the correct density by including crossed terms involving different functions, which, however, are not proper eigenstates of the one-electron Hamiltonian of the problem. Of course, this process leaves no clue of the importance of the different crossed terms in such a construction. It is, thus, impossible, although commonplace, to tell the extent and the manner by which the *electron density* has delocalized in comparison to its quasi-classical (interference-free) density by a mere inspection of the *molecular orbital shape*.

It was Ruedenberg’s seminal work, “The Physical Nature of the Chemical Bond”,⁸ that first tackled the issue of extracting this kind of information, among other things, from wave functions of a general form. By expressing the first and second order reduced density matrices (RDMs) in terms of properly selected atomic-like orbitals, Ruedenberg has shown that one could, in principle, compute the interference contribution to the energy and investigate its importance. Special attention was given to the analysis of bonding in H_2 and H_2^+ , demonstrating that the interference component is, indeed, responsible for the delocalization of electron density to the bond region and, ultimately, for chemical bonding.⁸ This electron density change promotes a reduction of the kinetic energy (in comparison to the kinetic energy of the corresponding quasi-classical density) and a lower increase of the potential energy, leading to a net energy drop. The **total** kinetic energy ultimately increases, while the **total** potential energy lowers, leading to the correct virial

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relation. This behavior of the total energy has been attributed to a contraction of electron density toward the nuclei, which is allowed by the kinetic energy drop promoted by the interference effect.^{8,9}

In this work, we investigate the nature of the conjugate π bonds in the 1,3-butadiene molecule in light of the interference effect. To this end, we use the generalized product function energy partitioning (GPF-EP).²⁰ The GPF-EP scheme, which is based on McWeeny's GPFs,²¹ allows the calculation of the interference energy arising from different bonds separately, while avoiding the need to arbitrarily partition the wave function in atomic orbitals. This is done by choosing modern valence bond wave functions (such as GVB) to construct the GPF. Such wave functions are constituted of uniquely defined atomic-like orbitals generated by self-consistent optimization. This partitioning approach was recently applied to investigate bonding in the N₂ molecule, revealing that two nitrogen atoms do not bind in the absence of quantum mechanical interference, despite the considerable electrostatic contributions to the energy found by other authors.²²

A brief discussion of both the equations and the interpretation of the GPF-EP is presented next. A more thorough discussion can be found elsewhere.²⁰

Generalized Product Function Energy Partitioning

A GPF is a special kind of approximate wave function constructed from the antisymmetrized product of strongly orthogonal wave functions, each one describing a different number of electrons. Examples of GPFs are the Hartree–Fock and GVB-PP wave functions. The RDMs of GPFs are such that the total energy can be expressed in terms of the RDMs of the individual groups. Consequently, the total energy can be divided in intragroup and intergroup contributions.²¹ For example, one could construct a GPF for the ethylene molecule in which each pair of electrons participating in a bond would be ascribed to a different electron group described at the GVB level, while all the core electrons would be included in a different electron group, described at the HF level.

We have recently shown that using modern valence bond (such as GVB) wave functions for electron groups makes it possible to partition the energy in four distinct terms, leading to the GPF-EP scheme:

$$E[\text{tot}] = E[\text{ref}] + E[\text{x}] + E[\text{I}] + E[\text{II}] \quad (1)$$

where $E[\text{ref}]$ is the energy associated with the quasi-classical (interference-free) electron density and pair-density of the electron groups, $E[\text{x}]$ is the energy contribution due to the antisymmetrization of electron indexes pertaining to different groups and can be understood as a correction to $E[\text{ref}]$, and $E[\text{I}]$ and $E[\text{II}]$ are the first-order and second-order interference contributions to the energy, respectively. Both the reference $E[\text{ref}]$ and interference $E[\text{I}]$ energies contain kinetic, electron–nucleus, and electron–electron potential contributions. $E[\text{ref}]$ also includes the nucleus–nucleus potential energy. On the other hand, $E[\text{x}]$ and $E[\text{II}]$ contain only electron–electron potential contributions. $E[\text{II}]$ has also been referred to as an “interference density self-interaction” in the literature and is usually quite small.

It is important to emphasize that there is no need, in this case, to commit to any particular criterion for choosing atomic orbitals, since the nonorthogonal orbitals in GVB are, within a given basis set, uniquely defined one-electron functions, generated by a self-consistent procedure.

In the GPF-EP scheme, it becomes possible to separate in a simple manner each of these terms in intragroup and intergroup contributions, with the exception of the nucleus–nucleus potential energy.

$$E[\text{ref}] = \sum_{\mu=1}^{\eta} E^{\mu}[\text{ref}] + \sum_{\mu<\nu} E^{\mu,\nu}[\text{ref}] + \frac{1}{2} \sum_{\text{A,B}}^M \frac{Z_{\text{A}} Z_{\text{B}}}{r_{\text{AB}}} \quad (2)$$

$$E[\text{x}] = \sum_{\mu<\nu} E^{\mu,\nu}[\text{x}] \quad (3)$$

$$E[\text{I}] = \sum_{\mu=1}^{\eta} E^{\mu}[\text{I}] \quad (4)$$

$$E[\text{II}] = \sum_{\mu=1}^{\eta} E^{\mu}[\text{II}] + \sum_{\mu<\nu} E^{\mu,\nu}[\text{II}] \quad (5)$$

In eqs 2–5, η is the number of electron groups while μ and ν are the indexes for the μ th and ν th electron groups. Terms containing one group index are intragroup contributions, and terms containing two group indexes are intergroup contributions. For example, the quasi-classical contributions, which are given by $E[\text{ref}]$, can be divided in three distinct types: terms in the first and second summation are intragroup and intergroup terms, respectively, and the third term is the nuclei repulsion potential. The prime over the summation symbol indicates that terms with equal indexes are not included. The expressions for obtaining each term have been compiled in the Supporting Information.

In many cases, it will be useful to consider a sum of some of the quantities above. For instance, usually, we shall be interested in the quasi-classical energy corrected due to proper symmetrization (i.e., the sum of $E[\text{ref}]$ and $E[\text{x}]$). In such cases, we shall use a notation including both labels inside the square brackets (e.g., $E[\text{ref+x}]$).

To get a clearer picture of the effect of interference in the electron density, one can plot the interference density, which is negative in regions where density is removed, and positive in regions where density is added. The expression for the interference density of the μ th electron group is given by

$$\rho_I^{\mu} = \sum_{r,s}^{N^{\mu}} \left\{ \phi_r^{\mu} \phi_s^{\mu} - \frac{1}{2} S_{rs} [(\phi_r^{\mu})^2 + (\phi_s^{\mu})^2] \right\} p(r|s) \quad (6)$$

where ρ_I^{μ} is the interference density, N^{μ} is the number of electrons in the group, ϕ_r^{μ} and ϕ_s^{μ} are the r th and s th orbitals pertaining to the μ th group, S_{rs} is the overlap integral between the orbitals r and s , and $p(r|s)$ is the first-order reduced density matrix expressed in the orbital basis.

Computational Details

All geometry optimizations and relaxed scans were carried out at the GVB-PP level with Dunning's cc-pVDZ basis set, using the JAGUAR 7.5 program.²³ The GPF-EP energy partitioning was carried out at the PES points obtained in the previous steps, using a wave function with the sigma bonds described at the GVB-PP level and the π bonds described at the GVB (or, equivalently, spin-coupled) level, which is identical

TABLE 1: Interference Energy Contributions in Ethylene

	$E[I]$ (kcal/mol)	$E[II]$ (kcal/mol)	$E[I+II]$ (kcal/mol)
C–H	−86.25	0.55	−85.70
σ C–C	−91.80	0.26	−91.54
π C–C	−49.03	0.87	−48.15

TABLE 2: Interference Energy Contributions in *s-trans*-1,3-Butadiene

	$E[I]$ (kcal/mol)	$E[II]$ (kcal/mol)	$E[I+II]$ (kcal/mol)
C–H _a ^a	−87.00	0.51	−86.50
C–H _b ^a	−86.91	0.51	−86.40
C–H _c ^a	−87.35	0.51	−86.84
σ C–C (1,2)	−92.32	0.26	−92.06
σ C–C (2,3)	−92.95	0.41	−92.54
π	−81.22	−2.88	−84.10

^a C–H_a and C–H_b bonds involve terminal carbon atoms; C–H_c refers to bonds involving carbon atoms 2 or 3; the hydrogen atom in the C–H_a bond is in trans position relative to the hydrogen in the C–H_c bond.

to a GVB-PP calculation without the perfect pairing and strong orthogonality approximations. The wave functions were constructed and optimized with the VB2000/GAMESS package.^{24,25} A stand-alone code was devised to obtain the GPF-EP.²⁶ The interference density plots were drawn with GNUPLOT.

Results and Discussion

Throughout this section, we shall need a convention when referring to the different C–C bond types in butadiene. Carbon atoms are numbered from 1 to 4, starting from one of the terminal ones. Bonds involving carbon atoms will, correspondingly, be named using these indexes (for instance, the middle C–C bond is the C2–C3 bond).

Interference Energy in the 1,3-Butadiene and Ethylene Molecules. Tables 1 and 2 show the calculated first and second-order interference contributions for ethylene and *s-trans*-1,3-butadiene from all bonds at the calculated equilibrium geometries. The “ π ” entry refers to the electron group containing all π orbitals, where the two possible spin-couplings are allowed to properly describe any conjugative effects. A table including all contributions for both ethylene and 1,3-butadiene has been included in the Supporting Information section.

The total interference energy values of both C–H and C–C σ bonds differ at most by 1.14 kcal/mol for C–H bonds and by 1.00 kcal/mol for the C–C σ bonds, evidencing the transferability of this quantity for chemically similar bonds in the two different molecules. The second-order contributions are quite small for all σ bonds, reaching at most 0.55 kcal/mol, for a C–H σ bond in ethylene. Interference between the p-like orbitals in ethylene contributes considerably less to the energy, resulting in an energy decrease not much larger than half the contribution stemming from interference in the C–C σ bond.

What is more interesting, however, is the interference contribution of the π bonds in 1,3-butadiene. The $E[II]$ component is now stabilizing in character and, though still small, presents a much larger value than in the π bond in ethylene. Since second-order interference changes to the electron density affect only electron–electron interactions, it is reasonable to expect it to increase when the number of electrons increases. The $E[I]$ component, on the other hand, contributes much less to the energy (almost 17 kcal/mol less) than one would expect by multiplying the π contribution of ethylene by 2. This result is better understood by separating the total interference energy $E[I]$ into the contributions arising from interference among each pair

TABLE 3: Energy Contributions of Interference between Each Orbital Pair in the Conjugated π Bonds of *s-trans*-1,3-Butadiene

	$E[I]$ (kcal/mol)
π C–C (1,2)	−48.91
π C–C (2,3)	6.24
π C–C (1,3)	4.28
π C–C (1,4)	1.79

of p-like orbitals in the 1,3-butadiene molecule. Only four distinct pairings are possible and the contributions for each one of them are presented in Table 3. We shall designate them using the same number labels used for the carbon atoms.

The interference energy of an orbital pair of type (1,2), which corresponds to one of the π bonds in 1,3-butadiene, is, in fact, quite similar to that of the π bond in ethylene, smaller by only 0.11 kcal/mol. In a distinct fashion, contributions stemming from interference in the other orbital pairings are destabilizing, the highest being for pair (2,3), specifically that corresponding to the carbon atoms involved in the C–C middle bond. Since all quantum mechanical contributions to the energy of the π electrons are isolated in this term, it becomes evident that there is no covalent effect responsible for the ground state properties of 1,3-butadiene (i.e., no stabilization by “electron delocalization”).

To drive this point further, we have plotted the interference densities of the π electron group for both ethylene and 1,3-butadiene in the *s-trans* conformation. Figures 1–4 are interference density contour diagrams for ethylene and butadiene.

As can be seen in parts a and b of Figure 1, similarly to the σ bond in the H₂ and H₂⁺ species,^{12,14} electron density in the ethylene π bond is displaced from regions close to the carbon nuclei toward the middle of the bond by the interference effect. Comparison of Figure 1a,b, and an inspection of Figure 2 evidence that in the π bond of ethylene, electron density is displaced not merely toward the middle of the bond but also outward in relation to the plane containing the molecule.

Parts a and b of Figure 3 show interference density plots for 1,3-butadiene analogous to those for ethylene (Figure 1a,b), revealing that the interference density of each π bond behaves in a fashion similar to the interference density in the ethylene π bond. On the other hand, interference actually removes electron density from the region between carbon atoms 2 and 3 instead of increasing it, at both small and large distances from the molecule plane, as can be clearly seen from the inspection of Figure 4. This goes against the notion that there is bond delocalization in 1,3-butadiene and that this effect is somehow responsible for the characteristic properties of similar conjugated molecules.

A discussion of the reasons behind the failings of the traditional view of the role of delocalization in butadiene is now necessary. The simplest valence bond argument considers two covalent resonant structures (Figure 5). The structure in Figure 5a, which corresponds to the singlet coupling of each pair of electrons involved in a π bond, is the most important structure and is taken as a reference where no bond delocalization occurs. On the other hand, the structure Figure 5b, which involves the singlet coupling of electrons from different bonds, has a smaller, but relevant, contribution and promotes bond delocalization. Most works that address the question of delocalization in butadiene do so by (explicitly or implicitly) attempting to quantify the relative contribution of the structure in Figure 5b, either directly (e.g., by means of structure coefficients) or indirectly (e.g., by calculating the energy difference between a

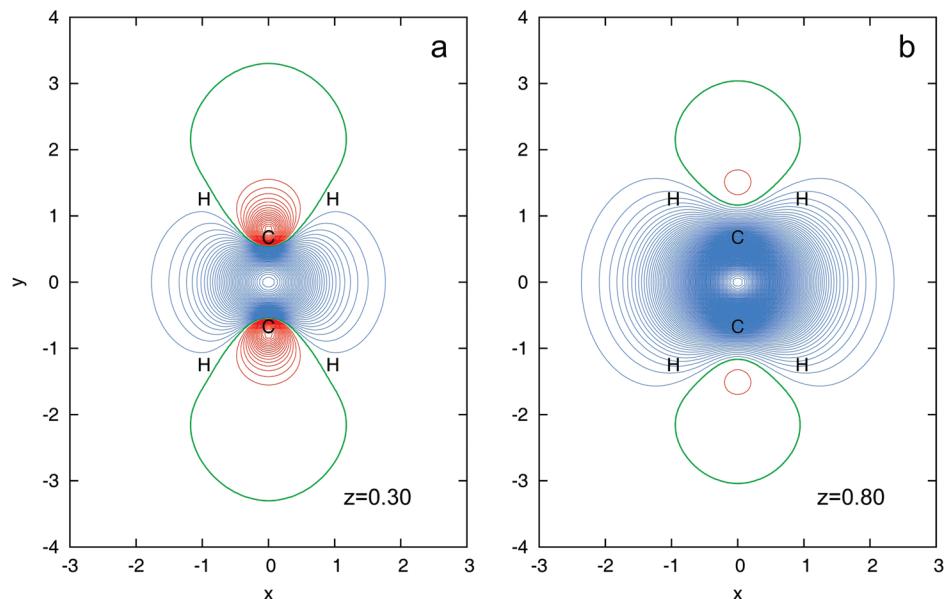


Figure 1. Interference density contour diagram for the ethylene π bond, plotted in a spatial cut section parallel to the plane of the molecule within a distance z , in angstroms. The green line corresponds to zero interference density; the blue line adjacent to it corresponds to the density value $\rho_i = +0.0002 \text{ V}^{-1}$, followed by incremental $s = +0.0002 \text{ V}^{-1}$ steps. The corresponding values for the red lines are $\rho_i = -0.0004 \text{ V}^{-1}$ and $s = -0.0002 \text{ V}$. Key: (a) $\rho_{\min} = -0.0036 \text{ V}^{-1}$, $\rho_{\max} = +0.0080 \text{ V}^{-1}$; (b) $\rho_{\min} = -0.0004 \text{ V}^{-1}$, $\rho_{\max} = +0.0196 \text{ V}^{-1}$. Coordinates in angstroms.

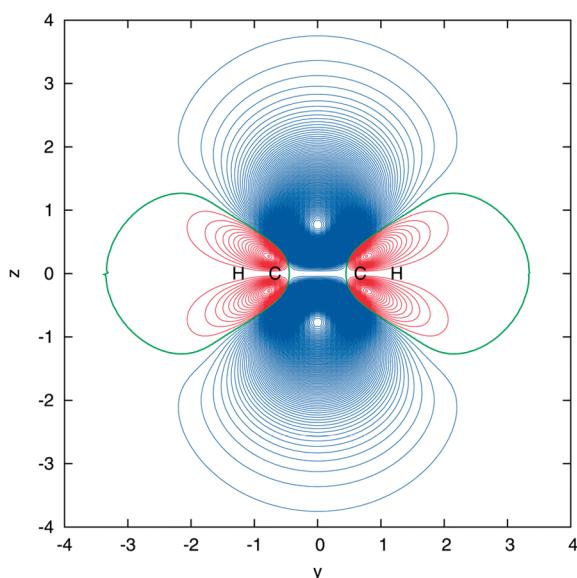


Figure 2. Interference density contour diagram for the ethylene π bond, plotted in a spatial cut section perpendicular to the plane of the molecule, containing both carbon atoms. Blue line: $\rho_i = +0.0002 \text{ V}^{-1}$, $s = +0.0002 \text{ V}^{-1}$. Red line: $\rho_i = -0.0002 \text{ V}^{-1}$, $s = -0.0002 \text{ V}^{-1}$; $\rho_{\min} = -0.0038 \text{ V}^{-1}$, $\rho_{\max} = +0.0196 \text{ V}^{-1}$.

wave function with the two structures and another without the structure in Figure 5b). Although this kind of argument is quite appealing due to its intuitiveness, it stumbles in its choice of “nondelocalized” reference. More specifically, the density of the resonance structure in Figure 5a contains terms between orbitals in different bonds that are not null and that favor an overall removal of density from the region between the C2 and C3 atoms. This is a nonremovable effect, present in the mathematical structure of any bonding scheme involving spatially close singlet-coupled electron pairs (e.g., He–He, H₂–H₂) a fact that had already been hinted at in Goddard’s work.¹⁶ In other words, *the very structure taken as reference contains many terms that remove density from the region between the middle carbon atoms, and the small “delocalizing”*

contribution of the second resonance structure is not enough to counter this effect. Thus, despite the fact that the wave function used in this work for butadiene contains all the spin-coupled structures needed to properly describe it (i.e., all the resonance structures), the total quantum mechanical term of the density expression does not promote bond delocalization and instead removes density from the region between the C2 and C3 carbon atoms.

An investigation of the other contributions to the total energy is now necessary to obtain a better understanding of the geometric features of butadiene. The section that follows presents an analysis of the process of homolytic breakage of the C–C single bond in view of the GPF-EP.

Energy Partition along the Dissociation Path of 1,3-Butadiene. The total energy partitioning in quasi-classical and interference contributions is presented in Figure 6. Each of the energy parts is presented relative to its value at a C2–C3 distance of 4.0 Å. It is seen that $E[\text{ref}+x]$, which stands for the total interference-free energy, goes up as the fragments approach, increasing by approximately 24.00 kcal/mol at a C2–C3 distance of 2.40 Å before starting to decrease, reaching a minimum of −15.80 kcal/mol at a C2–C3 distance of about 1.48 Å, which is quite close to the measured bond distance.²

Similarly to what happens in diatomics like H₂ and N₂, most of the energy drop resultant from bond formation stems from the interference effect.^{12,22,26} In this particular case, the interference energy $E[I]$ amounts to about 85.5% of this energy and is by far the most important of the two contributions. Interestingly, it varies very little in the vicinity of the equilibrium distance. Thus, even though the interference energy is extremely important for the formation of the single bond, the final distance between the two carbon atoms is ultimately a consequence of the quasi-classical contribution $E[\text{ref}+x]$.

The most important contributions to the total interference energy $E[I+II]$, namely, the first-order interference energy of both the C2–C3 bond and the π electron group, are shown in Figure 7, relative to their values at the dissociated bond limit. The variations of all the other interference contributions along

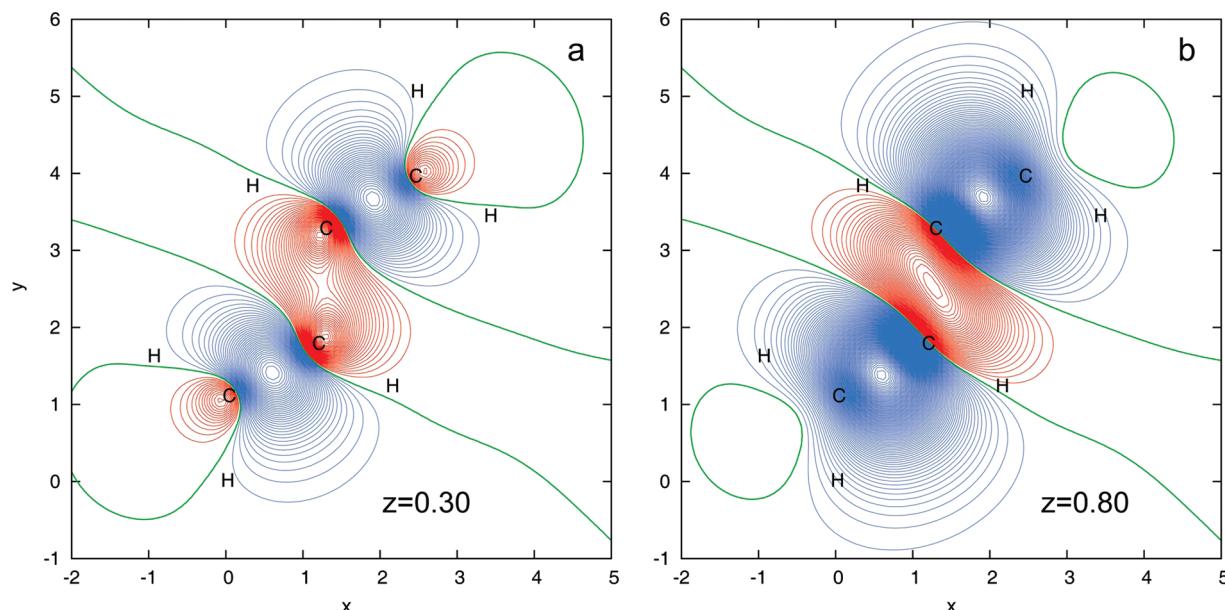


Figure 3. Interference density contour diagram for the *s-trans*-1,3-butadiene π -electron group. Follows the same parameters of Figure 1, differing only in the minimum and maximum values of the interference density. Key: (a) $\rho_{\min} = -0.0066 \text{ V}^{-1}$, $\rho_{\max} = +0.0072 \text{ V}^{-1}$; (b) $\rho_{\min} = -0.0074 \text{ V}^{-1}$, $\rho_{\max} = +0.0170 \text{ V}^{-1}$.

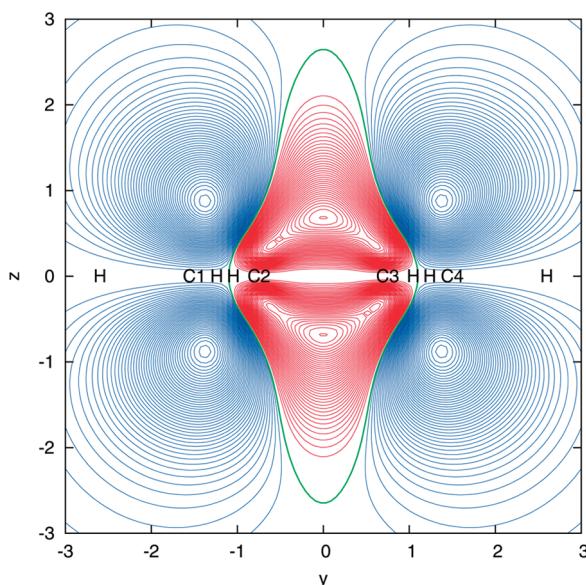


Figure 4. Interference density contour diagram for the *s-trans*-1,3-butadiene π -electron group, plotted in a spatial cut section perpendicular to the plane of the molecule, containing carbon atoms C2 and C3. Blue line: $\rho_i = +0.0002 \text{ V}^{-1}$, $s = +0.0002 \text{ V}^{-1}$. Red line: $\rho_i = -0.0004 \text{ V}^{-1}$, $s = -0.0002 \text{ V}^{-1}$; $\rho_{\min} = -0.0078 \text{ V}^{-1}$, $\rho_{\max} = +0.0088 \text{ V}^{-1}$.

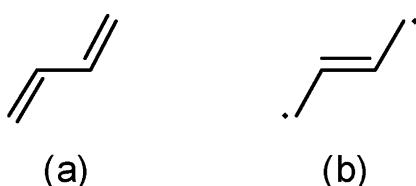


Figure 5. Covalent resonance structures for butadiene.

the potential energy surface are comparatively small and have not been included in the figure.

As expected, the interference energy contribution of the C2–C3 single bond increases greatly in magnitude as the two fragments approach, starting at a C2–C3 distance of about 3.8 Å and reaching a maximum at about 1.3 Å. On the other hand,

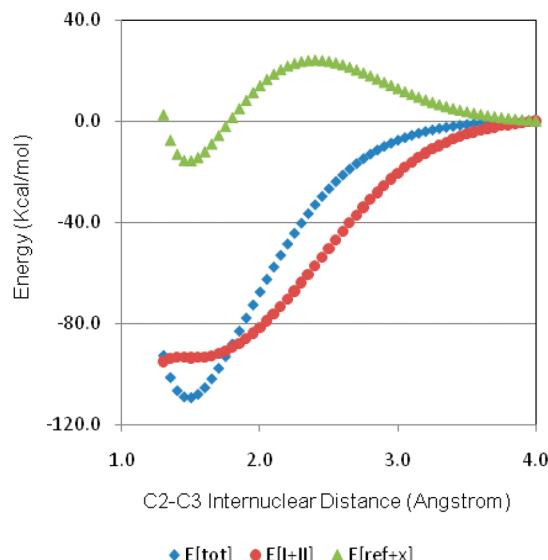


Figure 6. Energy partitioning along the C2–C3 bond-breakage path on the potential energy surface.

the interference contribution in the π electron group, which has a value of -99.67 kcal/mol at 4.00 \AA , originating from the π bond in each fragment, does not vary significantly until a C2–C3 distance of approximately 2.5 \AA , where it starts to decrease in magnitude, reaching the value of -81.22 kcal/mol at the equilibrium geometry, a change that is destabilizing by 18.45 kcal/mol . Hence, quantum mechanical contributions stemming from π bond conjugation are *not* stabilizing and cannot be directly linked to the shortening of the C2–C3 bond. Interestingly, this mirrors some findings concerning bonding in the benzene molecule, where the traditional stabilizing role attributed to the π electrons has been questioned.²⁷

The mechanism through which the density changes promoted by interference affect the total energy can be investigated by partitioning the interference energy of the σ C2–C3 bond and the π electron group into its kinetic and potential parts ($T[I]$ and $V[I]$, respectively). As the σ C2–C3 bond forms, interference promotes a kinetic energy lowering at the same time it

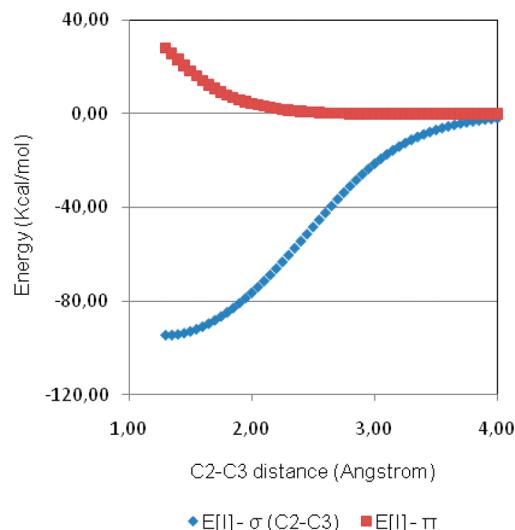


Figure 7. Contributions to the interference energy along the C2–C3 bond-breakage path on the potential energy surface.

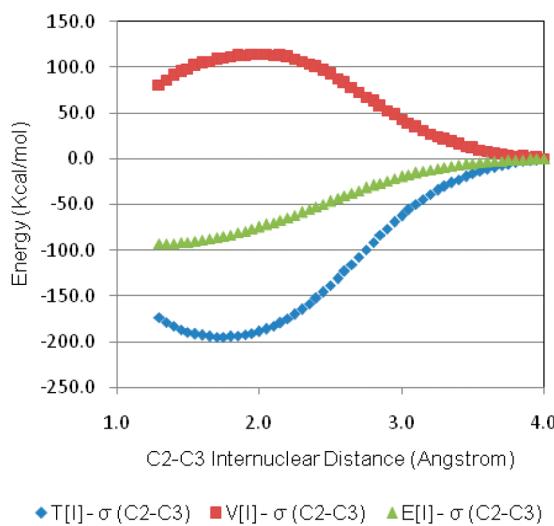


Figure 8. Partitioning of the interference energy in its kinetic $T[I]$ and potential energy $V[I]$ contributions for the C2–C3 σ bond along the C2–C3 bond-breakage path.

induces a potential energy increase, as can be seen in Figure 8. The quasi-classical contributions behave in the opposite way, with a kinetic energy increase of ~ 420 kcal/mol, possibly originating from density contraction. This is the same mechanism identified originally by Ruedenberg for simpler molecules,¹² which appears to be quite general.^{12,20,22,26}

The quantities $T[I]$ and $V[I]$ associated with π electrons behave quite differently. Figure 9 shows that, as the p-like orbitals involved in the two different π bonds approach, interference promotes an increase of the kinetic energy and a lowering of the potential energy. Once again, the interference kinetic energy change is larger in the module, leading to the energy increase identified both in Table 2 and in Figure 6. Contrary to what happens to the C2–C3 σ bond, the quasi-classical kinetic energy contribution experiences a relatively small decrease of approximately 54 kcal/mol.

Conformational Analysis along the C1–C2–C3–C4 Torsional Angle of 1,3-Butadiene. The results presented in the previous sections already suggest a clear picture regarding bonding in conjugated dienes. No evidence of electron density accumulation between carbon atoms 2 and 3 in 1,3-butadiene due to interference between π orbitals has been found. On the

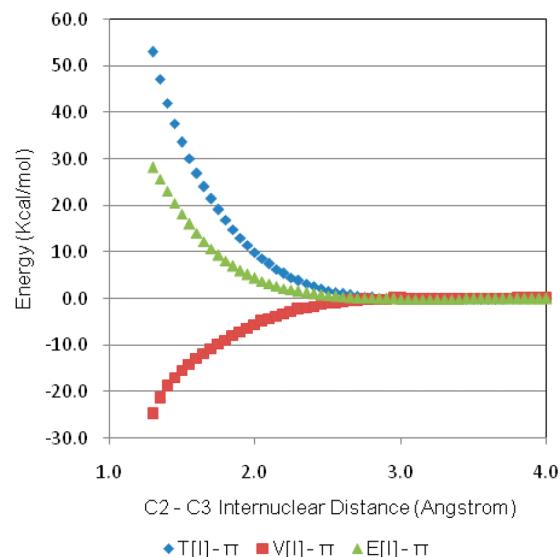


Figure 9. Partitioning of the interference energy in its kinetic $T[I]$ and potential energy $V[I]$ contributions for the π electrons along the C2–C3 bond-breakage path.

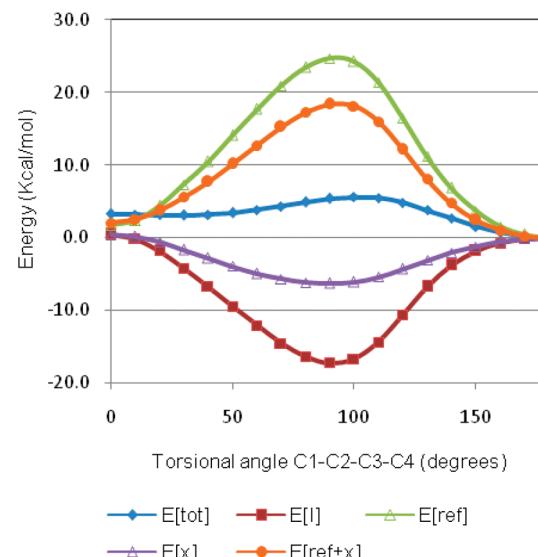


Figure 10. Energy partitioning and conformational analysis of rotation along the C1–C2–C3–C4 torsional angle.

contrary, interference between the p-like orbitals centered in these atoms actually *increases the energy by removing electron density from the region between the two atoms*. It would be reasonable to speculate, then, that the interference energy $E[I]$ should decrease (increase in magnitude) as one leaves the planar geometry along the C1–C2–C3–C4 torsional angle, while the corrected quasi-classical energy $E[\text{ref}+\text{x}]$ should increase faster, causing the formation of the rotational barrier. This is precisely what happens, as can be seen in Figure 10, where all energy contributions are shown relative to those for the *s-trans* conformation:

Rotation along the all-carbon torsional angle presents four distinct extreme points: two minima, corresponding to the *s-trans* conformation, at 180°, and a *gauche* conformation, at about 30°, and two maxima, corresponding to the *s-cis* conformation at 0° and another *gauche* conformation at about 100°.

As can be seen in Figure 11, the origin of the drop observed in the interference energy profile $E[I]$ as the molecule leaves its planar geometry is attributable to a corresponding drop in the interference energy profile of the π electron group, caused

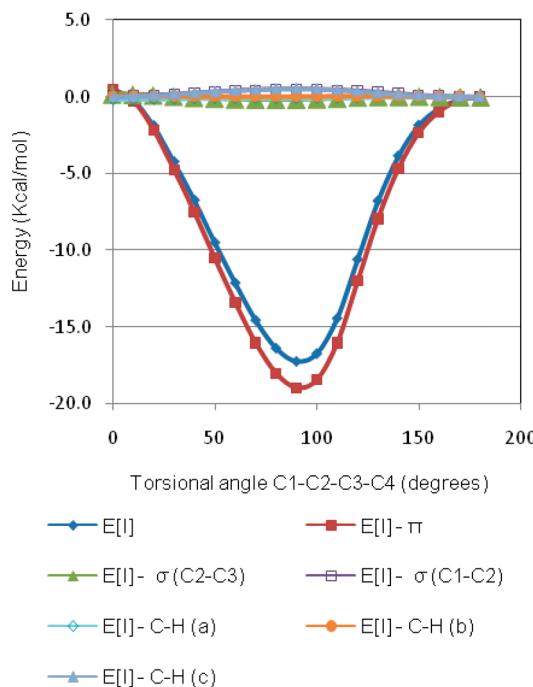


Figure 11. Partitioning of the total interference energy in its contributions by an electron group along the C1–C2–C3–C4 torsional angle.

by the loss of conjugation between π bonds, which reduces the positive (destabilizing) cross-bond contributions (see also Table 3), and consequently increases $E[I]$ in the module. As expected, the interference contributions from other bonds do not change appreciably during rotation. It is important to emphasize that we use the term “conjugation” here strictly in the sense of the alternation of single and double bonds in a plane, with no electron delocalization implied.

The rotational barrier has its origin in the reference energy $E[\text{ref}]$, a quantity composed of many mutually canceling intragroup and intergroup terms that can vary greatly along the rotation path. Assigning a particular effect to explain the barrier formation becomes tentative at best, making it difficult to ascertain whether a given quasi-classical model for the barrier is correct. Nevertheless, we proceed with a simple analysis that appears to reveal an important aspect of the problem.

We first partition the reference energy $E[\text{ref}]$ into its kinetic and potential contributions, as shown in Figure 12. The variations of the total reference potential energy $V[\text{ref}]$ along the rotational path are greatly surpassed in importance by the variation of the total reference kinetic energy $T[\text{ref}]$, which has a profile qualitatively similar to that of $E[\text{ref}]$.

The quantity $T[\text{ref}]$ has an important characteristic in that its value depends only on the form of the orbitals, being a functional of the quasi-classical density obtained by the simple sum of the squares of orbitals. Hence, the dramatic rise of the reference energy as the molecule distorts to an out-of-plane geometry comes, forcefully, from some important distortion in orbital shape. To identify the origin of the change in $T[\text{ref}]$, we have plotted the variations of the reference kinetic energy of each electron group along the torsional rotation path, as can be seen in Figure 13.

Despite the large number of different contributions to $T[\text{ref}]$, the change in the quasi-classical kinetic energy of the π electron group is clearly the most important one, and the only one contributing significantly to the increase of the quasi-classical kinetic energy. Thus, even though there is no density delocal-

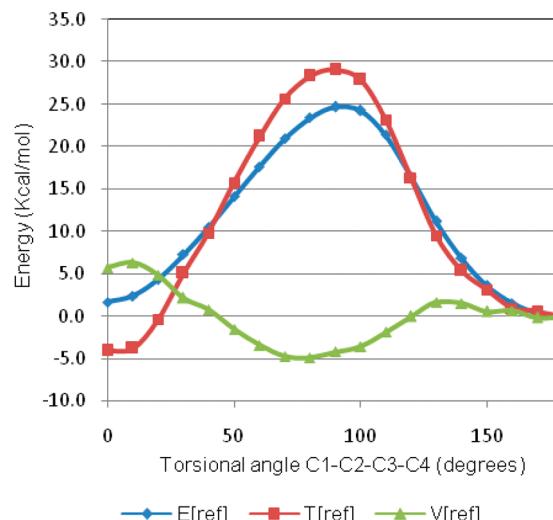


Figure 12. Partitioning of the reference energy in its kinetic and potential energy contributions along the C1–C2–C3–C4 torsional angle.

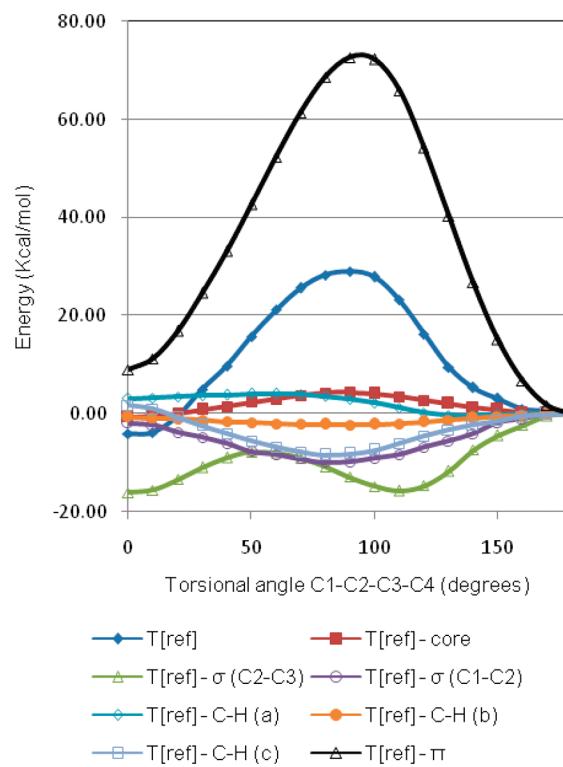


Figure 13. Partitioning of the reference kinetic energy in its contributions by electron group along the C1–C2–C3–C4 torsional angle.

ization in butadiene, electrons participating in the π bonds of butadiene appear to have an important role in shaping the rotational barrier by means of some quasi-classical effect involving orbital change, such as polarization. Further investigation is needed to obtain a better understanding of the problem.

Conclusions

The concept of bond delocalization was found to be unsuitable for the description of conjugated compounds like 1,3-butadiene. The results obtained demonstrate that orbital interference actually removes density from the middle C–C bond, making the two π bonds in 1,3-butadiene more localized, not less. This effect is shown to increase the energy, instead of lowering it

and is not responsible for any extra stabilization of the molecule. The previous attribution of a role to delocalization in butadiene originated from a simplistic reasoning in terms of resonance structures.

The energy lowering induced by interference is, quantitatively, the most important contribution to the formation of the potential well along the C2–C3 bond stretching coordinate of the 1,3-butadiene molecule. However, due to the flatness of the interference profile near the C2–C3 equilibrium distance, the quasi-classical contributions are the deciding factor in establishing the final bond length. The mechanism for the C2–C3 bond formation is analogous to that reported for H₂ and H₂⁺, with interference promoting a kinetic energy drop accompanied by a smaller increase in the potential energy. On the other hand, interference between orbitals involved in different π bonds raises the energy by increasing the kinetic energy, while decreasing the potential energy by a smaller amount.

The rotational barrier along the torsional angle C1–C2–C3–C4 in 1,3-butadiene is a consequence of quasi-classical changes of the energy and not of any quantum mechanical delocalization. In fact, the stabilizing contribution of the interference energy increases as the molecule leaves a planar conformation. The quasi-classical kinetic energy change experienced by the π electrons might be a sign that orbital polarization plays a role in the formation of the rotational barrier, though this has yet to be confirmed.

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Supporting Information Available: Equations of the GPF-EP method, as well as tables containing all contributions for the equilibrium geometries of ethylene and *s-trans*-1,3-butadiene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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