

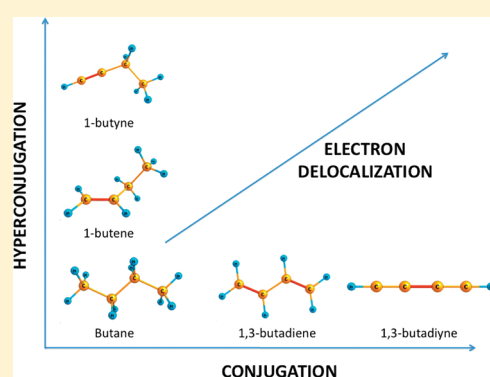
# Understanding Conjugation and Hyperconjugation from Electronic Delocalization Measures

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## S Supporting Information

**ABSTRACT:** The concepts of conjugation and hyperconjugation play an important role to provide an explanation for several fundamental phenomena observed in organic chemistry. Because these effects cannot be directly measured experimentally, their assessment became a primary concern for chemists from the very beginning. In general, the stabilization produced by both phenomena has been studied by means of isodesmic reactions and energy based analysis such as the energy decomposition analysis. In recent years, electronic delocalization measures have been successfully applied to elucidate the nature of chemical bonding and the aromatic character of all kind of molecules. Because conjugation and hyperconjugation stabilizations are strongly linked to the concept of electron delocalization, this paper will give an account of both effects from the point of view of electronic delocalization measures calculated within the framework of the quantum theory of atoms in molecules.

In particular, we focus our attention in the controversial case of the stabilization by conjugation in 1,3-butadiene and 1,3-butadiyne. Unexpectedly, theoretical calculations based on the scheme proposed by Kistiakowsky to quantify the extent of stabilization due to conjugation predicted that the conjugation of 1,3-butadiyne was zero. Subsequent energetic analyses contradicted this observation. These studies pointed out the presence of hyperconjugation stabilization in the hydrogenated product of 1,3-butadiyne and 1,3-butadiene that were used as reference systems in the Kistiakowsky's scheme. Consequently, the extra stabilization of 1-butyne due to hyperconjugation hides the stabilization by conjugation of 1,3-butadiyne. Our results based on electron delocalization measures confirm both the presence of conjugation in 1,3-butadiene and 1,3-butadiyne and hyperconjugation stabilization in their respective hydrogenated products, 1-butene and 1-butyne.



## 1. INTRODUCTION

The concepts of conjugation and hyperconjugation have been extensively employed to rationalize the structure, stability, and reactivity of several organic compounds. Conjugation basically involves interactions between  $\pi$ -orbitals, although its definition has been extended to p-orbitals to cover lone pair interactions with the  $\pi$ -system. The concept of hyperconjugation, which was introduced by Mulliken in 1939, accounts for the interaction between two orbitals with  $\pi$ -symmetry where one or both of them come from a saturated moiety.<sup>1,2</sup> It can also be defined as the interaction between the orbitals involved in a  $\sigma$ -bond (usually C–H or C–C) with those related to an adjacent  $\pi$ -bond (usually C=C) or another  $\sigma$ -bond. Both conjugation and hyperconjugation effects lead to stabilizing interactions that influence the geometry, electron density, dissociation energies, or nuclear magnetic resonance properties among many other physicochemical observables.<sup>3</sup> For instance, it has been shown that hyperconjugation effects are decisive to explain C–H bond dissociation energy differences in alkanes.<sup>4</sup>

Despite their importance and widespread use, neither conjugation nor hyperconjugation can be experimentally directly measured. Therefore, many theoretical works have been devoted to find methodologies that can help us to study the role played by these effects. Thus, several tools have been used to characterize them, including isodesmic reactions,<sup>5–9</sup> energy decomposition analyses (EDA),<sup>10–16</sup> valence bond theory,<sup>17,18</sup> the Laplacian of the charge density and the ellipticity as derived from the atoms-in-molecules theory,<sup>19,20</sup> natural bond orbital (NBO) analyses,<sup>21,22</sup> the concept of protobranching,<sup>23</sup> and the block-localized wave function (BLW) method.<sup>23,24</sup> The use of isodesmic reactions may lead to contradicting results (see for instance refs 21 and 16) because in isodesmic reactions it is difficult to isolate the conjugation

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and hyperconjugation stabilizations from other effects.<sup>8,13,14,23,25–27</sup> In addition, different isodesmic reactions may provide significantly different results for the same species.<sup>25</sup> These drawbacks have been partially solved by the EDA that allows a direct estimation of conjugation and hyperconjugation effects by analyzing the interaction energy between different fragments of the molecule<sup>13,14</sup> and by NBO and BLW approaches. Although the electron conjugation is represented by the electronic delocalization along the  $\pi$ -system, there have been very few attempts to address this effect from electron delocalization measures. In this context, Bader and co-workers proposed to analyze the electron density at a bond critical point to study conjugation and hyperconjugation effects of C–C bonds in hydrocarbons.<sup>19</sup>

One of the most striking examples of the conjugation and hyperconjugation effects shows in the analysis of the  $\pi$ -conjugation stabilization in polyenes and polyynes. In 1936, Kistiakowsky proposed a method to evaluate the conjugation stabilization of 1,3-butadiene that consists on the calculation of the energy difference between its two hydrogenation steps.<sup>28</sup> In 2003, Rogers et al. applied Kistiakowsky's scheme to quantify the conjugation stabilization of 1,3-butadiyne.<sup>26</sup> Unexpectedly, they found that the stabilization produced by two conjugated triple bonds was zero. This finding triggered subsequent energetic studies that analyzed the connection between conjugation and hyperconjugation effects in the two hydrogenation steps proposed by Kistiakowsky.<sup>8,13</sup> These works concluded that Kistiakowsky's scheme is not adequate to determine conjugation energy in butadiynes because it does not take into account the role of hyperconjugation in 1-butyne, the first hydrogenated product.

In this work, we put forward a new method to quantify conjugation and hyperconjugation effects from electron delocalization measures. Unlike isodesmic reactions, the method proposed in the present work does not rely on reference systems. The method is applied to compare the strengths of  $\pi$ -conjugation stabilization in 1,3-butadiene and 1,3-butadiyne, to refute Rogers' observation, and to corroborate the results of Houk<sup>8</sup> and Frenking<sup>13</sup> from the electron delocalization viewpoint. Subsequently, the role played by hyperconjugation in 1-butene and 1-butyne is discussed. We anticipate here that our results show that there is a good correlation between the results from EDA and those derived from electron delocalization measures.

## 2. METHODOLOGY

The analysis of the electronic distribution in molecules has occupied a central position in chemistry since the seminal work of Lewis.<sup>29</sup> After the advent of quantum mechanics, the quantification of electron delocalization became one of the challenges for theoretical chemists to characterize the electronic structure of molecules. Electron delocalization plays a prominent role in several fundamental phenomena such as chemical bond and aromaticity.<sup>30</sup> These phenomena are important to explain the structure, stability, magnetic properties, and reactivity of several organic and inorganic compounds.<sup>31</sup> Coulson was one of the first who used quantum mechanics to calculate the extent of electron delocalization between two regions of the molecule to unravel the electronic structure of some polyenes and aromatic molecules.<sup>32</sup> The electron delocalization is linked to the classical notion of bond order, which has evolved to the concept of electron sharing index (ESI), one of the most used electronic structure descriptors to characterize the interaction between

pairs of atoms. The most popular measures of electron delocalization use two-electron quantities such as the pair-density, the conditional probability, or the exchange–correlation density (XCD).<sup>33</sup> The work of Wiberg,<sup>34</sup> was the first to define an ESI based on the XCD. In a landmark paper of 1975, Bader and Stephens<sup>35</sup> described how the XCD can be used to quantify the delocalization or sharing of electrons over different regions of the molecular space; this measure was going to be called the delocalization index (DI) by Fradera, Austen, and Bader in 1999.<sup>36</sup> The DI is obtained by double integration of the XCD ( $\Gamma_{XC}(\vec{r}_1, \vec{r}_2)$ ) over the regions of atoms A and B:

$$\delta(A,B) = -2 \int_A \int_B \Gamma_{XC}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (1)$$

Other definitions of ESIs are available in the literature, related in one way or another to the original definition of the DI by Bader and Stephens.<sup>37–43</sup> The calculation of the ESI needs a scheme to define the domains of the atoms in the molecule. In this study we will use the quantum theory of atoms in molecules (QTAIM) molecular space partition introduced by Bader,<sup>44</sup> which defines the atomic regions from the condition of zero-flux gradient in the density.

For monodeterminantal closed-shell wave functions the DI reads

$$\delta(A,B) = 4 \sum_{i,j}^{\text{occ.MO}} S_{ij}(A) S_{ij}(B) \quad (2)$$

The summations in eq 2 run over all occupied molecular orbitals.  $S_{ij}(A)$  is the overlap between molecular orbitals  $i$  and  $j$  within the basin of atom A.  $\delta(A,B)$  provides a quantitative idea of the number of electrons delocalized or shared between atoms A and B, and they are strictly positive for single-determinant wave functions. To study the effect of  $\pi$ -conjugation on the electron delocalization, we split the value of the DI into  $\sigma$  and  $\pi$  components. This separation is only strictly possible for planar systems with only  $\sigma$ - and  $\pi$ -occupied orbitals where  $S_{\sigma\pi}(A) = 0$  and, thus,  $\delta(A,B)$  can be exactly split into  $\sigma$  and  $\pi$  contributions.

$$\delta(A,B) = \delta_{\sigma}(A,B) + \delta_{\pi}(A,B) \quad (3)$$


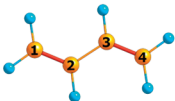
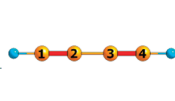
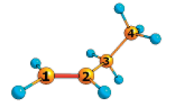
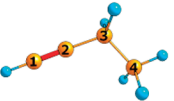
The definition of DI can also be extended to analyze the amount of electrons shared between more than two regions. These are called multicenter indices and they were defined by Giambiagi and co-workers<sup>45</sup> and extended to QTAIM by Boicichio et al.<sup>46</sup> For the conjugation and hyperconjugation analysis we are interested in four-center delocalization indices (4c-DIs), which at the monodeterminantal closed-shell level read

$$\delta(A,B,C,D) = 16 \sum_{i,j,k,l}^{\text{occ.MO}} S_{ij}(A) S_{jk}(B) S_{kl}(C) S_{li}(D) \quad (4)$$

Planar species also allow for an exact separation of  $\sigma$  and  $\pi$  contributions of these multicenter indices. Unlike their two-component counterparts at the monodeterminantal level, 4c-DIs can take either positive or negative values.

In last years, the use of multicenter indices has gained popularity as a tool to study the nature of chemical bonding and to analyze aromaticity.<sup>47–49</sup> Multicenter indices have been used to differentiate between three-center two-electron (3c–2e) and three-center four-electron (3c–4e) interactions; the 3c–2e bond takes positive 3c-DI values, whereas 3c–4e shows negative 3c-DIs.<sup>50</sup> Moreover, multicenter indices perform remarkably

**Table 1.** Values of Two-Center Delocalization Indices (2c-DI) and Four-Center Delocalization Indices (4c-DI) for Butane, 1,3-Butadiene, 1,3-Butadiyne, 1-Butene, and 1-Butyne Calculated at the B3LYP and CCSD Levels of Theory<sup>a</sup>

Conjugation	butane		1,3-butadiene		1,3-butadiyne		1-butene		1-butyne	
										
<b>2c-DI</b>	B3LYP	CCSD	B3LYP	CCSD	B3LYP	CCSD	B3LYP	CCSD	B3LYP	CCSD
$\delta(C_1-C_2)$	0.993	0.840	1.769	1.426	2.608	2.074	1.837	1.458	2.744	2.145
$\delta_\pi(C_1-C_2)$			0.768		1.672					
$\delta(C_1-C_3)$	0.049	0.038	0.078	0.046	0.102	0.059	0.069	0.047	0.080	0.047
$\delta_\pi(C_1-C_3)$			0.037		0.073					
$\delta(C_1-C_4)$	0.012	0.007	0.114	0.053	0.212	0.082	0.025	0.013	0.031	0.016
$\delta_\pi(C_1-C_4)$			0.107		0.211					
$\delta(C_2-C_3)$	0.976	0.827	1.122	0.943	1.300	1.081	1.016	0.863	1.064	0.896
$\delta_\pi(C_2-C_3)$			0.175		0.359					
$\delta(C_2-C_4)$	0.049	0.038	0.078	0.046	0.102	0.059	0.057	0.045	0.064	0.051
$\delta_\pi(C_2-C_4)$			0.037		0.073					
$\delta(C_3-C_4)$	0.993	0.840	1.769	1.426	2.608	2.074	0.983	0.834	0.975	0.830
$\delta_\pi(C_3-C_4)$			0.768		1.672					
$d(C_2-C_3)$	1.533	1.532	1.456	1.469	1.365	1.385	1.503	1.508	1.461	1.474
<b>4c-DI</b>										
$\delta(C_1-C_2-C_3-C_4)$	-0.0045	-0.0034	-0.0798	-0.0452	-0.1678	-0.0929				
$\delta_\pi(C_1-C_2-C_3-C_4)$			-0.0775		-0.1675					

<sup>a</sup> For planar systems, 2c-DI and 4c-DI have been split into their  $\sigma$  and  $\pi$  contributions, only  $\delta_\pi$  values are given.  $d(C_2-C_3)$  is the bond distance between  $C_2$  and  $C_3$ . DI are given in electrons and distances in angstroms.

well as aromaticity descriptors. In particular, they were used to describe the aromaticity of all-metal clusters.<sup>51,52</sup>

In some particular cases, we have computed DIs and 4c-DIs at the correlated level with CCSD method. CCSD pair density matrix and higher-body matrices are not generally N-representable, and therefore, to obtain the correlated versions of the DIs and multicenter indices, we have performed the following substitution in eqs 2 and 4:

$$S_{ij}(A) \rightarrow \frac{\sqrt{n_i n_j} S_{ij}^{\text{NO}}(A)}{2} \quad (5)$$

where  $S_{ij}^{\text{NO}}(A)$  is now the atomic overlap matrix (AOM) of atom A in terms of natural orbitals and the summations in eqs 2 and 4 run over the whole set of natural orbitals, instead of only the occupied molecular orbitals. This substitution is an approximation of the actual quantities, which is reasonably good in the DI case.<sup>53</sup> To the best of our knowledge it has not been tested yet for 4c-DIs.

In the last part of this work, the electron delocalization between two different fragments of the molecule has been analyzed. Two or more atoms in the molecule define the fragments. The same eqs 2 and 4 are used to calculate DIs and multicenter indices for molecular fragments ( $F_1 = A_1, \dots, A_n$ ) by only replacing the atomic overlaps,  $S_{ij}(A)$ , by the appropriate fragment overlaps:

$$S_{ij}(F_1) = \sum_k^n S_{ij}(A_k) \quad (6)$$

To our knowledge this is the first time that a measure of delocalization between fragments based on DIs is employed.

### 3. COMPUTATIONAL DETAILS

All calculations have been performed with the Gaussian 03 package.<sup>54</sup> The optimized geometries have been obtained in the framework of density-functional theory (DFT) using the B3LYP<sup>55</sup> functional, which combines the three-parameter Becke's exchange nonlocal functional<sup>56</sup> and the Lee–Yang–Parr's correlation nonlocal functional.<sup>57</sup> The 6-311++G(d,p) basis set has been used for all calculations.<sup>58,59</sup> In some cases, we have also performed CCSD/6-311++G(d,p) calculations to obtain optimized geometries at correlated level.

Calculation of atomic overlap matrices (AOM) and computation of DIs and four-center electron sharing indices (4c-ESI) have been performed with the AIMPAC<sup>60</sup> and ESI-3D<sup>61</sup> collection of programs.<sup>62</sup> Calculation of these DIs with the density functional theory (DFT) cannot be performed exactly because the electron-pair density is not available at this level of theory.<sup>63</sup> As an approximation, we have used the Kohn–Sham orbitals obtained from a DFT calculation to compute Hartree–Fock-like DIs through eq 2. In practice the values of the DIs obtained using this approximation are generally closer to the Hartree–Fock values than correlated DIs obtained with a configuration interaction method.<sup>53</sup>

### 4. RESULTS AND DISCUSSION

In 1936, Kistiakowsky and co-workers proposed a method for quantifying the stabilization energy due to conjugation of polyenes based on the calculation of the difference between the heat of hydrogenation obtained when going from 1,3-butadiene to



1-butene and from 1-butene to butane.<sup>28</sup> Because 1,3-butadiene is stabilized by conjugation, the energy released in the first step should be significantly lower than in the second hydrogenation step. In 2003, Rogers et al. decided to apply Kistiakowsky's scheme to analyze the  $\pi$ -conjugation stabilization in 1,3-butadiene and larger extended polyynes from the theoretical point of view.<sup>26,27</sup> In principle, one expects higher  $\pi$ -conjugation stabilization in 1,3-butadiene than in 1,3-butadiyne but, surprisingly, they found that the stabilization due to conjugation in polyynes was almost zero. Consequently, a lengthy debate started trying to elucidate the reason for the lack of stabilization due to conjugation in 1,3-butadiyne.<sup>8,13,27</sup> First, one must bear in mind that Kistiakowsky's scheme does not take into account phenomena such as nuclear and electronic reorganization or hyperconjugation. Subsequent energetic studies analyzed the connection between conjugation and hyperconjugation effects, concluding that Kistiakowsky's scheme is not a reliable way to determine conjugation energy in butadiynes because it does not account for the hyperconjugation stabilization of 1-butyne. Therefore, when Kistiakowsky's scheme is used, the strength of hyperconjugation of 1-butyne hides the conjugation stabilization of 1,3-butadiyne. The calculation of the stabilization by conjugation of 1,3-butadiene is also affected by this phenomenon, but the hyperconjugation of 1-butene is lower than in 1-butyne and does not compensate the conjugation stabilization as it does in butadiynes. To sum up, Rogers and co-workers found that 1,3-butadiene is significantly more stabilized by  $\pi$ -conjugation than 1,3-butadiyne, whereas analyses based on isodesmic reactions,<sup>8</sup> proto-branching,<sup>23</sup> and EDA<sup>13</sup> methods show the opposite trend. In addition, in certain agreement with Rogers results, anisotropy of the induced current density (ACID) calculations predict lower conjugation stabilization for 1,3-butadiyne with respect to 1,3-butadiene, although the strength of conjugation assigned to 1,3-butadiyne is not zero.<sup>64</sup>

Can the electron delocalization measures help us to assess the controversial topic of  $\pi$ -conjugation stabilization in butadienes and butadiynes? This question will be addressed in the Results and Discussion, which lays out as follows. First, we analyze the consequences of  $\pi$ -conjugation stabilization in conjugated 1,3-butadiene and 1,3-butadiyne systems, and second, we discuss the effect of hyperconjugation for their respective hydrogenated products, i.e., 1-butene and 1-butyne. Finally, we propose a new way to analyze the strength of  $\pi$ -conjugation in polyenes and polyynes by analyzing the  $\pi$ -electron delocalization.

#### A. Conjugation in 1,3-Butadiene and 1,3-Butadiyne.

*I. Decreasing the Saturation: Butane—1,3-Butadiene—1,3-Butadiyne.* Table 1 provides the values of DIs between different carbons of the molecule obtained at the B3LYP and CCSD levels of theory. First we will focus on the analysis of bonded pairs of atoms. As shown in Table 1, the electron delocalization between  $C_1$  and  $C_2$  increases when going from butane to 1,3-butadiyne, i.e., 0.993, 1.769, and 2.608 e. Obviously, this increment of electron sharing can be associated with the transition from a single bond in butane to a triple bond in 1,3-butadiyne. To assess the effect of conjugation, the electron delocalization between the central  $C_2$ — $C_3$  single bond gives us relevant information. It can be seen from the values of Table 1 that the number of electrons shared,  $\delta(C_2, C_3)$ , increases from butane to 1,3-butadiyne, 0.976, 1.122, and 1.300 e. These results correlate well with the decrease of the  $C_2$ — $C_3$  distance when the saturation of the system is reduced. The DI values obtained at the CCSD level of theory (Table 1) confirm the

previous trends observed at the B3LYP level. The inclusion of electron correlation leads to significant decrease of DI values, as it was previously observed by comparing CISD and B3LYP values.<sup>53</sup> In the case of planar systems such as 1,3-butadiene and 1,3-butadiyne one can isolate the  $\pi$ -delocalization associated with  $\pi$ -conjugation stabilization from the rest of the effects. As above shown by DI values, when the saturation of the system is reduced, the  $\delta_\pi(A, B)$  contribution predicts an increment of electron delocalization either in  $\delta_\pi(C_1, C_2)$  or in  $\delta_\pi(C_2, C_3)$ . In all the cases, the number of electrons delocalized is higher in 1,3-butadiyne than in 1,3-butadiene. In contrast to the observations of Rogers and co-workers based on Kistiakowsky's scheme, the increase of electron sharing can be related to the strengthening of conjugation when going from butane to 1,3-butadiyne. Consequently, DIs indicate that conjugation in 1,3-butadiyne is more important than in 1,3-butadiene. This observation is in agreement with EDA and BLW analysis,<sup>13,23</sup> but in contradiction with ACID results.<sup>64</sup>

Next, we study nonbonding interactions in these species; with the results summarized in Table 1. In the case of butane, we observe a progressive decrease of electron delocalization when going from  $\delta(C_1, C_2)$  to  $\delta(C_1, C_3)$  and to  $\delta(C_1, C_4)$ , 0.993, 0.049, and 0.012 e, respectively, associated with the increment of distance between carbons. Interestingly, in the cases of 1,3-butadiene and 1,3-butadiyne, the electron delocalization in  $C_1$ — $C_4$  is larger than that in  $C_1$ — $C_3$ , 0.114 e vs 0.078 e in the former and 0.212 e vs 0.102 e in the latter. This is reminiscent of benzene, which showed more electrons shared between atoms in para position than in meta position.<sup>37,65,66</sup> In addition, the amount of electron sharing between  $C_1$ — $C_4$  is almost twice in 1,3-butadiyne than in 1,3-butadiene (0.212 e vs 0.114 e). Thus, there are more electrons shared between the terminal carbons of the molecule when we have two conjugated triple bonds than when two double bonds are connected by a single C—C bond. These results agree with resonance stabilization calculations of Kollmar that show that the stabilization is nearly double in 1,3-butadiyne than in 1,3-butadiene.<sup>67</sup> In addition, EDA calculations assigned a conjugation stabilization of  $-45.0$  kcal/mol for 1,3-butadiyne and  $-19.5$  kcal/mol for 1,3-butadiene.<sup>13</sup>

*II. Conjugated versus Unconjugated Systems.* To deepen our understanding of the consequences of conjugation in 1,3-butadiene and 1,3-butadiyne, we compare these conjugated systems with their hydrogenated products, i.e., 1-butene and 1-butyne (Table 1). First, we focus our attention on bonded pairs of atoms. As can be seen from Table 1, there are more electrons delocalized between  $C_1$  and  $C_2$  in the case of 1-butene and 1-butyne than in their conjugated analogues. This result may be explained by the fact that electrons are more localized in the double bond region of 1-butene and 1-butyne than in 1,3-butadiene and 1,3-butadiyne, where the electrons are delocalized through the other carbons of the molecule due to the effect of conjugation. The same conclusion can be extracted from the analysis of  $\delta(C_2, C_3)$ , because the electrons are more delocalized in conjugated molecules than in their nonconjugated analogues (the value of the DI is higher in the former than in the latter as Table 1 shows). In the four cases, the value of  $\delta(C_2, C_3)$  is larger than in butane. In contrast to conjugated molecules, in 1-butene and 1-butyne the value of DIs progressively decrease when going from  $\delta(C_1, C_2)$  to  $\delta(C_1, C_4)$ . The value of  $\delta(C_1, C_4)$  is about 4 times larger in 1,3-butadiene than in 1-butene, but it is 8 times larger in 1,3-butadiyne than in 1-butyne.

*III. Analysis of Conjugation from Multicenter Indices.* In  $\pi$ -conjugated 1,3-butadiene and 1,3-butadiyne electrons are delocalized

**Table 2.** Values of Two-Center Delocalization Indices (2c-DI) and Four-Center Delocalization Indices (4c-DI) for Butane, 1-Butene, and 1-Butyne Calculated at the B3LYP and CCSD Levels of Theory<sup>a</sup>

Hyperconjugation	butane		1-butene		1-butyne	
2c-DI	B3LYP	CCSD	B3LYP	CCSD	B3LYP	CCSD
$\delta(\text{C}_1\text{--H}_5)$	0.009	0.008	0.014	0.012	0.029	0.015
$\delta(\text{C}_1\text{--H}_6)$	0.009	0.008	0.024	0.013	0.029	0.015
$\delta(\text{C}_1\text{--C}_3)$	0.049	0.038	0.069	0.047	0.080	0.047
$\delta(\text{C}_1\text{--C}_4)$	0.012	0.007	0.025	0.013	0.031	0.016
$\delta(\text{C}_2\text{--H}_5)$	0.042	0.033	0.043	0.034	0.054	0.043
$\delta(\text{C}_2\text{--H}_6)$	0.042	0.033	0.048	0.038	0.054	0.043
$\delta(\text{C}_2\text{--C}_3)$	0.976	0.827	1.016	0.863	1.064	0.896
$\delta(\text{C}_2\text{--C}_4)$	0.049	0.038	0.057	0.045	0.064	0.051
4c-DI						
$\delta(\text{C}_1\text{--C}_2\text{--C}_3\text{--C}_4)$	-0.0045	-0.0034	-0.0133	-0.0085	-0.0182	-0.0114
$\delta(\text{C}_1\text{--C}_2\text{--C}_3\text{--H}_5)$	-0.0005	-0.0003	-0.0013	-0.0009	-0.0191	-0.0121
$\delta(\text{C}_1\text{--C}_2\text{--C}_3\text{--H}_6)$	-0.0005	-0.0003	-0.0142	-0.0092	-0.0191	-0.0121

<sup>a</sup> DI units are electrons.

among four carbon atoms, and thus 4c-DI seems to be an ideal tool to evaluate the strength of conjugation in such systems. Table 1 lists the results obtained for butane, 1,3-butadiene, and 1,3-butyne. As expected, we observe an increase of  $\delta(\text{C}_1\text{C}_2\text{C}_3\text{C}_4)$  when going from butane to 1,3-butyne. Interestingly, butane presents a value of  $\delta(\text{C}_1\text{C}_2\text{C}_3\text{C}_4)$  close to zero ( $-0.0045$  e) because this molecule is not stabilized by  $\pi$ -conjugation and, thus, only few electrons are delocalized among the four carbons of the molecule. On the other hand, conjugated 1,3-butadiene and 1,3-butyne molecules show values of  $-0.0798$  and  $-0.1678$  e. Remarkably, the amount of electron delocalization among the four carbons in butadiene is twice as large as in butadiene. This result is in agreement with previous energy-based calculations of Kollmar and Cappel et al.<sup>13,67</sup> As Table 1 shows, the values of  $\delta(\text{C}_1\text{C}_2\text{C}_3\text{C}_4)$  and  $\delta_\pi(\text{C}_1\text{C}_2\text{C}_3\text{C}_4)$  are practically the same because almost only  $\pi$ -electrons are delocalized through the four carbons of the chain. The values of  $\delta(\text{C}_1\text{C}_2\text{C}_3\text{C}_4)$  obtained at CCSD level show the same trends as the ones given by B3LYP, although CCSD 4c-DIs are lower as expected.

#### B. Hyperconjugation in 1-Butene and 1-Butyne.

*I. Analysis from Delocalization Indices.* As previously mentioned, the conjugation stabilization of 1,3-butyne calculated using the Kistiakowski's scheme is zero.<sup>26</sup> Jarowski et al. pointed out that the scheme proposed by Kistiakowski does not take into account the hyperconjugation stabilization present in 1-butene and 1-butyne.<sup>8</sup> This extra stabilization of the first hydrogenated products leads to an underestimation of the stabilization produced by conjugation, to the point that this stabilization is zero for 1,3-butyne. In the same paper, Jarowski and co-workers used isodesmic reactions to assign hyperconjugation stabilization of 2.4 and 4.9 kcal/mol for 1-butene and 1-butyne, respectively. However, in isodesmic reactions difficulties arise when we try to isolate the desired effect. Recently, more sophisticated energetic analysis such as EDA, protobranching, and BLW have been used to

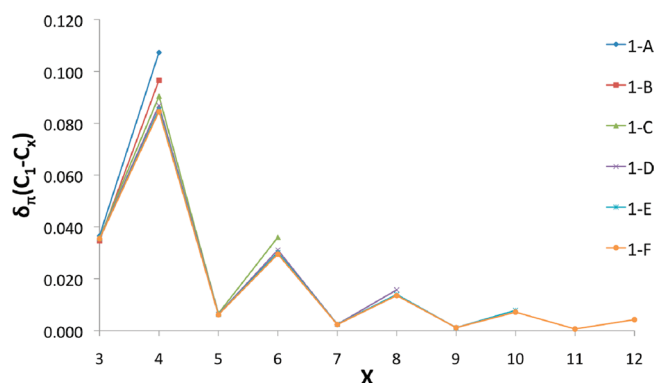
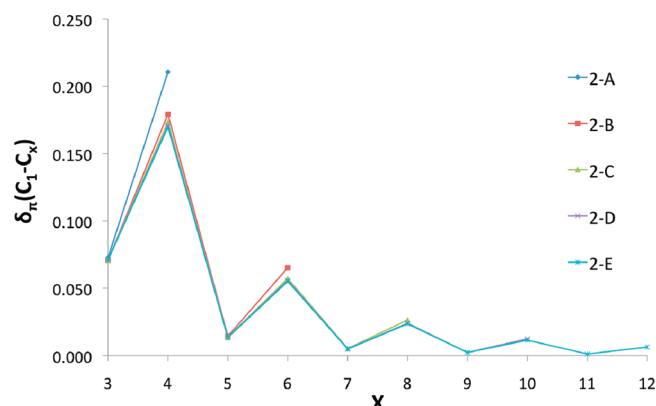
quantify the extent of hyperconjugation in some saturated and unsaturated compounds.<sup>13,14,23</sup> In the second part of this paper, we propose to study the hyperconjugation from the point of view of electron delocalization measures. To assess hyperconjugation in 1-butene and 1-butyne, an analysis of delocalization and multi-center indices has been performed.

Table 2 presents the results obtained from the analysis of the DIs for butane, 1-butene, and 1-butyne. The hyperconjugation stabilization in 1-butene and 1-butyne comes from the interaction between the  $\pi(\text{C}_1\text{--C}_2)$  orbital and the  $\sigma^*(\text{C}_3\text{--H})$  and  $\sigma^*(\text{C}_3\text{--C}_4)$  orbitals as well as from the interaction of the  $\sigma(\text{C}_3\text{--H})$  and  $\sigma(\text{C}_3\text{--C}_4)$  orbitals with the  $\pi^*(\text{C}_1\text{--C}_2)$  orbital. Thus, we analyze the DIs between the carbon atoms implied in the  $\pi$  orbital and carbons and hydrogens that form the  $\sigma$  bonds (Table 2). In all cases, we observe an increase of electron delocalization when going from butane to 1-butene, and from the latter to 1-butyne. For example, the number of electrons delocalized between  $\text{C}_1$  and  $\text{H}_5$  is 0.009 e in butane, 0.014 e in 1-butene, and 0.029 e in 1-butyne. These results can be explained by a stronger interaction between the orbitals of the  $\pi$  system and those of the  $\sigma$  bonds and, thus, an increment of hyperconjugation. Among all DIs, the most interesting value is the DI between  $\text{C}_2$  and  $\text{C}_3$ . Sometimes the presence of hyperconjugation has been linked to structural changes, in particular, the distance between  $\text{C}_2$  and  $\text{C}_3$  becomes shorter when the effect of hyperconjugation is stronger.<sup>3,13,14</sup> This shortening of the  $\text{C}_2\text{--C}_3$  distance provoked by the orbital interaction is typical of hyperconjugation and increases the number of electrons shared between these two regions. Consequently, the value of  $\delta(\text{C}_2\text{C}_3)$  progressively increases from butane to 1-butyne, i.e., 0.976, 1.016, and 1.064 e. According to energetic analysis,<sup>8</sup> stabilization by hyperconjugation is higher in 1-butyne than in 1-butene; the DIs corroborate this trend. However, from the analysis of 2c-DIs

**Table 3.** Values of Two-Center Delocalization Indices (2c-DI),  $\delta(C_1-C_x)$  (Where  $x = 2, \dots, n$ ) and  $\delta(C_2-C_3)$ , for Polyenes Calculated at the B3LYP Level of Theory<sup>a</sup>

	trans-1,3-butadiene (1-A)		cis-1,3-butadiene (1-B)		1,3,5-hexatriene (1-C)		1,3,5,7-octatetraene (1-D)		1,3,5,7,9-decapentaene (1-E)		1,3,5,7,9,11-dodehexaene (1-F)	
	total	$\pi$	total	$\pi$	total	$\pi$	total	$\pi$	total	$\pi$	total	$\pi$
$\delta(C_1-C_2)$	1.769	0.768	1.785	0.783	1.748	0.748	1.740	0.740	1.736	0.737	1.734	0.735
$\delta(C_1-C_3)$	0.078	0.037	0.072	0.035	0.077	0.036	0.077	0.036	0.077	0.035	0.077	0.035
$\delta(C_1-C_4)$	0.114	0.107	0.106	0.097	0.097	0.090	0.093	0.087	0.092	0.085	0.091	0.085
$\delta(C_1-C_5)$					0.008	0.007	0.008	0.006	0.007	0.006	0.007	0.006
$\delta(C_1-C_6)$					0.036	0.036	0.031	0.031	0.030	0.030	0.030	0.030
$\delta(C_1-C_7)$							0.003	0.002	0.002	0.002	0.002	0.002
$\delta(C_1-C_8)$							0.016	0.016	0.014	0.014	0.014	0.014
$\delta(C_1-C_9)$									0.001	0.001	0.001	0.001
$\delta(C_1-C_{10})$									0.008	0.008	0.007	0.007
$\delta(C_1-C_{11})$											0.001	0.001
$\delta(C_1-C_{12})$											0.004	0.004
$\delta(C_2-C_3)$	1.122	0.175	1.102	0.157	1.144	0.194	1.151	0.201	1.155	0.204	1.157	0.205

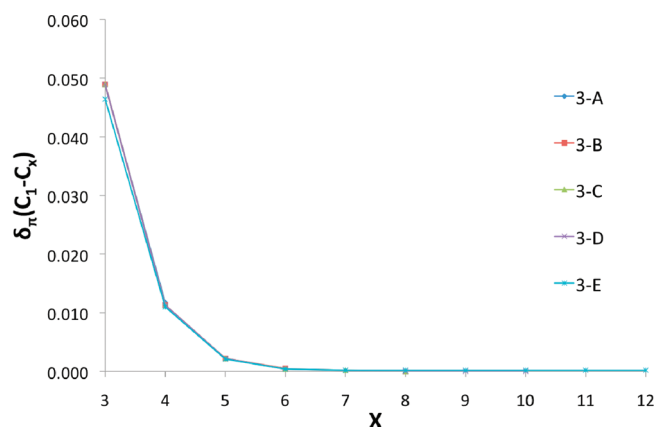
<sup>a</sup> For planar systems, 2c-DI has been split into its  $\sigma$  and  $\pi$  contributions; only  $\delta_\pi$  are listed in this table. DI units are electrons.

**Figure 1.** Evolution of  $\delta_\pi(C_1-C_x)$  (where  $x = 3, \dots, n$ ) in polyenes, from 1,3-butadiene (1-A) to 1,3,5,7,9,11-dodehexaene (1-F). Units are electrons.**Figure 2.** Evolution of  $\delta_\pi(C_1-C_x)$  (where  $x = 3, \dots, n$ ) in polyenes, from 1,3-butadiene (2-A) to 1,3,5,7,9,11-dodehexaene (2-E). See Table S1, Supporting Information, for  $\delta_\pi(C_1-C_x)$  values. Units are electrons.

one cannot isolate the electron delocalization due to hyperconjugation stabilization because this phenomenon involves more than two centers. Thus, higher order electron sharing indices have to be used to assess this effect.

**II. Analysis from Multicenter Indices.** Hyperconjugation in 1-butene and 1-butyne involves both the  $C_1-C_2$  and the  $C_3-H_5$ ,  $C_3-H_6$ , and  $C_3-C_4$  bonds. Because four atoms are involved in any of these interactions, the values of four-center multicenter indices have been calculated and summarized in Table 2. One of the advantages of this method with respect to energy based analyses is that it allows studying separately the hyperconjugation contribution of each C–H or C–C bonds. Let us start with 1,3-butadiene molecule where no hyperconjugation is expected. In this molecule, the  $C_3-H_5$   $\sigma$ - and  $C_1-C_2$   $\pi$ -orbitals are orthogonal and, consequently, hyperconjugation should be zero. According to these expectations, the value of the  $\delta(C_1, C_2, C_3, H_5)$  (not shown in Table 2) is practically zero,  $-0.0009$  e, indicating no electron delocalization among these four atoms. In contrast to

1,3-butadiene, 1-butene and 1-butyne present hyperconjugation. In 1-butyne, where the strength of the hyperconjugation effect is expected to be larger, the values of  $\delta(C_1, C_2, C_3, H_5)$  are  $-0.0191$  e for each C–H  $\sigma$  bond, whereas the interaction between  $C_1-C_2$  and  $C_3-C_4$  bonds,  $\delta(C_1, C_2, C_3, C_4)$ , gives a value of  $-0.0182$  e. These results show that the C–H and C–C bonds practically contribute the same to the electron delocalization due to hyperconjugation effect. Cappel and co-workers observed the same trends by means of EDA analysis when comparing the strengths of hyperconjugation stabilization of C–H ( $-20.1$  kcal/mol) and C–C ( $-20.6$  kcal/mol) bonds in propyne and 3,3-dimethyl-1-butyne, respectively.<sup>13</sup> On the other hand, 1-butene is not symmetric and, therefore, both C–H bonds do not equally contribute to the hyperconjugation stabilization. Interestingly, the  $C_3-H_5$   $\sigma$  bond is almost orthogonal to the  $\pi$   $C_1-C_2$  bond. Therefore, the value of the  $\delta(C_1, C_2, C_3, H_5)$  is  $-0.0013$  e showing almost no electron delocalization among these four centers. On the contrary, the remaining  $C_3-H_6$



**Figure 3.** Evolution of  $\delta_{\pi}(C_1, C_x)$  (where  $x = 3, \dots, n$ ) in  $n$ -alkanes, from  $n$ -butane (3-A) to  $n$ -dodecane (3-E). See Table S2, Supporting Information, for  $\delta_{\pi}(C_1, C_x)$  values. Units are electrons.

$\sigma$ -bond is better oriented to interact with the  $C_1$ – $C_2$   $\pi$ -bond as the value of  $-0.0142$  e for the  $\delta(C_1, C_2, C_3, H_6)$  shows. In addition, the value of  $\delta(C_1, C_2, C_3, C_4)$  is  $-0.0133$  e, which is significantly lower than the one found in 1-butyne. As previously expected, these results show that the strength of hyperconjugation in 1-butyne is larger than in 1-butene. Finally, the strength of the hyperconjugation in butane is much weaker, as indicated from the values of  $\delta(C_1, C_2, C_3, H_5)$  and  $\delta(C_1, C_2, C_3, C_4)$ , i.e.,  $-0.0005$  e for C–H and  $-0.0045$  e for C–C bonds. Thus, electronic multicenter indices represent a good tool to characterize the strength of hyperconjugation.

**C. Conjugation in Large Polyenes and Polyynes.** A few methods have been proved useful to evaluate the strength of conjugation without taking into account reference compounds or isodesmic reactions. Recently, Fernández and Frenking<sup>14</sup> proposed a direct measure of the energy of stabilization due to conjugation based on EDA analyses.<sup>10–12</sup> This methodology consists in dividing the molecule into different fragments and analyzing the interaction energy between them. The total interaction energy can be expressed as the sum of three different contributions:  $\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}$ , which are electrostatic attraction, Pauli repulsion, and orbital interaction energies, respectively. The latter term in planar systems can be split into  $\sigma$ - and  $\pi$ -contributions. Because  $\pi$ -conjugation is characterized by the interaction of  $\pi$ -orbitals, they suggest using the values of  $\Delta E_{\pi}$ , which arise from the interacting fragments, as a measure of the strength of conjugation. The performance of this method was studied with satisfactory results for large polyenes, from 1,3-butadiene to *all-trans*-1,3,5,7,9-decapentene, and for some silicon compounds analogues of 1,3-butadiene.<sup>14</sup> In the last part of this section, we aim to propose a measure of the strength of  $\pi$ -conjugation based on electron delocalization measures. To this end, we analyze the electron delocalization patterns of large polyenes, polyynes and some silicon compounds proposed by Fernández et al. and we compare our results with theirs.<sup>14</sup>

First, we focus on the analysis of polyenes (Table 3). We start by comparing the effects of conjugation in *trans*-1,3-butadiene and *cis*-1,3-butadiene. Here it is worth noticing that planar *cis*-1,3-butadiene is not an energy minimum; however, the planar system is chosen to study its  $\pi$ -delocalization. As Table 3 shows, the electron delocalization between  $C_1$  and  $C_2$  is slightly higher in *cis*- than in *trans*-butadiene whereas there are more electrons shared

**Table 4.** Amount of Electron Delocalization between Two Different Fragments of the Molecule,  $\delta_{\pi}(F_1, F_2)^a$

	$\delta_{\pi}(F_1, F_2)$	$\Delta E_{\pi}$
<i>trans</i> -1,3-butadiene	0.355	−19.5
<i>cis</i> -1,3-butadiene	0.323	−17.2
1,3,5-hexatriene	0.406	−22.0
1,3,5,7-octatetraene	0.424	−23.0
1,3,5,7,9-decapentaene	0.433	−23.4
<i>trans</i> -1-silabutadiene	0.439	−24.8
<i>trans</i> -2-silabutadiene	0.261	−12.0
1,4-disilabutadiene	0.570	−32.8
1,3-disilabutadiene	0.318	−16.4
2,3-disilabutadiene	0.225	−8.8

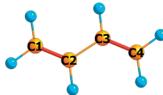
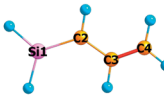
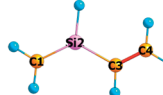
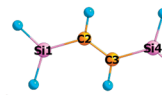
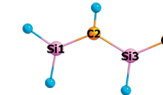
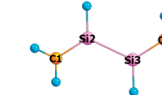
<sup>a</sup> Values of the  $\Delta E_{\pi}$  extracted from the work of Fernández and Frenking.<sup>14</sup>  $\delta_{\pi}(F_1, F_2)$  units are electrons and  $\Delta E_{\pi}$  are given in kcal/mol.

between  $C_2$  and  $C_3$  in the latter than in the former system. The higher delocalization between the carbons involved in the central C–C bond is associated with higher conjugation. This is corroborated by the nonbonded delocalization indices  $\delta(C_1, C_3)$  and  $\delta(C_1, C_4)$  that are higher in the case of *trans*-1,3-butadiene. Consequently, in the *cis* form the electrons are more localized in the double bond region, whereas the electrons are more delocalized through the molecule in the case of *trans*-butadiene. This is in agreement with EDA results that assign a higher stabilization due to conjugation to the *trans*- (19.5 kcal/mol) than the *cis*-1,3-butadiene (17.2 kcal/mol).<sup>14</sup>

Let us now discuss the electron delocalization patterns of large polyenes (Table 3). First, we observe that, when the number of conjugated bonds increases, the values of  $\delta(C_1, C_2)$  and  $\delta_{\pi}(C_1, C_2)$  decrease, and the number of electrons delocalized between  $C_2$  and  $C_3$  rises. This observation can be linked to the increase of electron delocalization through the carbon chain when the number of conjugated moieties increases. In the previous section we have seen how, in the case of 1,3-butadiene and 1,3-butadiyne, there are more electrons delocalized between  $C_1$  and  $C_4$  than between  $C_1$  and  $C_3$ , despite the distance between carbons being shorter in the latter. Interestingly, in 1,3,5-hexatriene the same trend is observed but it is also extended; that is, there are more electrons delocalized between  $C_1$  and  $C_4$  than in the case of  $C_1$  and  $C_3$ , but also the number of electrons shared is significantly higher between  $C_1$  and  $C_6$ , 0.036 e, than between  $C_1$  and  $C_5$ , 0.008 e. Thus, when the molecule presents conjugated bonds, a strong link exists between the first and the last carbon of the chain. As shown from the values in Table 3 and depicted in Figure 1, larger polyenes reproduce exactly the same alternation pattern. We observe peaks of electron delocalization at even positions and minima at odd positions (Figure 1). In addition, the values of Table 3 show that, when the distance between carbons increases, the percentage of  $\pi$ -delocalization becomes larger, to the point that there is only  $\pi$ -delocalization when the numbers of electrons delocalized between  $C_1$  and the last carbons of the chain are compared (after  $C_4$  the electron delocalization comes only from the  $\pi$ -component). Remarkably, we previously observed the same trends in aromatic organic compounds whereas the patterns reversed in antiaromatic systems that, in contrast to aromatic and conjugated systems, had electron delocalization maxima in odd positions.<sup>68</sup> Recently, in the field of conceptual DFT, Sablon and co-workers observed the same alternation pattern when analyzing the atom-condensed



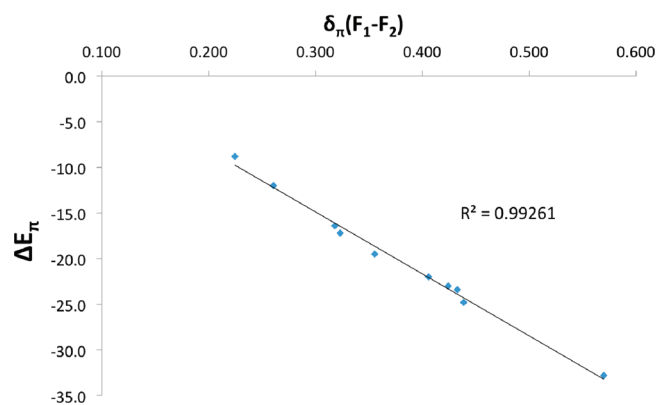
**Table 5.** Values of Two-Center Delocalization Indices (2c-DI), Where X = C and Si, for Silicon Analogues of *trans*-1,3-Butadiene Calculated at the B3LYP Level of Theory<sup>a</sup>

	1,3-butadiene		1-sila-butadiene		2-sila-butadiene		1,4-disila-butadiene		1,3-disilabutadiene		2,3-disilabutadiene	
												
	total	$\pi$	total	$\pi$	total	$\pi$	total	$\pi$	total	$\pi$	total	$\pi$
$\delta(X_1-X_2)$	1.769	0.768	1.097	0.545	1.106	0.556	1.056	0.507	1.115	0.540	1.246	0.652
$\delta(X_1-X_3)$	0.078	0.037	0.043	0.024	0.161	0.082	0.074	0.052	0.020	0.010	0.098	0.041
$\delta(X_1-X_4)$	0.114	0.107	0.110	0.106	0.075	0.067	0.122	0.119	0.075	0.070	0.075	0.064
$\delta(X_2-X_3)$	1.122	0.175	1.235	0.247	0.616	0.095	1.384	0.348	0.666	0.144	0.856	0.078
$\delta(X_2-X_4)$	0.078	0.037	0.108	0.063	0.035	0.016	0.074	0.052	0.178	0.094	0.098	0.041

<sup>a</sup> For planar systems, 2c-DI has been split into its  $\sigma$  and  $\pi$  contributions, only  $\delta_\pi$  are represented in this table. DI units are electrons.

linear response kernel in some aromatic compounds whereas no alternation was observed for their unconjugated analogues.<sup>69</sup> The same conclusions can be extracted from the analysis of delocalization indices when molecules with conjugated triple bonds are studied (Table S1, Supporting Information and Figure 2). In contrast to polyenes and polynes, in large n-alkanes (Table S2, Supporting Information) the alternation patterns are not observed. Figure 3 shows a progressive decrease of  $\delta(C_1, C_x)$  (where  $x = 3, \dots, n$ ) when the distance between carbons increases. In addition, there are no electrons delocalized from carbons separated by more than 3 atoms in n-alkanes.

From the analysis of DIs between atoms one can get a nice picture of how the electrons are shared in molecules; however, it is difficult to obtain a quantitative measure of the strength of conjugation similar to that provided in previous studies based on energetic analyses. To overcome this limitation, we propose to analyze the number of  $\pi$ -electrons delocalized between two different fragments of the molecule,  $\delta_\pi(F_1, F_2)$ . The molecular fragments are similar to the ones defined by Fernández and Frenking when they evaluated the stabilization due to conjugation using EDA,<sup>14</sup> but without taking into account the hydrogen atoms; i.e., the first fragment ( $F_1$ ) contains  $C_1$  and  $C_2$  ( $F_1 = C_1, C_2$ ), whereas the remaining carbon atoms of the molecule form the second fragment ( $F_2 = C_3, C_4, \dots, C_n$ , where  $n$  is the total number of carbons of the polyene). All results are presented in Table 4. According to EDA values, the strength of  $\pi$ -conjugation stabilization in polyenes increases when the number of conjugated bonds rises (Table 4). Interestingly, the same trend is reproduced by the values of  $\delta_\pi(F_1, F_2)$  that show a progressive increment of  $\pi$ -electron delocalization when going from *trans*-1,3-butadiene to 1,3,5,7,9-decapentene, 0.355, 0.406, 0.424, and 0.433 e. Remarkably,  $\delta_\pi(F_1, F_2)$  also predicts a stronger  $\pi$ -conjugation stabilization in *trans*- than in *cis*-butadiene, 0.355 e versus 0.323 e, in agreement with EDA analysis (Table 4), but opposite to ACID calculations which assign critical isosurface values of 0.0744 and 0.0755 to the *trans* and *cis* isomers, respectively.<sup>64</sup> In the case of polynes,  $\delta_\pi(F_1, F_2)$  values show stronger  $\pi$ -conjugation, which is twice as large in polyenes; e.g., 0.715 e is delocalized in 1,3-butadiene and 0.355 e in 1,3-butadiene (see Table S3, Supporting Information, for  $\delta_\pi(F_1, F_2)$  results of polynes). This finding is consistent with the values obtained by Kollmar and Fernández et al. for 1,3-butadiene and 1,3-butadiyne.<sup>14,67</sup>

**Figure 4.** Plot of  $\delta_\pi(F_1, F_2)$  values versus  $\Delta E_\pi$  values obtained from ref 14.  $\delta_\pi(F_1, F_2)$  units are electrons and  $\Delta E_\pi$  are given in kcal/mol.

This study is complemented with the analysis of some silicon analogues of 1,3-butadiene (Table 5). As pointed out by several authors, the substitution of carbon by silicon atoms in 1,3-butadiene can lead to either an increase or a decrease of the  $\pi$ -conjugation stabilization depending on the position and the number of carbon atoms replaced by silicon.<sup>14,70</sup> The strength of  $\pi$ -conjugation stabilization of *trans*-1-silabutadiene and *trans*-2-silabutadiene with respect to *trans*-1,3-butadiene has been a topic of controversy in the past years. According to resonance energy calculations, Trinquier et al. predicted a lower stabilization for 1-silabutadiene in comparison with 1,3-butadiene whereas a higher stabilization for 2-silabutadiene was reported.<sup>70</sup> By means of isodesmic reactions the same authors found that both 1- and 2-silabutadienes are less stable than their all-carbon conjugated analogues. On the other hand, Fernández and co-workers observed the opposite results;<sup>14</sup> i.e., 1-silabutadiene is more stable (−24.8 kcal/mol) than 1,3-butadiene (−19.5 kcal/mol) whereas 2-silabutadiene is less stable (−12.0 kcal/mol). They linked these observations to the polarization of  $\pi$ -orbitals toward the carbon atom in the C=Si bonds. To solve this controversy, we decided to perform the  $\pi$ -electron delocalization analysis of these molecules. In 1-silabutadiene there are more electrons delocalized,  $\delta_\pi(\text{Si}_1, \text{C}_4) = 0.106$  e, between the terminal atoms of the molecule than in 2-silabutadiene,  $\delta_\pi(\text{C}_1, \text{C}_4) = 0.067$  e (Table 5). In addition, the electron sharing between the



central atoms of the molecule is larger in 1-silabutadiene,  $\delta_{\pi}(C_2, C_3) = 0.247e$ , than in the Si—C bond of 2-silane molecule,  $\delta_{\pi}(Si_2, C_3) = 0.095e$ . Therefore, according to DI the effect of conjugation is larger in 1-silabutadiene than in 2-silabutadiene. These results are confirmed by  $\delta_{\pi}(F_1, F_2)$  values (where  $F_1 = C_1/Si_1, C_2/Si_2$  and  $F_2 = C_3/Si_3, C_4/Si_4$ ), which show higher strength of  $\pi$ -conjugation in 1-silabutadiene than in 1,3-butadiene, 0.439 e versus 0.355 e, whereas 2-silabutadiene presents lower electron delocalization, 0.261 e, than butadiene (Table 4). Remarkably, the  $\delta_{\pi}(F_1, F_2)$  values confirm EDA results. Moreover, the  $\pi$ -conjugation has been assessed for three *trans*-disilabutadienes. In all cases,  $\delta_{\pi}(F_1, F_2)$  reproduces EDA results; that is, 1,4-disilabutadiene presents larger  $\pi$ -conjugation stabilization than 1,3-butadiene, whereas the  $\pi$ -electrons of 1,3- and 2,3-disilabutadiene are less delocalized through the molecule (Table 4). Finally, to assess the performance of  $\delta_{\pi}(F_1, F_2)$ , the correlation between  $\delta_{\pi}(F_1, F_2)$  and  $\Delta E_{\pi}$  (correlation coefficient  $R^2 = 0.992$ ) was studied for the above-mentioned polyenes and silicon compounds (Table 4 and Figure 4). Altogether,  $\delta_{\pi}(F_1, F_2)$  performs remarkably well to analyze the strength of  $\pi$ -conjugation. As compared to EDA analysis, this method has the advantage that allows using any desired fragment (even non linked atoms can form a unique fragment) and as many fragments as one may like without increasing the computational cost.

## 5. CONCLUSIONS

In the present work, we have used the so-called delocalization and multicenter indices to assess the strength of conjugation in 1,3-butadiene and 1,3-butyne. Because the effect of conjugation is strongly linked to the  $\pi$ -electron delocalization, the values of DIs and multicenter indices have been split into their  $\sigma$  and  $\pi$  contributions. Our results show an increase of electron delocalization when going from butane to butadiene, and from butadiene to butadiyne. Particularly interesting are the values of multicenter indices because they allow easily calculating the strength of conjugation through the evaluation of the electron sharing among the four carbon atoms of the molecule. In line with BLW and EDA analyses, the values of multicenter indices show that the electron delocalization is more than double in 1,3-butyne than in 1,3-butadiene. Interestingly, the calculation of multicenter indices requires neither reference systems nor dividing the molecule into different fragments.

To broaden the scope of the quantification of hyperconjugation, in this work we have used DI and multicenter indices to assess the role played by hyperconjugation in 1-butene and 1-butyne. Two-center DIs show an increase of hyperconjugation when going from butane to 1-butene and from 1-butene to 1-butyne; these values are in agreement with previous energy calculations. However, the analysis of 2c-DI does not allow a direct measure of the strength of hyperconjugation. Because hyperconjugation is a four-center interaction between  $\pi$  C—C and  $\sigma$  C—H or C—C bond orbitals, we have computed the four-center multicenter indices among these four atoms. Interestingly, the values of 4c-DI are zero when  $\pi$  and  $\sigma$  bond orbitals are orthogonal and show a significant increment of electron sharing when the strength of the  $\pi$ — $\sigma$  interaction increases. In contrast to EDA and BLW methods, from the analysis of multicenter indices one can assess the strength of hyperconjugation of each C—H and C—C  $\sigma$ -bonds of the molecule.

In the last part of this paper, we have proposed a new measure of the strength of conjugation stabilization based on calculating

the amount of  $\pi$ -electrons shared between two fragments of the molecule,  $\delta_{\pi}(F_1, F_2)$ . To this end,  $\delta(F_1, F_2)$  values between fragments have been computed for the first time. In this case, we have used fragments similar to the ones defined by Fernández et al. to calculate the strength of conjugation by means of EDA analyses.<sup>14</sup> Moreover, the  $\delta(F_1, F_2)$  values can be calculated for any desired fragment (even non linked atoms can form a unique fragment) and as many fragments as one may like without increasing the computational cost. This method has been applied to evaluate the stabilization by conjugation in *trans*- and *cis*-1,3-butadiene, large polyenes, polyyenes, *n*-alkanes, and silicon analogues of 1,3-butadiene. We have seen that  $\delta_{\pi}(F_1, F_2)$  values predict that the conjugation strength of *trans*-butadiene is higher than in the *cis* form. These results are in agreement with EDA<sup>14</sup> and opposite to ACID calculations.<sup>64</sup> In addition, we have observed an increment of the strength of conjugation when the number of conjugated moieties increases, i.e., when going from *trans*-1,3-butadiene to *trans*-1,3,5,7,9,11-dodehexaene. The same results have been shown for large polyyenes. Interestingly, polyenes and polyyenes show the same alternation patterns of electron delocalization that have been observed for aromatic compounds. Finally, the conjugation strength in silicon analogues of 1,3-butadiene has been also studied. From the analysis of  $\delta_{\pi}(F_1, F_2)$ , we have reported that 1-silabutadiene and 2-silabutadiene are more and less conjugated, respectively, than 1,3-butadiene. These observations are in agreement with previous EDA calculations<sup>14</sup> and opposite to the observations of Trinquier and co-workers.<sup>70</sup> To assess the performance of  $\delta_{\pi}(F_1, F_2)$ , we have plotted the values of  $\delta_{\pi}(F_1, F_2)$  against the values of  $\Delta E_{\pi}$  obtained within the framework of the EDA. Remarkably, we observed a very good correlation between electron delocalization measures and EDA values.

## ■ ASSOCIATED CONTENT

**S** Supporting Information. Tables S1 and S2 with DIs values of polyenes and *n*-alkanes and Table S3 with  $\delta_{\pi}(F_1, F_2)$  values of polyyenes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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