Electron Delocalization in Linearly π-Conjugated Systems: A Concept for Quantitative Analysis

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Abstract: Donor- and/or acceptor-substituted π-conjugated systems represent an important class of compounds in organic chemistry. However, up to now, a general method to quantitatively address the efficiency of a conjugated path is still missing. In this work, a novel computational approach based on deletion energies and on second-order orbital interaction energies in a natural bond orbital (NBO) scheme is employed to quantitatively assess ("measure") delocalization energies. Moreover, the purpose of this work is to assess the efficiency of distinct π-conjugated paths, that is, *geminal*, *cis*, and *trans*, as well as to predict the impact of substituents on a given backbone. This study is focused on various mono-, di-, tri-, and tetrasubstituted tetraethynylethenes (TEEs). These model systems are suitable for our analysis, because they offer distinct conjugation paths within the same molecule, and can also be substituted in multiple ways. Differences between conjugation paths, the effect of neighbor paths, and the impact of donor and acceptor substituents on the various paths are discussed.

Keywords: conjugation • delocalization energy • density functional calculations • donor–acceptor systems • local properties

Introduction

Tetraethynylethene (TEE, 3,4-diethynylhex-3-ene-1,5-diyne), diethynylethene (DEE, (*E*)-hex-3-ene-1,5-diyne), and their derivatives represent a class of compounds of great interest due to the acetylenic scaffolding that provides carbon-rich compounds with very interesting physicochemical properties. In fact, these systems, as well as other polyethynylethenes,[1] give access to advanced materials for electronic and photonic applications, such as chromophores with nonlinear optical properties of higher order,[2] molecular photochemical switches,[3] and extensive π-conjugated polymers.[4]

The *trans* and *geminal* DEEs as well as TEE have been studied both theoretically and experimentally, because of their use as building blocks of linearly conjugated polymers, that is, polyacetylenes (PAs), polydiacetylenes (PDAs), and polytriacetylenes (PTAs).[5–9] Moreover, they show two relevant characteristics. First, they allow through- (or *trans)* and cross- (or *geminal*) conjugation. Second, they can easily be functionalized with a wide range of donor and acceptor substituents. The presence of donor and acceptor substituents has a strong effect on the properties of these systems.[10–12]

In this article we present a novel method, based on the NBO analysis of Weinhold,[13] that allows us to quantify the delocalization energy (σ or π) of distinct conjugation paths within a given molecule. Furthermore, the method allows us to address the issue of quantifying donor/acceptor substituent effects on given backbones, and, finally, to evaluate the effect of neighboring paths on the conjugation path under consideration. In this work, we study simple model compounds, such as TEE substituted with NO_2, CHO, and CN (acceptors), and OH, OCH_3, and NH_2 (donors).

The NBO analysis offers a way to quantify electron delocalization in terms of intramolecular donor–acceptor interactions. In our method, we "measure" the delocalization energy by applying the orbital deletion procedure described in reference [5]. The orbitals deleted are the π* (or σ*) NBOs responsible for the delocalization. The difference between the total energies before and after the deletion gives the delocalization energy (E_{deloc}), which represents the deviation from the idealized Lewis structure. The term E_{del}, therefore, is closely related to the non-Lewis (NL) contribution to the total energy along the conjugation path consid-

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DOI: 10.1002/chem.200400313

ered, that is, $E_{\text{deloc}}=E_{\text{NL}}=E_{\text{del}}$. These non-Lewis contributions can be approximated by the sum of second-order interaction energies between the strongly occupied Lewis type NBOs (donor orbitals) and the weakly occupied non-Lewis NBOs (acceptor orbitals) involved in the path. These interactions are responsible for the loss of occupancy of the donor in favor of the acceptor orbitals, and, hence, for the departure from the idealized Lewis type structure description. In other words, they represent the non-Lewis corrections to the natural Lewis structure, that is, $\sum_{ij} E_{\text{SOIE}_{ij}}=E_{\text{NL}}$. Thus, these second-order perturbation energies and the deletion energies can be viewed as tools to evaluate delocalization by means of single orbital interactions.

In the section "Results and Discussion" we present the method in more detail and use the approach outlined here to predict the impact of donor/acceptor substituents on distinct paths within the same system, as well as to characterize the differences between the cross- *(geminal)* and through- (*trans)* conjugation paths.

Results and Discussion

The method of analysis: The complete information contained in the first-order reduced density matrix $\gamma(\mathbf{r}|\mathbf{r}')$ of an N electron LCAO-MO (LCAO-MO = linear combination of atomic orbitals to molecular orbitals) wavefunction Ψ can be obtained by solving the eigenvalue equations [Eq. (1)] in which θ_i are natural orbitals and n_i is their occupancy.

$$\hat{\gamma}\theta_i = n_i\theta_i \tag{1}$$

By searching for the highest occupancy eigenorbitals in each diatomic region, one finds the optimal natural bond orbitals (NBOs) $\theta_i^{(\text{AB})}$. This set of high-occupancy NBOs, each taken doubly occupied, is considered to represent the "natural Lewis structure" of the molecule. Moreover, the transformation from LCAO-MOs to NBOs also produces orbitals that are unoccupied in the Lewis description. The most important of these orbitals are usually the antibonding σ^* and π^*. These weakly occupied (non-Lewis) NBOs represent the irreducible departure from the idealized Lewis picture. The energy associated with these orbitals is calculated by deleting them from the NBO basis set and by recomputing the total energy (E'_{tot}) in the reduced orbital space.

The total energy (E_{tot}) can, therefore, be expressed as sum of Lewis (L) and non-Lewis (NL) contributions [Eq. (2)] in which E_{L} and E_{NL} are given by Equations (3) and (4), respectively.

$$E_{\text{tot}} = E_{\text{L}} + E_{\text{NL}} \tag{2}$$

$$E_{\text{L}} = E'_{\text{tot}} \tag{3}$$

$$E_{\text{NL}} = E_{\text{tot}} - E'_{\text{tot}} \tag{4}$$

In linearly π-conjugated systems, the π^* and σ^* NBOs are considered to be responsible for electron delocalization. The energy associated with their deletion may thus be used as a measure of delocalization.

In this picture, the delocalization energy (E_{deloc}) is then obtained as Equation (5):

$$E_{\text{deloc}} = E_{\text{NL}} - E_{\text{strain}} - E_{\text{Rydberg}} \tag{5}$$

If the contributions of the Rydberg orbitals (E_{Rydberg}) are negligible, and if the steric repulsion (E_{strain}) is very small, then we get Equation (6).

$$E_{\text{deloc}} = E_{\text{NL}} = E_{\text{del}} \tag{6}$$

Therefore, E_{del} or E_{NL} are equivalent to E_{deloc} and may, for example, be used to quantitatively assess the delocalization energy differences in conformational isomers.[5,13]

In a previous study,[5] we showed that E_{del} can be decomposed into σ and π contributions by using the same procedure on specific orbitals [Eq. (7)].

$$E_{\text{del}} = E_{\text{del}}(\sigma) + E_{\text{del}}(\pi) \tag{7}$$

In cases in which the in-plane π orbitals ($\pi_{\parallel}$) can only interact with the σ framework, but not with the perpendicular orbitals ($\pi_{\perp}$), the delocalization energy can be further expressed as Equation (8) with $E_{\text{del}}(\sigma_{\parallel})$ as defined in Equation (9).

$$E_{\text{del}} = E_{\text{del}}(\sigma_{\parallel}) + E_{\text{del}}(\pi_{\perp}) \tag{8}$$

$$E_{\text{del}}(\sigma_{\parallel}) = E_{\text{del}}(\sigma + \pi_{\parallel}) \tag{9}$$

This means that the energy associated with $\sigma_{\parallel}$ is calculated by deleting all the σ^* and $\pi^*_{\parallel}$ orbitals simultaneously.

This approach [Eq. (8)] has the advantage of giving an energy-based measure for in-plane conjugation ($E_{\text{del}}(\sigma_{\parallel})$) and vertical π-conjugation ($E_{\text{del}}(\pi_{\perp})$). It even allows us to quantitatively analyze the efficiency of conjugation in a given path within the same system.

In non-aromatic compounds, the non-Lewis contributions are typically very small relative to the Lewis type ones, they amount to less than 1%. The corrections to the Lewis type picture can thus be approximated by second-order perturbation theory.

In this case, we examine all possible interactions between filled Lewis type NBOs (donor orbitals) and weakly occupied non-Lewis type NBOs (acceptor orbitals), and evaluate their relevance by means of second-order perturbation theory. These donor–acceptor interactions are responsible for the loss of occupancy in filled NBOs, and measure the deviation from the idealized Lewis structure. Therefore, they are also referred to as "delocalization corrections" to the natural Lewis structure. The second-order interaction energy (SOIE) for a pair of donor and acceptor NBOs, labeled i and j, is given by Equation (10) in which q_i is the donor orbital occupancy, ε_i and ε_j are orbital energies, and F(i,j) is the corresponding element of the Fock matrix in the NBO basis.

$$E(2) = E_{\mathrm{SOIE}_{ij}} = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_i - \varepsilon_j} \qquad (10)$$

For a system of two pairs of π orbitals (π_i and π_j), the leading second-order interaction terms are: $\pi_i \rightarrow \pi^*_j$: SOIE_{ij}; $\pi_j \rightarrow \pi^*_i$: SOIE_{ji}

The $\pi_i \rightarrow \pi^*_i$ and $\pi_j \rightarrow \pi^*_j$ are usually very small and do not play an important role. The sum of SOIEs corresponds to the non-Lewis contribution to the total energy [Eq. (11)]

$$E_{\mathrm{NL}} = E_{\mathrm{SOIE}_{ij}} + E_{\mathrm{SOIE}_{ji}} + \text{higher order terms} \qquad (11)$$

From the above discussion, we can conclude that Equation (12) is valid, and as long as higher order contributions can be neglected, this leads to Equation (13).

$$\sum_{ij} E_{\mathrm{SOIE}_{ij}} = E_{\mathrm{NL}} \qquad (12)$$

$$E_{\mathrm{del}} = \sum_{ij} E_{\mathrm{SOIE}_{ij}} \qquad (13)$$

The approaches to calculate delocalization energies are summarized in Figure 1, in which we schematically show the relationship between E_{deloc} (or E_{conj}), E_{NL}, E_{del}, and $\sum_{ij} E_{\mathrm{SOIE}_{ij}}$.

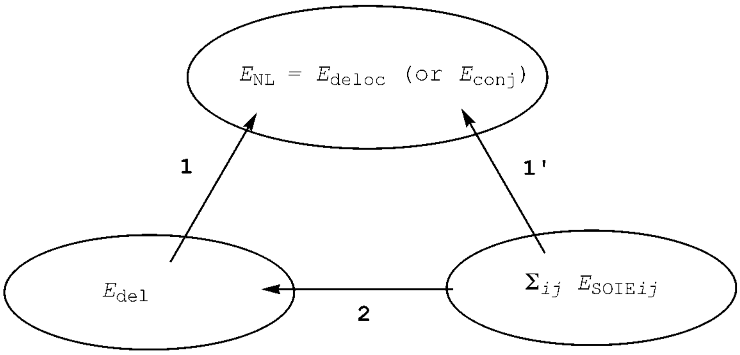


Figure 1. The relationship between conjugation energy, E_{del}, and $\sum_{ij} E_{\mathrm{SOIE}_{ij}}$. Both E_{del}, and $\sum_{ij} E_{\mathrm{SOIE}_{ij}}$ allow us to "measure" the total or the local conjugation energy (**1**,**1**′); the results, however, may not be identical (higher order corrections). The SOIE approach further allows us to identify the donor/acceptor orbital interactions responsible for the conjugation energies observed (**2**).

In summary, whereas E_{NL} just gives the total delocalization energies, both the E_{del} and the sum of second-order energies ($\sum_{ij} E_{\mathrm{SOIE}_{ij}}$) approaches allow to "measure" distinct conjugation paths, looking at delocalization as a local property. Moreover, the SOIE approach further allows us to identify the donor–acceptor orbital interactions responsible for the conjugation energies observed.

In the present text, we will refer to delocalization energy or π-conjugation energy (E_{deloc} or E_{conj}, respectively) without distinction between E_{del} and $\sum_{ij} E_{\mathrm{SOIE}_{ij}}$ unless otherwise mentioned.

1,3-Butadiene—an illustration of the method: We applied the above method to one of the simplest examples of a π-conjugated system, 1,3-butadiene (Figure 2), with the goal to reproduce the *cis–trans* rotational barrier solely based on the change in the delocalization energy. We will show that the approximations expressed by Equations (6) and (13) are accurate. We need to remind the reader that the planar *cis* structure is a transition state, and that the minimum for the *cis* structure is found at a torsional angle of 30.9° (steric repulsion). Similarly, the maximum of the rotational barrier is shifted towards the *trans* structure, and occurs at 100°.

Figure 2. The *trans* and *cis* 1,3-butadiene. π_i and π_j are the two out-of-plane occupied orbitals, π_i^* and π_j^* are the corresponding unoccupied ones.

Figure 3 displays E_{tot} and E_{del} as a function of the torsional angle ϕ. E_{del} is calculated by removing all the antibonding orbitals simultaneously (σ* and π*). The graph shows that in the range of 180 to 90°, that is, from the *trans* structure to the region slightly beyond the maximum, E_{tot} and E_{del} are nearly identical, indicating that Equation (6) is accurate. Moreover, the results show that the Lewis component of the energy (E_{L}) remains constant during the rotation, and that the energy variation is exclusively due to the non-Lewis component (E_{NL}), that is, the rotational barrier of 1,3-butadiene is entirely due to changes in the delocalization energy. On the other hand, in the range of $0 < \phi < 80°$ the discrepancy between $E_{\mathrm{del}}(\phi)$ and $E_{\mathrm{tot}}(\phi)$ is noticeably larger due to steric repulsion; this means that E_{strain} [Eq. (5)] is no longer negligible. Furthermore, it is worth noting that both curves exhibit the maximum at the exact same angle; this means

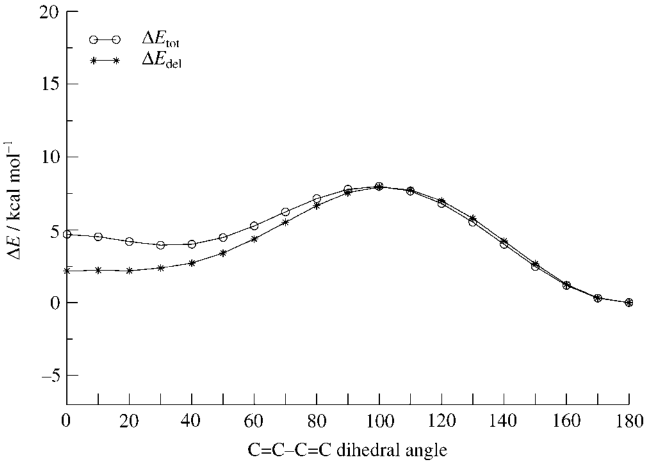


Figure 3. The calculated E_{tot} and E_{del} as function of the C=C–C=C dihedral angle. The energies are computed for all the structures obtained after a rotation of 10° about the single central bond. All energies are calculated with respect to the *trans* isomer (180°), which is taken as reference structure.

that the deletion approach predicts the transition state to occur at the correct dihedral angle.

Figure 4 shows the accuracy of the relationship between the sum of E_{SOIE} and E_{del} as well as E_{NL}. We find that all energies show the same pattern, and that they compare reasonably well also in a quantitative way. It is also evident that the E_{del} calculated from the sum of the single π_D^* deletions compares more favorably with E_{SOIE} than the deletion energies obtained by removing all the π_D^* orbitals simultaneously. In the first case, both E_{del} and E_{SOIE} consider only single orbitals, whereas in the latter case the deletion energy also takes into account the coupling between orbitals, which in general has the effect of reducing the interaction energy. Moreover, from Figure 4 we see that the discrepancy between the $\sum_{ij} E_{SOIE_{ij}}$ and E_{del} is larger for those structures with a dominant π–π out-of-plane conjugation. In fact the most significant energy difference is found for the *trans* isomer (180°) and the planar *cis* one (0°), in which the out-of-plane conjugation is purely given by π–π interactions. This indicates that for these geometries the second-order energies are insufficient to accurately describe these interactions, and that higher order terms should be taken into account [Eq. (11)].

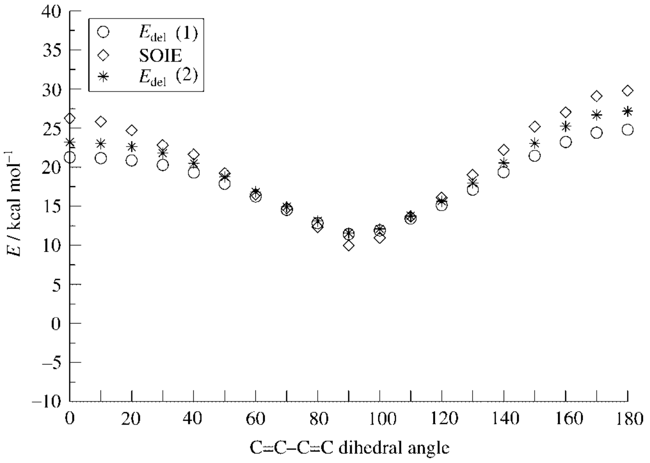
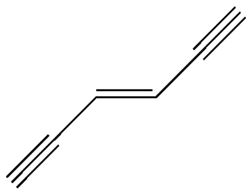
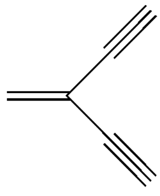


Figure 4. The SOIE, $E_{del}(1)$ calculated by deletion of all π orbitals simultaneously, and $E_{del}(2)$ calculated as sum of deletion of single orbitals, as function of the C=C–C=C dihedral angle.

***trans* and *geminal* diethynylethene (DEE)**: We have shown[5] that the deletion approach allows us to discriminate between *geminal* and *trans* paths in pairs of isomers, such as the *trans* and *geminal* DEEs (**1a** and **1b**). By breaking the delocalization energies into contributions for each type of bond, that is, $\pi_{\perp}$, $\pi_{\parallel}$, and σ, we can show that the difference between *trans* and *geminal* conjugation in **1a** and **1b** is mainly due, as expected, to the vertical π conjugation ($\pi_{\perp}$ conjugation). The deletion energy difference ΔE_{del} calculated as the energy difference between the *trans* and *geminal* isomers (**1a**, **1b**) amounts to 5.42 kcal mol^{-1} in favor of the *trans* isomer, which compares to a difference of 4.81 kcal mol^{-1} in total energy. Looking at single orbital contributions, we find that $\Delta E_{\perp}$ is 5.45 kcal mol^{-1} in favor of **1a**, whereas $\Delta E_{\sigma_{\parallel}}$ favors **1b** by 0.35 kcal mol^{-1}. However, closer inspection of the σ deletion energies reveals that there are also considerable differences in the in-plane σ conjugation. In fact, we observed that the deletion of all the σ_S^* orbitals (corresponding to the single C–C bonds) amounts to 15.96 kcal mol^{-1} in favor of **1b**, whereas the deletion of all the σ_{HD}^* orbitals (corresponding to C–H bonds) favors **1a** by 12.54 kcal mol^{-1}. These contributions are interestingly high, but due to their opposite effect they cancel each other.



1a



1b

In summary, the difference in stability between the cross and through conjugation is controlled by the vertical π delocalization. However, the in-plane σ conjugation should be exploited to differentiate *geminal* and *trans* isomers.

Tetraethynylethene (TEE) and its derivatives

Scope of the study and notation: Tetraethynylethene (TEE) and its substituted derivatives offer an example of compounds with several distinct conjugation paths within the same molecule. The donor/acceptor-substituted TEEs furthermore allow us to address the effect of donor/acceptor functionalization on a specific path.

For this purpose, we studied the complete set of mono-, di-, tri-, and tetra-substituted TEEs (TEE-*n*X, *n* = 1–4, Figure 5). The substituents considered are NO_2, CN, CHO (acceptor groups), and OH, OCH_3, NH_2 (donor groups). None of these compounds has been studied experimentally. However, in the context of the validation of the analysis, it is sufficient to compare among computed data.

The notation used in the following discussion is explained in Table 1 and Figure 5. Three types of paths are distinguished: *trans* (*a*) *geminal* (*b*), and *cis* (*c*). We refer to the pure ethynyl unit (-C≡C–H) as E, and to the ethynyl unit with a substituent (-C≡C–X) as X. We will not investigate *cis* conjugation (*c*) any further in the present study, since the focus of this work is on through (*cis*, *trans*) versus cross (*geminal*) conjugation. Through conjugation will be represented by *trans* conjugation. Moreover, the specific path considered is referred to as conjugation path, whereas the other is always referred to as neighbor path. For example, if the *geminal* XX path (*a'*) in **2d** (Figure 5) is the analyzed conjugation path, the second *geminal* path EE (*a*) is the neighbor path. Finally, in the following discussion, we will label the orbitals according to the bond they are associated with, that is, π_D and π_T are the vertical occupied π orbitals of the double bonds (D) C=C and the triple bonds (T) C≡C, whereas π_D^* and π_T^* are the corresponding antibonding orbitals.

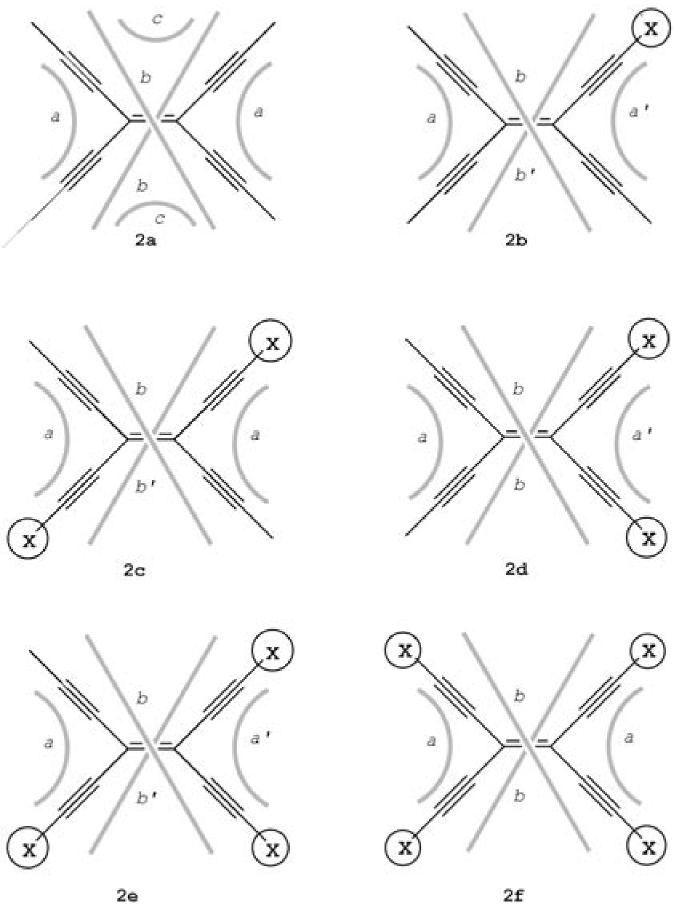


Figure 5. The tetraethynylethene derivatives (TEE-nX, $n=0$–4 (**2a-f**)) studied in the present work (X = H, NO_2, CHO, CN, OH, OCH_3, and NH_2). The grey-shaded lines indicate the conjugation paths (*trans* and *geminal*) (see also Table 1).

Table 1. The distinct paths (*geminal* and *trans* conjugation) in substituted and unsubstituted TEEs (TEE-nX with $n=0$–4). The labels *a* and *b* indicate *geminal* and *trans* paths, respectively. Non-equivalent *geminal* and *trans* paths are marked as *a'* and *b'*, respectively. The neighbor paths are indicated in parentheses.

n	Compound	Paths	Occurrence
0	**2a**	*a:* EE (EE)	2
		b: EE (EE)	2
1	**2b**	*a:* EE (EX)	1
		a': EX (EE)	1
		b: EE (EX)	1
		b': EX (EE)	1
2	**2c**	*a:* EX (EX)	2
		b: EE (XX)	1
		b': XX (EX)	1
2	**2d**	*a:* EE (XX)	1
		a': XX (EE)	1
		b: EE (EX)	2
3	**2e**	*a:* EX (XX)	1
		a': XX (EX)	1
		b: EX (XX)	1
		b': XX (EX)	1
4	**2f**	*a:* XX (XX)	2
		b: XX (XX)	2

Technical details on the analysis: For the comparison of SOIEs with deletion energies, one needs to carefully consider which orbital interactions have to be taken into account. Figure 6 shows the two *geminal* paths, that is, EX (*1*) and EE (*2*), in a generic monosubstituted TEE. For example, the deletion energy E_{del}(EX) of the *geminal* path (*1*) should correspond to the SOIE given by the sum of all $\pi_T \rightarrow \pi_D^*$ contributions, of the $\pi_D \rightarrow \pi_T^*$ contributions involved in the EX path, and of the contributions due to the substituents, that is, $Y_X \rightarrow \pi_T^*$. If X is a donor, Y_X stands for the donor lone pairs, whereas if X is an acceptor, Y_X stands for π_D^* or π_T^* depending on the nature of the substituents (see *a*, *a'*, *b*, and *c* in Figure 6, respectively). In the deletion procedure, removing the central π_D^* orbital in a specific path means deleting an orbital that is unavoidably affected by the neighbor path. Therefore, in order to have the appropriate comparison between E_{del} and E_{SOIE}, also the $\pi_T \rightarrow \pi_D^*$ contributions of the neighbor path need to be taken into account. Finally, the $\pi_T \rightarrow Y_X^*$ contributions do not need to be considered because the antibonding orbitals of X do not play an important role in characterizing the substituent effects on the backbone.

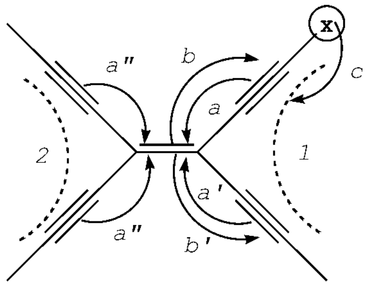


Figure 6. The g*eminal* conjugated paths for a monosubstituted tetraethynylethene molecule. *1* and *2* represent EX and EE conjugation paths, respectively. (*a*, *a'*, *a*“) are the $\pi_T \rightarrow \pi_D^*$ contributions; (*b*, *b'*) are the $\pi_D \rightarrow \pi_T^*$ contributions; (*c*) are the $X_{\mathrm{lonepair}} \rightarrow \pi_T^*$ or $\pi_{D(T)} \rightarrow \pi_T^*$ when X is a donor or an acceptor, respectively.

Through- (trans) versus cross- (geminal) conjugation: By comparing distinct *geminal* or *trans* paths within TEE-nX, ($n=1$–3), we observe considerable differences in the delocalization energies (Figure 7 and 8). These energy differences are also summarized in Table 2.

Table 2. The conjugation energy splitting [in kcal mol^{-1}] calculated at B3LYP/cc-pVDZ level for TEE-nX with $n=1$–3.

TEE-nX	Splitting	Acceptors			Donors		
		NO_2	CHO	CN	OH	OCH_3	NH_2
$n=1$							
geminal	EX-EE	15	13	18	34	34	11
trans	EX-EE	13	11	16	36	36	12
$n=2$							
geminal	XX-EE	30	25	35	68	67	22
trans	XX-EE	24	21	32	70	69	24
$n=3$							
geminal	XX-EX	15	11	18	34	33	11
trans	XX-EX	12	11	16	34	33	12

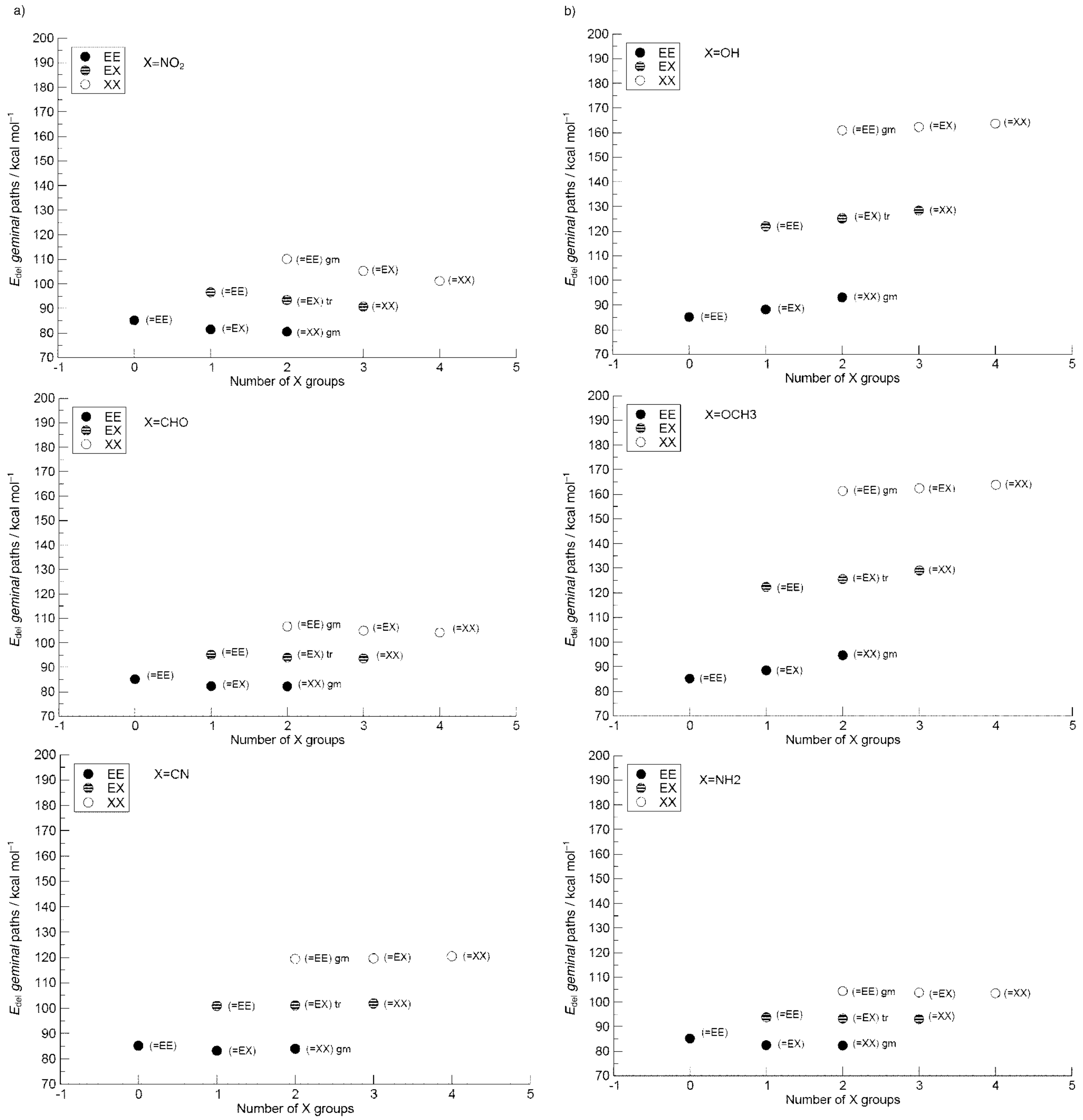


Figure 7. The *geminal* delocalization energies for all the TEE-*n*X, $n=0$–4. a) TEE-*n*X, with X = acceptor groups. b) TEE-*n*X, with X = donor groups. In the legend, full, striped, and empty circles represent the studied EE, EX, and XX conjugation paths, respectively, whereas the neighbor paths are displayed in parentheses.

For the *geminal* paths in the acceptor-substituted compounds, we observe conjugation energy splittings of 13–18, 25–35, and 11–18 kcal mol^{-1} for the mono-, di-, and trisubstituted systems, respectively. However, this splitting between *geminal* paths is even larger when donor groups are attached to TEE. With X = OH or OCH_3, the splittings are 34 kcal mol^{-1} for both TEE-X, about 68 kcal mol^{-1} for TEE-2X, and, lastly, about 34 kcal mol^{-1} for TEE-3X. TEE-*n*NH_2 ($n=1$–3) shows a behavior more similar to the acceptor groups than to the donor ones. In fact the energy splitting is rather small, that is, ≈11, 22, and 11 kcal mol^{-1} for the mono-, di-, and trisubstituted systems, respectively, compared to the other donors considered.

In Figure 8 we present the delocalization energies calculated for the *trans* paths of the same set of compounds. As also shown in Table 2, these results are similar to those obtained for the *geminal* pathways. In fact, for the acceptors, the energy splittings EX-EE, XX-EE, and XX-EX are in the range 11–16, 21–32, and 10–16 kcal mol^{-1} for the mono-, di-, and trisubstituted systems, respectively. For the donors these same conjugation energy differences are 36 kcal mol^{-1} for TEE-OH and TEE-OCH_3, about 70 kcal mol^{-1} for the

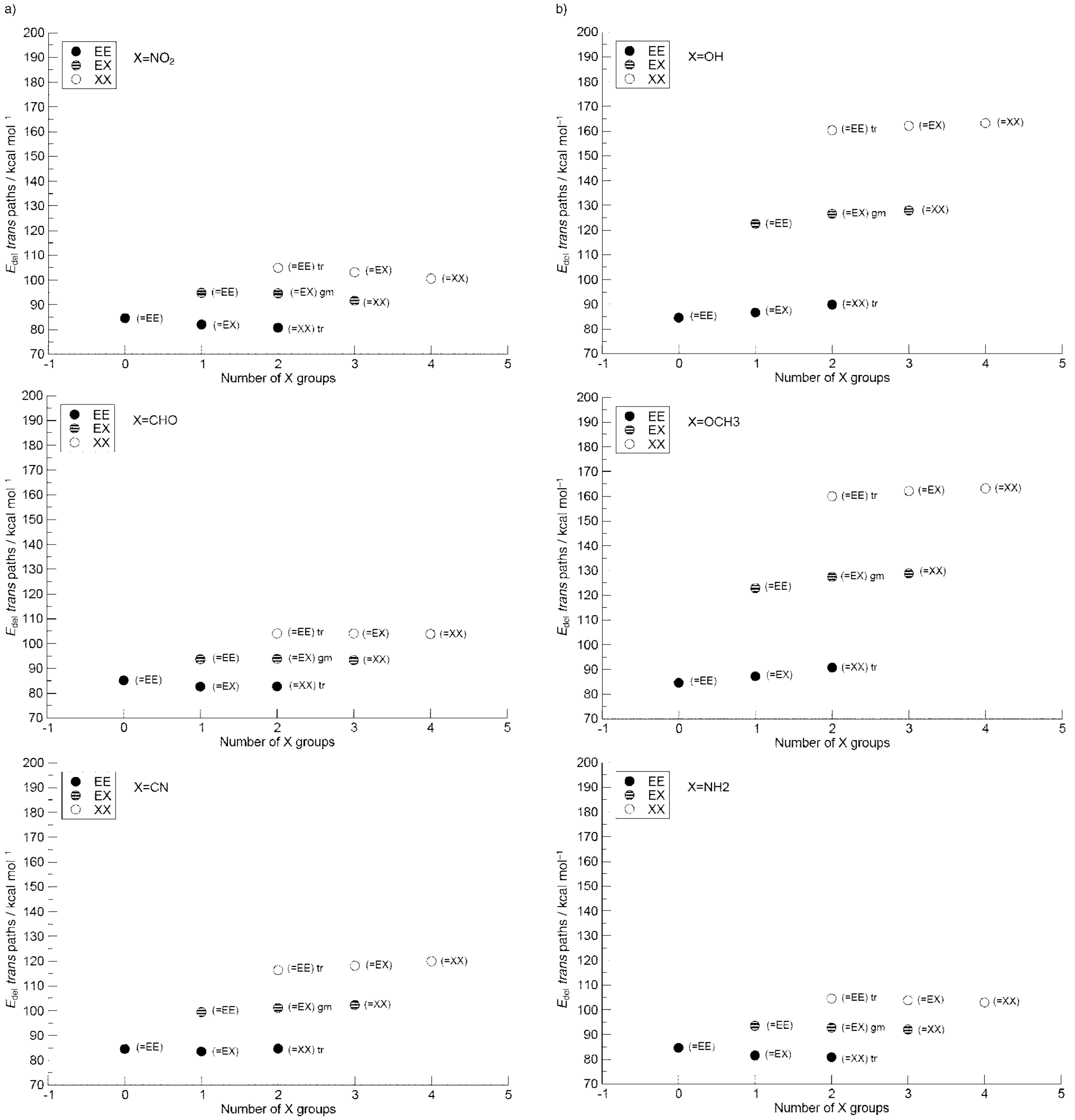


Figure 8. The *trans* delocalization energies for all the TEE-*n*X, $n = 0$–4. a) TEE-*n*X, with X = acceptor groups. b) TEE-*n*X, with X = donor groups. In the legend, full, striped, and empty circles represent the studied EE, EX, and XX conjugation paths, respectively, whereas the neighbor paths are displayed in parentheses.

disubstituted compounds, and about 34 kcal mol^{-1} for the trisubstituted ones. TEE-*n*NH$_2$ show very small delocalization energy splitting, that is, 12, 24, and 12 kcal mol^{-1} for $n =$ 1, 2, and 3, respectively.

These data show three different aspects. First, the delocalization energies in the TEEs substituted with donors are much larger than those in the TEEs with acceptors for both *trans* and *geminal* pathways. The analysis of the SOIE data show that this is due to the interactions between the π^*_T of the backbone (TEE) and the lone pairs of the donors. This interaction is much stronger than the one of the $\pi_{D(T)}$ of the acceptors with the π^*_T of the backbone. This is consistent with the fact that the electronic population which moves from the lone pairs of the substituents to the π^*_T of the backbone is much larger than the charge which moves from the $\pi_{D(T)}$ (of the substituents) into the π^*_T of the backbone. Second, each substituent shows a different strength. In the case of the acceptor groups, the largest splitting is observed for the CN group, whereas the weakest delocalization energy differences between paths are found for CHO in all cases (*geminal*, *trans*). This indicates that the CN substituent is the strongest among the three acceptors considered here, enhancing the π conjugation in TEE most effectively. For the donors (Figures 7b and 8b), there is not much difference in delocalization energies for the TEE-*n*OH and TEE-*n*OCH_3. Both of the two groups intensively enhance the π conjugation in TEE. Here NH_2 turns out to be a very weak π donor also showing some acceptor character. Third, we note that in the acceptor-substituted TEEs, the *geminal* paths are always more favorable by a few $kcal\,mol^{-1}$ than the *trans* ones, whereas in the donor-substituted TEE, the *trans* paths are preferred by 1–2 $kcal\,mol^{-1}$ with no exception.

In summary, for the class of compounds studied here, the conjugation is determined by the type of substituent (donor versus acceptor), whereas the type of path considered (through versus cross) has a minor influence only.

Impact of degree of substitution: The analysis of Figures 7 and 8 reveals two more distinct trends. First, we see a significant increase of E_{deloc} when increasing the number of substituents in a conjugation path ("direct trend"). Second, we observe only a small variation of E_{deloc} when increasing the number of substituents in the neighbor path ("indirect trend"). In both cases, the best *geminal* and *trans* paths are always the XX paths, independent of the type of neighbor and the type of substituents, that is, donor or acceptor. In the XX paths the interactions between the substituents and the π^*_T of the backbone are doubled, thus strongly enhancing conjugation. For example, the delocalization energies of the *geminal* EE and EX paths of the TEE-OH are 86 and 122 $kcal\,mol^{-1}$, respectively. The contribution of the lone pair interacting with the π^*_T of TEE amounts to 37 $kcal\,mol^{-1}$, which accounts for most of the difference between the two conjugation paths. In the case of *geminal* TEE-2OH we observe similar numbers for the EE path (88 $kcal\,mol^{-1}$), and a very strong delocalization for the XX path (158 $kcal\,mol^{-1}$), which is dominated by the interactions between the lone pairs of the X groups and the π^*_T of the backbone (74 $kcal\,mol^{-1}$). In summary, the higher the number of substituents in a path, the larger is the corresponding delocalization energy.

From a more detailed analysis of the data presented in Table 3, we observe that in the acceptor case, the energy difference of the *geminal* paths for the direct trend is 23 $kcal\,mol^{-1}$ on average for NO_2, 22 $kcal\,mol^{-1}$ for CHO, and 35 $kcal\,mol^{-1}$ for CN, whereas in the indirect trend the difference is 7, 2, and 1 $kcal\,mol^{-1}$ for NO_2, CHO, and CN, respectively. In the donor case, the energy variation in the direct trend is on average 74 and 73 $kcal\,mol^{-1}$ for OH and OCH_3, and 17 $kcal\,mol^{-1}$ for NH_2, whereas in the indirect trend it is 6 $kcal\,mol^{-1}$ for OH and OCH_3, and 2 $kcal\,mol^{-1}$ for NH_2. These data show that for a given conjugation path the neighborhood effects are small with respect to the substituent effects. In the case of the *trans* paths we observe similar numbers; however, for the direct trend the *trans* paths are slightly disfavored for TEE with acceptors, and slightly favored with the donors, whereas in the indirect trend the *geminal* paths are always favored with the only exception of TEE-*n*CN. Thus, in TEE (as backbone) the π conjugation in the *geminal* or *trans* path is enhanced by attaching donor groups rather than acceptor ones.

The NH_2 substituent represents a particular case. As known from the literature,[14] and from our own study, this substituent behaves as a π donor when attached to a phenyl group. Comparing the results obtained for our series of TEEs substituted with both donor and acceptor groups and TEE-*n*NH_2, it seems that the latter behaves more similarly to the acceptor groups rather than to the donor ones. By means of the SOIEs, it can be noted that the NH_2 is indeed a donor, but rather than being a π donor, like in the case of Ph-NH_2, it is a σ donor when attached to TEE.

Finally, we conclude from the data collected in Table 3, that the indirect trend, albeit small, consistently favors a less substituted neighbor path for the acceptor case and a more substituted neighbor path for the donor one. The only exceptions are CN and NH_2.

Table 3. The energy differences [in $kcal\,mol^{-1}$] in the direct and indirect trends calculated at B3LYP/cc-pVDZ level for TEE-*n*X with $n=0$–4. The degree of substitution *n* is shown in parenthesis in the first column.

Energy differences	Acceptors			Donors		
	NO_2	CHO	CN	OH	OCH_3	NH_2
direct trend						
geminal						
XX(2)–EE(0)	25	22	34	76	76	19
XX(3)–EE(1)	24	23	36	74	74	10
XX(4)–EE(2)	21	22	36	71	69	21
trans						
XX(2)–EE(0)	20	20	32	76	75	20
XX(3)–EE(1)	21	21	35	73	75	22
XX(4)–EE(2)	20	21	35	73	72	22
indirect trend						
geminal						
EE(2)–EE(0)	−5	−3	−1	8	9	−3
EX(3)–EX(1)	−6	−2	1	6	7	−1
XX(4)–XX(2)	−9	−2	1	3	2	−1
trans						
EE(2)–EE(0)	−4	−2	0.1	5	6	−4
EX(3)–EX(1)	−3	−0.4	3	5	6	−2
XX(4)–XX(2)	−4	−0.2	4	3	3	−2

In summary, for the acceptor as well as for the donor substituted TEEs (Figure 7 and 8) we observe a strong dependence of the conjugation energy on the degree of substitution, and on the type of substituents attached (donors versus acceptors). Somewhat surprisingly, the conjugation energy depends much less on the type of paths, that is, *trans* versus *geminal*. The impact of the neighboring path is clearly visible, but also much less pronounced.

Conclusions

A major focus of the present work was to validate our method of computing delocalization energies as presented in reference [5] by means of the second-order orbital interaction (SOIE) approach. The study shows that the deletion energies, which represent the delocalization energy compare rather well with the second-order perturbation energies, both depicting the non-Lewis contribution to the total energy of the systems considered (Figure 3). The main advantage of the SOIE approach is that it offers higher depth of analysis allowing us to identify the contributions to conjugation energies. However, in presence of very strong conjugation, higher order perturbative corrections can no longer be neglected; therefore, the deletion approach becomes quantitatively more accurate.

To illustrate the capabilities of the method, an extensive study of mono-, di-, tri-, and tetrasubstituted donor/acceptor TEEs was performed. We compared distinct conjugation paths, that is, *geminal* (cross) or *trans* (through), within the same molecule. We also analyzed the effect of each substituent on the TEE as backbone, and the impact of neighbor paths. From this analysis, we observed first that the conjugation is strongly dependent on the nature of the substituent (donor versus acceptor) rather than on the type of path considered (through versus cross). Second, we have found that the conjugation energy in a selected path is enhanced with increasing degree of substitution. In fact, the best *geminal* and *trans* paths are always the XX paths (X = donor or acceptor), regardless of the neighborhood. This is due to a strong contribution of the substituents into the π^*_T orbitals of the backbone, which is in general much larger with the donors than with the acceptors.

In this work we were restricting ourselves to model molecules, because our goal mainly was to test our novel approach by showing that deletion energies and second-order interaction energies can be used complementary to "measure" the delocalization energy in conjugated systems. By means of this method, we are able to understand why certain paths favor conjugation more than others. We are also able to quantify the effect of substituents on a backbone, and, therefore, to predict how to enhance conjugation (π or σ) in a specific path.

Computational Methods

In the present work, all calculations were performed at the DFT level of theory, using the nonlocal and hybrid Becke three-parameter Lee-Yang-Parr (B3LYP) functional.[15,16] The optimized geometries and the NBO data were obtained at B3LYP level together with 6-31G** basis set of Gaussian orbitals[17] for 1,3-butadiene and diethynylethenes, and with a correlation-consistent polarized valence double-ζ (cc-pVDZ) basis set[18] for the TEE and its derivatives.

All calculations were carried out using Gaussian 98 package.[19] The natural bond orbital analysis has been performed with the program NBO 5.0[20] included in Gaussian 98.

Acknowledgement

The research project was supported by the Swiss National Science Foundation through grant 200020–100346. The authors would like to thank Prof. F. Weinhold, Prof. F. Diederich, Dr. N. Moonen, and Dr. D. Bakowies for fruitful and stimulating discussions.

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Received: March 30, 2004