

Applications of natural orbitals for chemical valence in a description of bonding in conjugated molecules

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Abstract Natural orbitals for chemical valence (NOCV) were used to describe bonding in conjugated π -electron molecules. The ‘single’ C–C bond in *trans*-1,3-butadiene, 1,3-butadiene-1,1,4,4-tetra-carboxylic acid, 1,3,5,7-octatetraene, and 11-*cis*-retinal was characterized. In the NOCV framework, the formation of the σ -bond appears as the sum of two complementary charge transfer processes from each vinyl fragment to the bond region, and partially to the other fragment. The formation of the π -component of the bond is described by two pairs of NOCV representing the transfer of charge density from the neighboring ‘double’ C–C bonds. The NOCV eigenvalues and the related fragment-fragment bond multiplicities were used as quantitative measures of the σ - and π - contributions. The σ -component of the ‘single’ C–C bonds appears to be practically constant in the systems analyzed, whereas the π -contributions increase from butadiene (ca. 7.5%) to retinal (ca. 14%).

Keywords Natural orbitals for chemical valence · Deformation density · Bond orders · Conjugated hydrocarbons

Introduction

One of the main goals of theoretical chemistry is to understand the character of bonding in molecular systems. When interpreting the molecular structure in chemical terms, some intuitive quantities are often used. Although

proven useful, many of them are not observable in a quantum mechanical sense. The elusive nature of the basic chemical concepts, such as atom-in-molecule or chemical bond [1], implies the existence of numerous definitions of atomic charges [2–4], bond order indices [5–13], and localized bond orbitals [14–17].

We have recently introduced the concept of natural orbitals for chemical valence (NOVC) [18] that lead to a very compact description of bonding in terms of only a few orbitals localized in the bond region. Defined within the framework of the chemical valence theory of Nalewajski and Mrozek [8–13], NOCV are directly linked to the concepts of bond-orders and deformation density, $\Delta\rho$. It has been demonstrated that this set of orbitals is especially useful in describing bonding in transition metal complexes, as it allows for a direct separation of the ligand \rightarrow metal and metal \rightarrow ligand electron transfer processes. Thus, in the NOCV framework, it is possible to directly address the Dewar-Chatto-Duncanson donation/back-donation model [19, 20]. Accordingly, NOCV have recently been applied to characterize donor and acceptor properties of different ligands in the square-planar transition metal complexes [21].

Indeed, the scope of possible NOCV applications is not limited to transition-metal based systems. The main purpose of the present study was to verify the applicability of NOCV in a description of covalent bonding in organic molecules. As a test example, we selected ‘single’ carbon–carbon bonds in molecules with a conjugated π -electron system. Thus, the NOCV description of the middle C–C bond in *trans*-1,3-butadiene will be presented, followed by analysis of its derivatives—in which the π -component in the analyzed bond is expected to be more pronounced—such as 1,3-butadiene-1,1,4,4-carboxylic acid, 1,3,5,7-octatetraene, and 11-*cis*-retinal.

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Conjugative and hyperconjugative interactions are very often used in descriptions of energetic stability, geometries and bond energies of saturated and unsaturated hydrocarbons [22–34]. Conjugative stabilization is not a measurable quantity. Indirect methods of experimental evaluation of this effect in unsaturated hydrocarbons are usually based on measurements of the hydrogenation energies [35, 36]. The same approach is often used in theoretical estimations [31, 37–40]. However, it is possible to apply other theoretical models that allow for quantitative assessment of the conjugative interaction. For example, it has been recently demonstrated by Fernández et al. [41] that energy decomposition analysis (EDA) [42, 43] can be useful in determining the strength of π -conjugation in polyenes and their derivatives. In this report, we demonstrate the possible use of NOCV in the description of conjugated systems.

Theory and computational details

NOCV have been defined [18] as the eigenvectors of the chemical valence operator of the Nalewajski-Mrozek theory [8–13]:

$$\widehat{V}\varphi_i = v_i\varphi_i \quad i = 1 \dots N \quad (1)$$

with the valence operator matrix defined as:

$$V = 1/2\Delta\mathbf{P} \quad (2)$$

where $\Delta\mathbf{P}$ corresponds to the difference between the charge- and bond-order matrices of a molecule and its promolecule. At atomic resolution, the promolecule consists of isolated atoms placed in the same positions as in the molecule, while in the fragment-resolution it is built of non-interacting molecular fragments. It has been shown that NOCV are especially useful in describing the interactions between two molecular fragments. In the present study, the two-fragment resolution was also applied. Thus, we considered formation of the molecule $A-B$ from two molecular fragments, A and B .

One of the features of NOCV is that they can be grouped in pairs of complementary orbitals corresponding to the same eigenvalue with the opposite sign [18]:

$$\widehat{V}\varphi_{-k} = -v_k\varphi_{-k}, \quad \widehat{V}\varphi_k = v_k\varphi_k, \quad k = 1 \dots N/2 \quad (3)$$

It should be pointed out that, within each pair, both natural orbitals have fractional occupation numbers in the promolecule as well as in the molecule, as they differ from the molecular orbitals and the isolated fragment orbitals.

Taking into account Eq. 3, the deformation density, $\Delta\rho = \rho(\text{molecule}) - \rho(\text{fragments})$, can be expressed in the

NOCV representation as the sum of the pair-contributions [18]:

$$\Delta\rho(r) = \sum_{k=1}^{N/2} v_k [-\varphi_{-k}^2(r) + \varphi_k^2(r)] = \sum_{k=1}^{N/2} \Delta\rho_k(r) \quad (4)$$

Interpretation of NOCV follows from Eq. 4: an eigenvalue, v_k , corresponds to a fraction of electron density that is transferred from the φ_{-k} orbital to the φ_k orbital, when the molecule is formed from the fragments. Thus, complementary pairs of NOCV define decoupled channels for the electron transfer between the fragments. Therefore, in their character, NOCV are similar to the inter-reactant modes defined within charge sensitivity analysis, that describe changes in atomic electron populations [44].

One of the basic quantities in the Nalewajski-Mrozek theory of chemical valence [8–13] is the overall valence, V . For a given molecular system, the value of V corresponds to the number of chemical bonds in the system. In atomic resolution, a decomposition of V into diatomic contributions allows the bond-order indices (bond-multiplicities) to be defined [9, 11–13]. In the two-fragment resolution, the overall valence directly provides a measure of the fragment-fragment bond multiplicity.

The overall valence can be obtained as the expectation value of the valence operator [12]:

$$V = \langle \Psi | \widehat{V} | \Psi \rangle = \text{Tr}(\mathbf{P}\mathbf{V}) = \text{Tr}(\mathbf{P}1/2\Delta\mathbf{P}) \quad (5)$$

It has been shown by Nalewajski et al. [12] that

$$1/2 \text{Tr}(\mathbf{P}\Delta\mathbf{P}) = 1/4 \text{Tr}(\Delta\mathbf{P}^2) \quad (6)$$

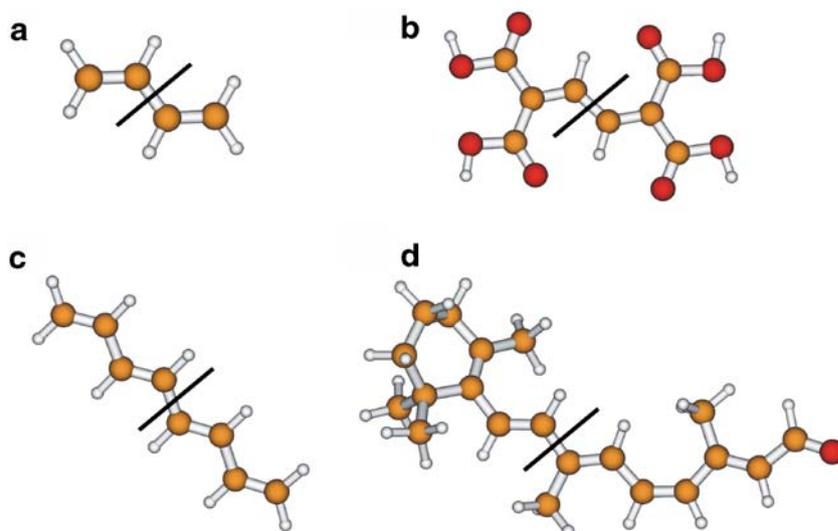
Thus, the overall chemical valence can be written in terms of the NOCV eigenvalues as:

$$V = \frac{1}{4} \sum_{i=1}^N v_i^2 \quad (7)$$

In all the DFT calculations presented here, the Amsterdam density functional (ADF) program [45–50] was used. The Becke-Perdew exchange-correlation functional [51–53] was applied. A ‘standard’ double-zeta STO basis with one set of polarization functions, included in the ADF program [45 and references therein], was used. The $1s$ electrons of C and O were treated as frozen core. Auxiliary s , p , d , and f STO functions, centered on all nuclei, were used to fit the electron density and obtain accurate Coulomb and exchange potentials in each SCF cycle. The influence of the basis set and the frozen core approximation on the results was tested for butadiene by performing additional calculations on the SZ/1s, TZP/1s, and DZP/all electron level.

The molecules investigated in the present work are presented in Fig. 1. For each system, the bond marked by a

Fig. 1 Molecules considered in the present work. The line dividing each molecule into two fragments indicates the bond characterized; the corresponding promolecule built of two non-interacting fragments was used



line dividing the molecule into two fragments was characterized.

In order to describe the middle C–C bond (‘single’) in *trans*-butadiene, formation of the molecule from a promolecule built of two non-interacting vinyl fragments, $-\text{CH}=\text{CH}_2$, was considered. Since the vinyl fragments have unpaired electron, the spin-resolved approach was applied. Namely, two sets of NOCV for spin alpha and beta were obtained from separate diagonalizations of the respective $\Delta\mathbf{P}^\alpha$ and $\Delta\mathbf{P}^\beta$ matrices. In the promolecular state, the opposite spin of the two unpaired electrons on the fragments, $\text{H}_2\text{C}=\text{CH}\uparrow$ and $\downarrow\text{HC}=\text{CH}_2$, was assumed as the most natural choice: in such a case the total number of spin alpha and beta electrons is preserved. Similarly, for the remaining molecules, a two-fragment promolecule was considered in each case, with the opposite spin of the unpaired electrons on the two fragments.

It should be pointed out that, in Eqs. 1–7, the spin restricted case (spin restricted molecule and spin-restricted fragments) was assumed for simplicity. The corresponding expressions for the spin-resolved approach can be easily obtained with $\Delta\mathbf{P}^\alpha$ and $\Delta\mathbf{P}^\beta$ matrices. However, the pre-factor 1/2 must be replaced by 1 (and, consequently, 1/4 by 1/2), since $\mathbf{P} = \mathbf{P}^\alpha + \mathbf{P}^\beta = 2\mathbf{P}^\alpha = 2\mathbf{P}^\beta$, and $\Delta\mathbf{P} = \Delta\mathbf{P}^\alpha + \Delta\mathbf{P}^\beta$ and thus

$$\begin{aligned} \text{Tr}(\mathbf{P}^\alpha \Delta\mathbf{P}^\alpha + \mathbf{P}^\beta \Delta\mathbf{P}^\beta) &= \text{Tr}([1/2\mathbf{P}]\Delta\mathbf{P}^\alpha + [1/2\mathbf{P}]\Delta\mathbf{P}^\beta) \\ &= \text{Tr}([1/2\mathbf{P}][\Delta\mathbf{P}^\alpha + \Delta\mathbf{P}^\beta]) = \text{Tr}(1/2\mathbf{P}\Delta\mathbf{P}) \\ &= 1/2 \text{Tr}(\mathbf{P}\Delta\mathbf{P}) \end{aligned} \quad (8)$$

In particular, Eq. 7 then takes the form

$$V = \frac{1}{2} \sum_{i=1}^N (v_i^\alpha)^2 + (v_i^\beta)^2 \quad (7a)$$

where v_i^α and v_i^β are the NOCV eigenvalues obtained from diagonalization of $\Delta\mathbf{P}^\alpha$ and $\Delta\mathbf{P}^\beta$ matrices.

Results and discussion

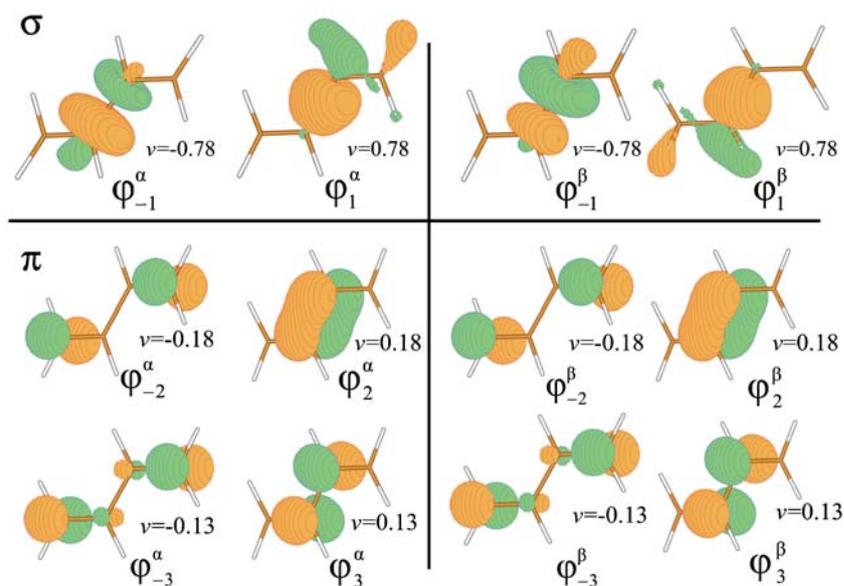
We will start the discussion with the NOCV description of the middle C–C bond (‘single’) in the butadiene molecule. The contours of NOCV characterizing this bond are shown in Fig. 2. The corresponding contributions to the deformation density $\Delta\rho$ are shown in Fig. 3. Table 1 lists the crucial NOCV eigenvalues for all the systems studied.

Within each spin-subset there are three pairs of complementary NOCV participating in bonding: one pair of σ -symmetry and two pairs of π -symmetry. As the middle C–C bond in butadiene has predominantly single-bond character, the eigenvalues corresponding to the NOCV with σ -symmetry are substantially higher (0.78) than those for π -symmetry (0.18 and 0.13). The σ - and π -contributions to the fragment-fragment bond-multiplicity (overall valence) from Eq. 7a are 1.21 and 0.10, respectively.

Let us first discuss the NOCV that contribute to σ -bonding. The first orbitals for each spin, φ_{-1}^α and φ_{-1}^β , exhibit antibonding character and each has a visibly larger contribution on one fragment. The complementary φ_1^α and φ_1^β orbitals are bonding, and each extends from the bond-region to the other fragment. Obviously, due to the symmetry of the butadiene molecule and the fragment-based promolecule, the overall shape of the spin α and spin β NOCV is the same, but they are localized on opposite fragments.

The contributions to the deformation density $\Delta\rho$ from the two pairs of the σ -NOCV are shown in the upper part of Fig. 3. It is clear from these plots that each pair describes the charge transfer from one fragment to the bond-region

Fig. 2 Natural orbitals for chemical valence (NOCV) characterizing the central C–C bond in butadiene. NOCV are grouped in pairs corresponding to the same eigenvalue with the opposite sign. For clarity, the two sets of spin-resolved NOCV, as well as the orbitals of the σ - and π -character are separated by *solid lines*. The contours corresponding to $|\phi|=0.1$ a.u. are plotted; the respective NOCV-eigenvalues (ν) are shown



and the C–H bonds on the other fragment. The shape of the ‘outflow-contour’ (negative $\Delta\rho$) corresponds roughly to the shape of the SOMO fragment orbital, with some participation of the terminal C–C bond. Thus, in the NOCV picture, the formation of the σ -bond is visualized as the sum of two complementary charge transfer processes from the two fragments. These charge-flow channels give rise to the overall σ -contribution to the deformation density, $\Delta\rho_\sigma$, shown in the upper part of Fig. 3b.

The NOCV that contribute to the π -bonding are practically identical for spin α and β . In each case, the first pair (φ_{-2}^α and φ_2^α , φ_{-2}^β and φ_2^β) comprises the orbital with a dominant contribution from terminal carbon atoms of the two fragments (φ_{-2}^α or φ_{-2}^β), and the π -bonding orbital, perfectly localized in the bond region (φ_2^α or φ_2^β). The density-difference contours of Fig. 3 ($\Delta\rho_2^\alpha$ and $\Delta\rho_2^\beta$) show

that such a pair describe a charge flow from the p -orbitals of the terminal carbon atoms to the bond-region. In the last pair of NOCV for each spin, both orbitals (φ_{-3}^α and φ_3^α , φ_{-3}^β and φ_3^β) exhibit antibonding character. From the $\Delta\rho$ -contributions of Fig. 3 ($\Delta\rho_3^\alpha$ and $\Delta\rho_3^\beta$), it is clear that these orbitals describe an intra-fragment polarization, with the charge outflow from the middle towards the terminal carbon atoms.

The overall π -contribution to the deformation density, $\Delta\rho_\pi$, is shown in the lower part of Fig. 3b (contour $\Delta\rho_\pi = 0.005$ a.u.). The lower density contour ($\Delta\rho_\pi = 0.002$ a.u.) is also presented in Fig. 4a. There, two plots show the outflow of electrons from the terminal C–C π -bonds (including the terminal carbon atoms) and the accumulation of the π -electron density in the middle C–C bond region.

Table 2 presents the NOCV values calculated for the *trans*-butadiene molecule with different basis sets (SZ,

Fig. 3 Contributions to the deformation density, $\Delta\rho = \rho(\text{molecule}) - \rho(\text{fragments})$ from the pairs of complementary NOCV (see Fig. 2), $\Delta\rho_k(r) = \nu_k [-\varphi_{-k}^2(r) + \varphi_k^2(r)]$ (a) and the total σ - and π -contributions to $\Delta\rho$ (b). The contours corresponding to $|\Delta\rho|=0.005$ a.u. are plotted. The *green* and *orange* contours correspond to positive and negative $\Delta\rho$, respectively

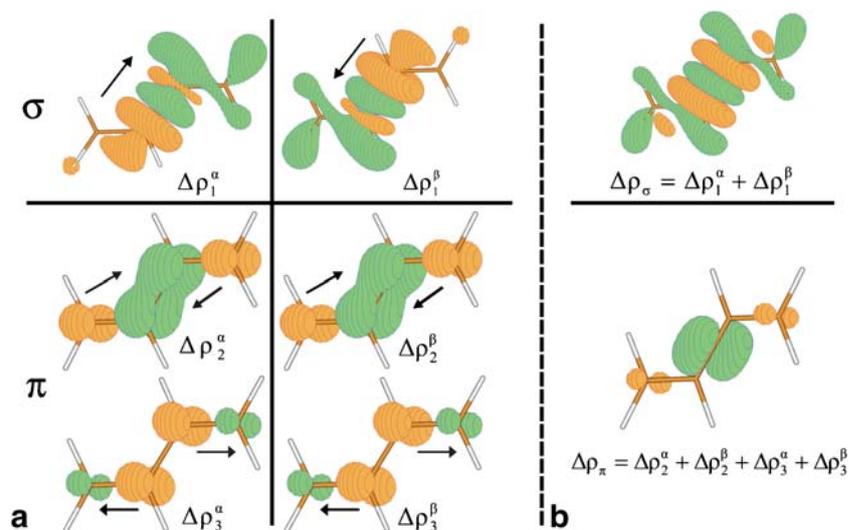


Table 1 Natural orbitals for chemical valence (NOCV) eigenvalues (v_1 , v_2 , v_3) and the corresponding contributions to the fragment-fragment bond multiplicity (b_σ , b_π)

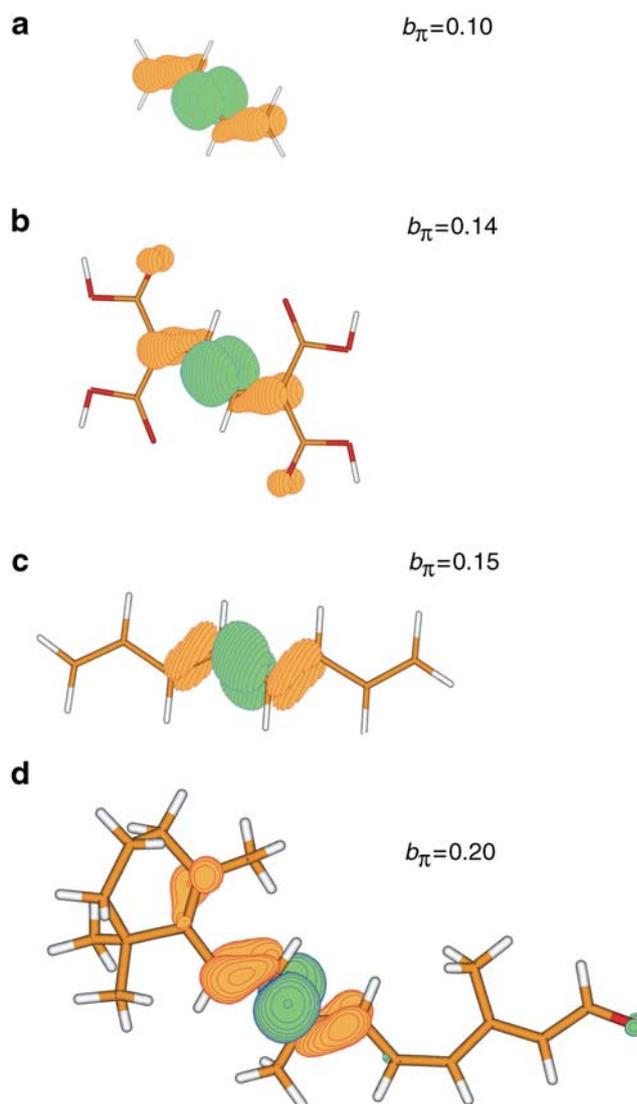
Molecule	σ -component		π -component	
	v_1	b_σ	v_2, v_3	b_π
H ₂ C=CH-CH=CH ₂	0.78	1.21	0.18, 0.13	0.10
(COOH) ₂ C=CH-CH-C(COOH) ₂	0.78	1.21	0.22, 0.17	0.14
H ₂ C=CH-CH=CH-CH=CH-CH=CH ₂	0.78	1.21	0.22, 0.15	0.15
11- <i>cis</i> -retinal	0.78	1.21	0.26, 0.18	0.20

DZP, TZP); the influence of the frozen core approximation was tested as well for DZP basis. The results clearly show that, even for a SZ basis set, the qualitative picture is identical. The results for DZP and TZP are practically the same (differences in the third decimal point). Also, the use of the frozen core approximation (1s frozen for non-hydrogen atoms) introduces a negligible error in NOCV eigenvalues (up to 0.002 a.u.)

In order to further test the applicability of NOCV in the description of conjugated π -electron systems, we determined the NOCV and their $\Delta\rho$ contributions for a few larger molecules in which the π -contribution in the ‘single’ C–C bond should be increased compared to butadiene. This set comprises 1,3-butadiene-1,1,4,4-tetra-carboxylic acid, 1,3,5,7-octatetraene, and 11-*cis*-retinal. In each case the qualitative picture of bonding in the NOCV framework is similar to butadiene. Namely, there are three pairs of NOCV in each spin subset: a σ -NOCV pair and two π -NOCV pairs; their general features are the same as for butadiene. Therefore, the NOCV contours will not be shown here. The NOCV eigenvalues are collected in Table 1 together with the corresponding σ - and π -contributions to the overall fragment-fragment bond multiplicity (overall valence). The contours of the respective $\Delta\rho_\pi$ contributions are compared in Fig. 4.

The results presented in Table 1 show that the σ -eigenvalue practically does not change for the systems studied here: in each case $v_1=0.78$. Thus, the corresponding σ -contribution to the fragment-fragment bond multiplicity remains constant, $b_\sigma = 1.21$.

The contours of the $\Delta\rho_\pi$ contributions shown in Fig. 4 exhibit the similar character of the π -electron density changes for all analyzed molecules. Namely, partial π -bond formation appears mostly at the expense of neighboring ‘double’ C–C bonds. Obviously, the changes in π -bonding must propagate further; they are too small, however, to appear on the 0.002 a.u. contour of electron density difference. Only in the case of tetra-carboxylic acid and the retinal molecule do noticeable changes emerge. In the

**Fig. 4** Comparison of the total π -contributions to the deformation density for the molecules studied in the present work. The contours corresponding to $|\Delta\rho_\pi| = 0.002$ a.u. are plotted. The green and orange contours correspond to positive and negative $\Delta\rho_\pi$, respectively**Table 2** The influence of basis sets and frozen core approximation on the NOCV eigenvalues corresponding to the σ and π components of the middle C–C bond in *trans*-butadiene

NOCV eigenvalues	Basis set / frozen core level			
	SZ / 1s	DZP / 1s	TZP / 1s	DZP
σ component:	0.746	0.780	0.782	0.782
v_1				
π component:	0.185, 0.121	0.178,	0.175,	0.177,
v_2, v_3		0.130	0.137	0.130

former case, a decrease in electron density of lone pairs of carboxyl oxygen atoms is visible, while in the latter case, the ‘double’ bond in the hexene ring is weakened.

From the three-dimensional contours shown in Fig. 4, it is difficult to compare the magnitude of the π -electron density changes. The numerical data in Table 1 allow for such a comparison. The π -NOCV eigenvalues and the π -bond multiplicity increase from butadiene ($v_\pi = 0.81, 0.13$; $b_\pi = 0.10$) to retinal ($v_\pi = 0.26, 0.18$; $b_\pi = 0.20$). Thus, the π -bond contribution in retinal is doubled compared to that of butadiene.

From the overall fragment-fragment bond-multiplicities, it may be concluded that the middle C–C bond in butadiene is ca. 92.5% σ -bond and ca. 7.5% π -bond. The analyzed C–C bond (‘single’) in the retinal molecule in a σ -bond in ca. 86% and π -bond in ca. 14%. The increase in π -bonding is reflected by the changes in the corresponding C–C bond lengths: in retinal the analyzed C–C bond is substantially shorter (1.438 Å) than in butadiene (1.451 Å).

It should be pointed out that the above NOCV result for butadiene is in good agreement with the estimation of Fernández et al. [41], based on EDA analysis, predicting ca. 8.6% of π -character.

Concluding remarks

In the present study, NOCV were used to describe bonding in conjugated π -electron molecules. The ‘single’ C–C bond in *trans*-1,3-butadiene, 1,3-butadiene-1,1,4,4-tetra-carboxylic acid, 1,3,5,7-octatetraene, and 11-*cis*-retinal was characterized. The results demonstrate that NOCV provide an attractive framework for the representation of covalent bonding. In the NOCV reference frame, the formation of the σ -bond appears as the sum of two complementary charge transfer processes from each vinyl fragment to the bond region, and partially to the other fragment. The formation of the π -component of the bond is described by two pairs of NOCV, representing the transfer of the charge density from the neighboring ‘double’ C–C bonds. The results also show that the NOCV eigenvalues and the related fragment-fragment bond multiplicities can be used as quantitative measures of the σ - and π - contributions. It was demonstrated that σ components of ‘single’ C–C bonds appear to be practically constant in the systems analyzed, whereas the π -contribution increases from butadiene (7.5%) to retinal (14%).

To conclude, the present results demonstrate the applicability of NOCV in the description of covalent bonds in organic molecules. A direct link to the deformation density and bond-multiplicity measures within one common theoretical framework is a distinctive feature of NOCV that makes them useful as a supplementary tool for analyzing the electronic structure of molecular systems.

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