Theoretical description of hydrogen bonding in oxalic acid dimer and trimer based on the combined extended-transition-state energy decomposition analysis and natural orbitals for chemical valence (ETS-NOCV)

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Abstract In the present study we have analyzed hydrogen bonding in dimer and trimer of oxalic acid, based on a recently proposed charge and energy decomposition scheme (ETS-NOCV). In the case of a dimer, two conformations, α and β, were considered. The deformation density contributions originating from NOCV’s revealed that the formation of hydrogen bonding is associated with the electronic charge deformation in both the σ—(Δρσ) and π-networks (Δρπ). It was demonstrated that σ-donation is realized by electron transfer from the lone pair of oxygen on one monomer into the empty ω»H/C0/O orbital of the second oxalic acid fragment. In addition, a covalent contribution is observed by the density transfer from hydrogen of H-O group in one oxalic acid monomer to the oxygen atom of the second fragment. The resonance assisted component (Δρπ), is based on the transfer of electron density from the π—orbital localized on the oxygen of OH on one oxalic acid monomer to the oxygen atom of the other fragment.

ETS-NOCV allowed to conclude that the σ(O—HO) component is roughly eight times as important as π (RAHB) contribution in terms of energetic estimation. The electrostatic factor (ΔEelstat) is equally as important as orbital interaction term (ΔEorb). Finally, comparing β-dimer of oxalic acid with trimer we found practically no difference concerning each of the O—HO bonds, neither qualitative nor quantitative.

Keywords ETS-NOCV · Extended transition state · Natural orbitals for chemical valence · Oxalic acid dimer and trimer · Resonance assisted hydrogen bonds

Introduction

Hydrogen bonding (HB) plays an important role in biochemistry [1, 2]. Accordingly, many attempts were made to describe HB-phenomenon in both experimental and theoretical laboratories [3–11]. For the purpose of understanding the nature of hydrogen bonding, theoretical approaches appeared to be of significant importance [12–19]. Especially, electrostatic-covalent HB model, derived by Gilli [20, 21] from the systematic analysis of structural and spectroscopic data, allowed to make a comprehensive classification of H-bonds in a different chemical classes: e. g., charge assisted hydrogen bonds, low barrier hydrogen bonds, dihydrogen bonds, and resonance-assisted hydrogen bonds (RAHBs). It clearly shows that different factors can influence the nature of hydrogen connections.

For the purpose of HB description, various energy decomposition analysis (EDA) were also used [22–25, 46]. In such decomposition schemes, the total interaction energy between interacting sub-systems is divided up into a few
chemically meaningful contributions (electrostatic, exchange, charge-transfer, relaxation, etc.). Despite great usefulness of these methods, as they allow to extract stabilizing and destabilizing factors, none of them provide direct, qualitative and quantitative, separated information about σ—and π-contributions. Such specific knowledge on the hydrogen bonding phenomenon can be useful in understanding the structures of bio-molecules and further in a description of reactivity.

We have recently developed the ETS-NOCV scheme by combining the extended transition state (ETS) [26, 27] energy decomposition approach with the natural orbitals for chemical valence (NOCV) density analysis method [28–34]. It was shown that ETS-NOCV is able to extract and directly quantify the crucial components (σ, π, δ, etc.) that participate in various types of chemical bonds including predominantly donor-acceptor and covalent interactions [35, 36]. Furthermore, we have shown that ETS-NOCV can also be useful in a description of weak bonds [35, 36], including intra—and inter-molecular hydrogen bonding. For example, we have found, based on the analysis of intermolecular bonding in Adenine-Thymine base pair, that ETS-NOCV provides separated, qualitative and quantitative information not only about both σ(O—HN) and σ(N—HN) interactions, but also about the resonance assisted hydrogen bonding contribution (π) [35].

The main goal of this article is to extend our study on weak intermolecular interaction by characterization of hydrogen bonding in the dimeric and trimeric systems consisting of both σ(O—HO) and π-interactions between the monomers. We will consider in our analysis the oxalic acid dimers exhibiting two different conformations α and β (1 and 2), Fig. 1. In addition, we will investigate oxalic acid trimers, 3 and 4, based on two different bond-partitioning, as indicated in Fig. 1. The purpose of doing so is to obtain a compact description of each O—HO interaction in trimer of oxalic acid. To the best of our knowledge this is the first study reporting on the character of bonding in the oxalic acid systems based on charge and energy decomposition analysis. All structures discussed here were fully optimized after initial guesses taken from the Cambridge Structural Database [37, 38]. For the sake of clarity of presentation we will use throughout our study the “α-dimer” and “β-dimer” terms to describe the oxalic acid dimers that exhibit two different conformations α and β, respectively.

**Computational methods**

As we mentioned in the previous paragraph, our analysis is based on the ETS-NOCV approach which is a combination of the extended transition state (ETS) [26, 27] method with the natural orbitals for chemical valence (NOCV) [28–34] scheme.

We shall start by presenting the basic concepts of the ETS method. In this scheme, the total bonding energy between the interacting fragments (ΔE_{total}) is divided into four chemically meaningful components Eq. 1:

\[
\Delta E_{\text{int}} = \Delta E_{\text{dist}} + \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}.
\]

The first component, referred to as the distortion term ΔE_{dist}, represents the amount of energy required to promote the separated fragments from their equilibrium geometry to the structure they will take up in the combined molecule. The second term, ΔE_{elstat}, corresponds to the classical electrostatic interaction between the promoted fragments as they are brought together to form A⋯B. Thus, our analysis is based on the bonding between the two close shell molecular fragments.

**Computational details**

All the calculations, within dDensity functional theory approach, were based on the Amsterdam density functional (ADF2009) program in which ETS-NOCV scheme was implemented [39–43]. The Becke-Perdew exchange-correlation functional [44, 45] was applied (BP86). A standard triple-zeta STO basis containing two sets of polarization functions was adopted for all of the elements (TZ2P). Auxiliary s, p, d, f, and g STO functions, centered on all nuclei, were used to fit the electron density. It was proven previously for similar systems [35, 46] that optimized structures and interaction energies based on BP86/TZ2P calculations are in line with the corresponding estimates obtained from the experiment and from high-level ab initio methods. The contours of deformation densities were plotted using ADF-GUI [47].

In our analysis each of the system is divided up into two individual fragments A and B, as shown schematically by a thick line in Fig. 1. Then we used the ETS-NOCV method to study the interaction between A and B, as they are brought together to form A⋯B. Thus, our analysis is based on the bonding between the two close shell molecular fragments.
the fragments and molecule. It should be emphasized that the meaning of where \( M \) pairs of complementary eigenfunctions (can be expressed in the NOCV representation as a sum of the second fragment (was treated as first fragment (4)尼斯 of gen bonding. In bonding analysis of 4 the middle monomer was treated as first fragment (a) and the terminal monomers as the second fragment (b) where the sum is over all the occupied and virtual molecular orbitals on the two fragments. It now follows from the ETS scheme that the \( \Delta E_{\text{orb}} \) term is given by [26, 27]

\[
\Delta E_{\text{orb}} = \sum_{k} \sum_{\mu} \Delta P_{\lambda \mu} F_{\lambda \mu}^{T}
\]

(3)

where \( F_{\lambda \mu}^{T} \) is a Kohn-Sham Fock matrix element that is defined in terms of a (transition state) potential that is mid between that of the combined fragments and the final molecule. It should be emphasized that the meaning of “transition state” in the ETS approach is completely different from that commonly used in the context of the transition state theory.

Turning next to the NOCV approach, we note that historically the natural orbitals for chemical valence (NOCV) [28–34] have been derived from the Nalewajski-Mrozek valence theory[48–54]. However, from a mathematical point of view the NOCV’s, \( \psi \), are simply defined as the eigenvectors,

\[
\psi_{i}(1) = \sum_{k} C_{i,k} \lambda(1)
\]

(4)

that diagonalize the deformation density matrix \( \Delta P \) introduced in Eq. 2. Thus,

\[
\Delta P \psi = \lambda \psi; \quad i=1,M
\]

(5)

where \( M \) denotes the total number of molecular orbitals on the fragments and \( C_{i} \) is a column vector containing the coefficients that defines the NOCV \( \psi_{i} \) of Eq. 4. It follows further [28–34] that the deformation density \( \Delta \rho \) of Eq. 2 can be expressed in the NOCV representation as a sum of pairs of complementary eigenfunctions \( \psi_{-k}, \psi_{k} \) corresponding to the eigenvalues—\( -v_{k} \) and \( +v_{k} \) with the same absolute value but opposite signs:

\[
\Delta \rho(r) = \sum_{k=1}^{M/2} v_{k} \left[ -\psi_{-k}^{*}(r) + \psi_{k}^{*}(r) \right] = \sum_{k=1}^{M/2} \Delta \rho_{k}(r).
\]

(6)

Expression (6) is the most important for the interpretation of NOCV, as it defines the charge-flow channels decomposing the overall deformation density. Therefore, in the present study we will not discuss the orbitals themselves, but only the respective deformation density contributions, \( \Delta \rho_{k} \). Examples of orbitals and their interpretation can be found elsewhere [28–30].

In the combined ETS-NOCV scheme [35, 36] the orbital interaction term (\( \Delta E_{\text{orb}} \)) is expressed in terms of NOCV’s as

\[
\Delta E_{\text{orb}} = \sum_{k=1}^{M/2} v_{k} \left[ -F_{-k,-k}^{T} + F_{k,k}^{T} \right]
\]

(7)

where the diagonal Kohn-Sham matrix elements are defined over NOCV’s with respect to the transition state (TS). The advantage of the expression in Eq. 7 for \( \Delta E_{\text{orb}} \) over that of Eq. 3 is that only a few complementary NOCV pairs normally contribute significantly to \( \Delta E_{\text{orb}} \). We see from the above Eqs. 6, 7 that for each complementary NOCV pair, representing one of the charge deformations \( \Delta \rho_{k} \), not only can visualize \( \Delta \rho_{k} \) but also provide the energy contributions to the bond energy from \( \Delta \rho_{k} \) [28–34].

The total bonding enthalpies (\( D_{e} = -\Delta E_{\text{mol}} \)) reported here do not include zero point energy additions, finite temperature contributions or basis set superposition error corrections. Our interest here has been to study the electronic nature of hydrogen bond formation through trends in the (electronic) bond enthalpy as revealed by our recently proposed ETS-NOCV procedure [35, 36].

**Results and discussion**

Let us start our discussion from a qualitative description of hydrogen bonding in \( \beta \)-dimer of oxalic acid (2), which is more stable (by 9.9 kcal mol\(^{-1}\)) compared to dimer exhibiting \( \alpha \)-conformation (1), Table 1. It is clear from Fig. 2 that three deformation density contributions, \( \Delta \rho_{\sigma}, \Delta \rho_{\pi}^{R,H,B} \) and \( \Delta \rho_{\text{pol}} \) based on complementary NOCV’s Eq. 6, describe the formation of two equivalent \( O\text{--}H \) interactions in 2. The dominant component \( \rho(O--H) \) originates from the donation of electron density from the lone pair of oxygen into the empty \( \rho_{H--O} \) characterizing
anti-bonding orbital of H-O bond in the oxalic acid monomer. In addition, density is shifted from hydrogen of H-O group of one oxalic acid monomer to oxygen of the second fragment. The density deformation ($\Delta \rho_{\sigma}$) in the $\sigma$-network of 2 gives rise to an orbital interaction stabilization of $\Delta E_{\text{orb}} = -7.7$ kcal mol$^{-1}$. We note that the participation of $\sigma$(O—HO) component (78% of $\Delta E_{\text{orb}}$) is roughly eight times as important as $\pi$-RAHB contribution (9.8% of $\Delta E_{\text{orb}}$). At the same time, the stabilizing effect (originating from $\Delta E_{\text{orb}}$ and $\Delta E_{\text{elstat}}$) is reduced by the repulsive interaction between the occupied carbonyl lone-pair orbital on one monomer and the occupied O-H bonding orbital on the other oxalic acid fragment, what is accordingly manifested by considerable Pauli repulsion contribution ($\Delta E_{\text{Pauli}}$) by 51.5 kcal mol$^{-1}$, Table 1. The total stabilization stemming from all bonding components Eq. 1, given per one hydrogen O—HO bond, is by $\Delta E_{\text{int}}/2 = -7.95$ kcal mol$^{-1}$.

Table 1: ETS-energy decomposition$^1$ (in kcal mol$^{-1}$) of the hydrogen bonding in 1–4

| Systems | $\Delta E_{\text{Pauli}}$ | $\Delta E_{\text{elstat}}$ | $\Delta E_{\text{orb}}$ | $\Delta E_{\text{dist}}$ | $\Delta E_{\text{int}}$ |
|---------|-------------------------|--------------------------|---------------------------|-------------------------|-------------------------|
| 1       | 12.3                    | -11.1                    | -7.7                      | 0.5                     | -6.0                    |
| 2       | 51.5                    | -36.7                    | -35.9                     | 5.3                     | -15.9                   |
| 3       | 51.7                    | -36.8                    | -36.3                     | 5.4                     | -15.9                   |
| 4       | 103.6                   | -74.4                    | -71.6                     | 10.7                    | -31.6                   |

$^1 \Delta E_{\text{int}} = \Delta E_{\text{Pauli}} + \Delta E_{\text{elstat}} + \Delta E_{\text{dist}} + \Delta E_{\text{orb}}.$

$^2$The labeling corresponds to Fig. 1.

The second stabilizing contribution in 2 comes from the electrostatic attraction ($\Delta E_{\text{elstat}}$) between the oxalic acid monomers. It amounts to $-36.7$ kcal mol$^{-1}$. Such an interaction is due to the stabilizing interaction between the $\delta^+ H$—$\delta^- O$ dipole of the HO bond in one monomer and the $\delta^- O$—$\delta^+ C$ dipole of the carbonyl group of the second oxalic acid fragment. Further stabilization comes from the fact that the electron density of one fragment only partially can shield the interaction of the nuclei on the same fragment from the electron density on the other fragment. The reduced shielding is due to intra-penetration of the two fragment densities. The reduced shielding is due to inter-penetration of the two fragment densities. It should be noted that $\sigma$(O—HO) component (78% of $\Delta E_{\text{orb}}$) is roughly eight times as important as $\pi$-RAHB contribution (9.8% of $\Delta E_{\text{orb}}$). At the same time, the stabilizing effect (originating from $\Delta E_{\text{orb}}$ and $\Delta E_{\text{elstat}}$) is reduced by the repulsive interaction between the occupied carbonyl lone-pair orbital on one monomer and the occupied O-H bonding orbital on the other oxalic acid fragment, what is accordingly manifested by considerable Pauli repulsion contribution ($\Delta E_{\text{Pauli}}$) by 51.5 kcal mol$^{-1}$, Table 1. The total stabilization stemming from all bonding components Eq. 1, given per one hydrogen O—HO bond, is by $\Delta E_{\text{int}}/2 = -7.95$ kcal mol$^{-1}$. 

Fig. 2 The contours of deformation density contributions $\Delta \rho_{\sigma}$, $\Delta \rho_{\text{RAHB}}$, $\Delta \rho_{\text{pol}}$ describing the hydrogen bonding between the monomers in 2. In addition the corresponding ETS-NOCC based energies (in kcal mol$^{-1}$) are shown. The numerically smallest contour values are ±0.001 a.u.
Table 1. It is made up from the orbital interaction stabilization, \( \Delta E_{\text{orb}}/2 = -17.95 \text{ kcal mol}^{-1} \) and destabilizing \((\Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{dist}})/2 = 10.0 \text{ kcal mol}^{-1} \).

The ETS results gathered in Table 1 lead to the conclusion that \( \alpha \)-conformation of oxalic acid dimer (1) is energetically less stable than the corresponding \( \beta \)-structure (\(|\Delta E_{\text{int}}| \) lower by 9.9 kcal mol\(^{-1}\)), as a result of changes in all of the bonding contributions defined in Eq. 1. The main reason of a relatively small stabilization from \( \Delta E_{\text{orb}} \) is that solely one O–HO bond is formed between the oxalic acid monomers. The qualitative picture of \( \sigma (\text{O—HO}) \) formation (see Fig. 3) is analogous to 2, with practically no participation (<1 kcal mol\(^{-1}\)) from the \( \pi \)-network. The lack of considerable RAHB contribution is related to the broken planarity in 1. The lower destabilization from Pauli term, as well as lower stabilization from electrostatic contribution for 1 originate from the fact that the monomers are further apart (by 0.2\( \text{Å} \)), compared to \( \beta \)-dimer (2). We should remark at this point that the experimental lattice energy estimations for \( \alpha \)-and \( \beta \)-conformations of oxalic acid in the crystal show that these two forms are roughly similar in stability [55]. This is consistent with our result. Apparently, the dimeric and trimeric structures are not appropriate as models of real, infinite, periodic crystals. However, it was not our intention. As it was stated in the Introduction section, the main goal of our investigation was to verify the applicability of our new ETS-NOCV scheme in a description of bonding in hydrogen bonded molecules that exhibit both \( \sigma (\text{O—HO}) \) and \( \pi \) (RAHB) interactions. It would be worthy to conduct in the future a similar energy decomposition analysis (ETS), as implemented in the BAND program [56], which is suitable for periodic calculations. Such an analysis could shed light on the origin of stability for both oxalic acid conformations in the crystal [55].

It is obvious from three deformation density contributions and their corresponding energies, depicted in Fig. 4, that there is practically no difference in the picture of O—HO bonding, neither qualitative nor quantitative when comparing to dimer 2 (Fig. 2). Furthermore, the data collected in Table 1 lead to the conclusion that not only electronic factor \( \Delta E_{\text{orb}} \), but as well the remaining contributions, i.e., Pauli repulsion, electrostatic and distorsion terms, are of the same magnitude, as in the case of 2. Accordingly, the total interaction energy, \( \Delta E_{\text{int}} \), in trimer 3 is exactly the same as for dimer 2. The same qualitative picture of bonding formation in 2 and 3 lead to the conclusion that NOCV’s exhibit a feature of localized orbitals, i.e. they reveal the same characteristics of a given bond when going from one molecule to another.

Up to this point we have analyzed the two O–HO interactions in trimer 3, i.e., the trimer was divided up into
two subsystems (A and B), as indicated in Fig. 1. For the purpose of simultaneous analysis of all four O—HO interactions that are present in β-oxalic acid trimer, we have considered another bonding situation 4. In such a bonding pattern we have used the middle β-oxalic acid as one fragment and the remaining two monomers as the second fragment. In such a way the formation of all four O—HO bonds connected to each monomer is described, Fig. 1.

It is clear from the deformation densities and the corresponding energies, presented in Fig. 5, that the total strength of four σ(O—HO) contributions is by −56.9 kcal mol⁻¹, whereas the resonance assisted hydrogen bonding component (RAHB) is by −6.5 kcal mol⁻¹. The remaining intra-fragment polarizations amounts to −8.2 kcal mol⁻¹. Further, an inclusion of other stabilizing (electrostatic) and destabilizing (Pauli repulsion and distortion term) factors gives rise to the total interaction energy by −31.6 kcal mol⁻¹, which is, in line with the intuition, nearly doubled in magnitude, compared to ΔE_int for system 3, Table 1. It confirms an equivalence of each O—HO interaction in trimer of oxalic acid.

To the best of our knowledge there is no available data in the literature on the character of bonding in dimer or trimer of oxalic acid. However, a few theoretical studies were reported recently for familiar molecules, i.e. for pyrrole-2-carboxylic acid and formic acid dimers, containing as well the two equivalent O—HO interactions, supported further by RAHB contribution [57, 58]. In these studies the electronic enthalpies (per one O—HO hydrogen bond) are −5.8 kcal mol⁻¹ and −8.5 kcal mol⁻¹ for formic and pyrrole-2-carboxylic dimers, respectively. We obtained the value of −7.9 kcal mol⁻¹ for β-dimer. In addition, similar qualitative picture of bonding formation based on the total deformation density contours was found by Beck et al. and Góra et al. [57, 58]. In the above studies, however, no information on the relative importance of σ—and π-contributions was provided. Recently, Guerra et al. reported for Adenine-Thymine and Guanine-Cytosine base pairs that the dominant contribution comes from the σ-component, whereas π-contribution adds very little stabilization [46]. This is a similar trend to our findings for oxalic acid molecules.

**Concluding remarks**

In the present study we have characterized hydrogen bonding in the dimer and the trimer of α—and β-oxalic acid, based on the recently proposed ETS-NOCV procedure. The main attention was paid to characterization of HB from both qualitative (by providing deformation density contributions, Δρσ and a quantitative (by providing energetic estimations ΔEk for each Δρσ) point of view.

We found based on the NOCV-deformation density contours that the formation of hydrogen bonding is associated with the electronic charge redistribution in both the σ—(Δρσ) and π-networks (Δρπ). It was shown that σ-donation is realized by electron transfer from the lone pair of oxygen on one monomer into the empty ρ HO orbital of the second oxalic acid fragment. In addition, a covalent contribution is observed by the density transfer from hydrogen of H-O group in one oxalic acid monomer to the oxygen atom of the second fragment. The resonance assisted component (Δρπ), RAHB, is based on the transfer of electron density from the π—orbital localized on the oxygen of OH on one oxalic acid monomer to the oxygen atom of the other fragment. The σ(O—HO) component is roughly eight times as important as π-contribution in β-oxalic acid dimer (2) and trimers (3,4). The electrostatic factor (ΔEelstat) is quantitatively as important as orbital interaction term (ΔErot). Finally, comparing β-dimer (2) with trimer of oxalic acid (3) we found practically no difference in the characteristics of each of the O—HO bonds, neither qualitative nor quantitative.
