On the stability of *cis*- and *trans*-2-butene isomers. An insight based on the FAMSEC, IQA and ETS-NOCV schemes

Ignacy Cukrowski[1)*], Filip Sagan[2)] and Mariusz Paweł Mitoraj[2)*]

[1)]Department of Chemistry, Faculty of Natural and Agricultural Sciences, University of Pretoria, Lynnwood Road, Pretoria 0002, South Africa.

[2)] Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, R. Ingardena 3, 30-060 Cracow, Poland.

*Corresponding authors:
E-mail: ignacy.cukrowski@up.ac.za
Landline: +27 12 420 3988
Fax: +27 12 420 4687

E-mail: mitoraj@chemia.uj.edu.pl
Landline: +48 12 663-2042

ABSTRACT:

In the present account the real space Fragment Attributed Molecular System Energy Change (FAMSEC) approach, Interacting Quantum Atoms (IQA) energy decomposition scheme as well as molecular orbitals based the Extended Transition State scheme coupled with Natural Orbitals for Chemical Valence (ETS-NOCV) have been, for the first time, successfully used to delineate factors of importance for stability of the 2-buthene conformers (*cis*-eq, *cis*-TS, *trans*-eq, *trans*-TS). Our results demonstrate that atoms of the controversial H--H contact in *cis*-eq (i) are involved in attractive interaction dominated by the exchange-correlation term, (ii) are weekly stabilized, (iii) show trends in several descriptors found in other typical H-bonds, and (iv) are part of most stabilized CH--HC fragment (*loc*-FAMSEC = -3.6 kcal/mol) with most favorably changed intrafragment interactions on *trans*-eq→*cis*-eq. Moreover, lower stability of *cis*-eq vs. *trans*-eq is linked with the entire HC=CH (ethylenic) fragment which destabilized *cis*-eq (*mol*-FAMSEC, +3.9 kcal/mol) the most. Although the H--H contact can be linked with smaller, relative to *trans*-, rotational energy barrier in *cis*-2-butene, we have proven that to rationalize this phenomenon one must account for changes in interactions between various atoms and fragments that constitute the entire molecule. Importantly, we discovered a number of comparable trends in fundamental properties of equivalent molecular fragments on a methyl group rotation; *e.g.*, interaction between BP-free H-atoms in *trans*-eq (involving C-H bonds of the methyl and ethylenic units) and BP-linked H-atoms in *cis*-eq. This proves that rotational energy barrier cannot be entirely (i) rationalize by the properties of or (ii) attributed to the H--H contact in *cis*-eq.

1. Introduction

Polar dihydrogen XH•••HY (X ≠ Y) bonds belong to important group of non-covalent interactions.[1-4] It has been proven that such interactions not only influence the stability of various materials, but they also determine reactivity.[3-4] Due to the fact that polar dihydrogen bonds (both inter- and intra-molecular ones) are found in various systems, one must also consider non-polar dihydrogen XH•••HX contacts to be stabilizing. Although, it is now quite well accepted by scientific community that inter-molecular CH•••HC contacts are weakly stabilizing due to the dominance of dispersion forces,[5-6] the opposite opinion is valid when considering intra-molecular CH•••HC interactions.[7-8] For example, Bader et al. concluded for the first time based on the QTAIM method on the stabilizing nature of intra-molecular CH•••HC interactions in the planar isomer of biphenyl.[7a] This work was then rebutted by Bickelhaupt et al.[8a] who claimed, based on the energy decomposition analysis (ETS), that the CH•••HC contacts in planar biphenyl are repulsive (which is in line with the classical text-book interpretation of the steric repulsion). In turn, Bader criticized[7c] the energy decomposition scheme that has been applied by Bickelhaupt et al. Further in depth studies by means of the Interacting Quantum Atoms (IQA) scheme[9] as well as by the FAMSEC method[7e] consistently point at stabilizing intra-molecular CH•••HC interactions in the planar biphenyl and its higher energy as compared with the twisted trans-isomer shall be attributed to the destabilization of the carbon atoms and particularly those of the bay. It shall be referenced that the similar debates are observed when considering homopolar BH•••HB interactions in hydrogen storage materials.[10-11] For example, we have recently reported,[10] in contradiction to the series of the cutting-edge articles by McGrady et al,[5,11cd] that the homopolar BH•••HB interactions in $LiNMe_2BH_3$ are destabilizing; interestingly, the inter-molecular homopolar CH•••HC interactions in $LiNMe_2BH_3$ appeared to be stabilizing.[10]

As far as homopolar CH•••HC interactions (both intra and intermolecular) are concerned one must emphasize that more and more evidences are reported in literature that highlight the stabilizing nature of such contacts.[6,7] Due to growing number of articles highlighting that alkyl groups (especially the bulky ones) are in fact dispersion donors, one must reconsider view on steric repulsion' as nicely summarized by Wagner and Schreiner.[6]

Very recently, Weinhold, Schleyer and McKee have concluded, WSM[12] based on the Natural Bond Orbitals (NBO) approach, supported by the steric–NBO analyses,[13] that the CH•••HC interactions are repulsive in the *cis* isomer of 2-butene, what intuitively explains:

(1) Why the *cis*-isomer is higher in energy as compared with the corresponding *trans*-isomer despite the fact that the CH•••HC bond path is noted in the former case.

(2) Why the barrier to internal methyl rotation in *cis*-2-butene is facile, by *ca*. +0.8 kcal/mol, whereas it is notably higher, *ca*. +2 kcal/mol for the *trans*-isomer.

A while later Matta, Sadjadi, Braden and Frenking, abbreviated as MSBF, revisited answers to the above questions (1-2) based on in depth description of the electronic structure including the analyses of changes in atomic energies upon rotations.[14] It has been concluded, contrary to WSM,[12] that: (i) CH•••HC interactions are stabilizing and the higher energy of *cis*-2-butene originates largely from the destabilization of the ethylenic C5=C7 fragment, (ii) in order to understand the barriers to methyl rotations one must take into account not only the changes in the atomic energies of the hydrogen atoms involved in the CH•••HC contact, but predominantly variations in the energies of all the remaining hydrogen and carbon atoms. These results clearly demonstrate that one shall not focus solely on arbitrary selected region of a molecule when rationalizing relative stabilities of its isomers – therefore, very careful and open-minded approach is warranted when intuitively applying unicorns (concepts) that are deeply rooted in chemistry.[15]

In the present study we hope to settle the above dispute by further and in depth characterization of the stability of *cis*- and *trans*-2-butene isomers by means of various tools suitable for description of (non)bonding situations which were not used in the previous studies.[12,14] We applied predominantly the fragment attributed molecular system energy change (FAMSEC) approach by Cukrowski[7e] which is rooted in the interacting quantum atoms (IQA) method by Pendás et al.[16] It has been proven that the FAMSEC scheme is well suited for an in depth analysis of the energy contribution made by interactions to relative energies of isomers regardless if they are of a (de)stabilizing nature and whether atoms involved are QTAIM or covalently (non)bonded. In the first implementation of FAMSEC,[7e] the common notion of classical intramolecular (i) stabilizing H•••N and H•••O interactions in the protonated forms of ethylenediamine (**Hen**) and ethanolamine (**Hea**), respectively, and (ii) destabilizing nature of steric O—O clash in the eclipsed form of glycol (**gc**) were fully recovered (Figure 1). Moreover, using the same methodology, the origin of the higher energy of the planar biphenyl, **bph**, relative to its twisted conformer and the nature of the H--H contacts was also explained –a comprehensive summary of relevant findings is included in the Supporting Information. Briefly and for convenience, $E_{\text{attr-loc}}^{\mathcal{G}}$ is the energy change of a molecular fragment $\mathcal{G}$ and $E_{\text{attr-mol}}^{\mathcal{G}}$ accounts for

this fragment energy contribution to a relative stability of a molecule on a structural change from the initial to final state.

Hence, encouraged by the successful implementation of FAMSEC, we decided to make use of this methodology in exploring the origin of the higher energy of *cis*-, relative to *trans*-2-butene as well as rotational energy barriers in the two isomers using FAMSEC/IQA-defined descriptors, among them energy contributions made by meaningful molecular fragments of these molecules, including the steric CH--HC clash. It was also of paramount importance to find out whether trends and energy contributions found from the FAMSEC-based analyses could be supported by a classical charge and energy partitioning scheme, ETS-NOCV.[17] It is important to emphasize that it is the first attempt to apply the two totally different approaches based on real space perspective and molecular orbitals based model of chemical bonding.
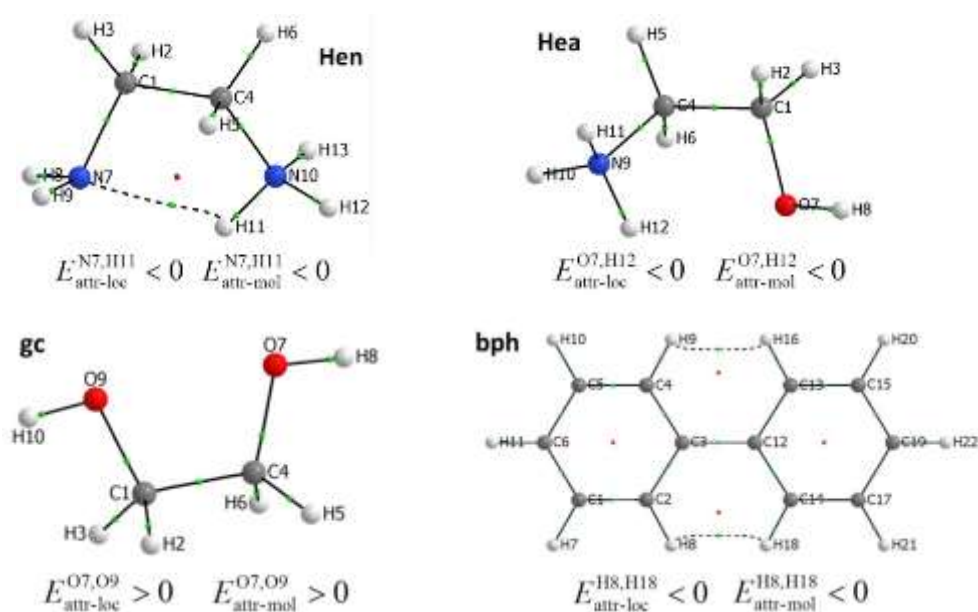

Figure 1. FAMSEC-defined energy terms obtained for (i) stabilizing intramolecular interactions in protonated forms of ethylenediamine (**Hen**) and ethanolamine (**Hea**), (ii) destabilizing steric clash O--O in the eclipsed form of glycol (**gc**) and (iii) steric contacts H--H in planar biphenyl (**bph**).[7e]

2. Computational details and methods

For the purpose of FAMSEC-based analysis, all structures were optimized using Gaussian 09, Revision D.01[18] at the MP2/6-311++G(d,p) level of theory. For the study of terminal methyl group rotational energy barrier, a relevant dihedral angle was changed by 60° and it was kept fixed during full energy optimization in Gaussian. A keyword 'density=current' was used to generate wavefunctions required for the QTAIM and IQA analyses. Molecular graph generation

5

and calculation of all energy terms within the QTAIM and IQA frameworks was carried out using Keith's AIMAll software[19] with default settings. Note that an accurate implementation of IQA requires well-defined second order density matrix but the Müller approximation of the two-electron density matrix in terms of natural orbitals of the one-electron density matrix is used in AIMAll software for post HF levels of theory. As a result, a systematic error in the IQA-recovered molecular energy is present, mainly in the computed self-atomic energies. However, systematic error cancellation took place during a comparative analysis performed in this study. To this effect, the computed difference in electronic energies of equilibrium structures, $\Delta E = E_{cis\text{-}eq} - E_{trans\text{-}eq} = 1.363$ kcal/mol, was overestimated at the MP2 level by 0.3 kcal/mol which is comparable with 0.2 kcal/mol at HF-level at which no approximation is made during IQA calculations implemented in AIMAll software. Moreover, the difference in electronic energy for *cis*-TS→*cis*-eq and *trans*-TS→*trans*-eq was reproduced by IQA to 0.0 and 0.3 kcal/mol, respectively. Hence, we concluded that the IQA-generated data at the MP2 level are perfectly suitable for comparative analyses of relative trends and conclusions arrived at must be seen as reliable and representative. The Extended Transition State coupled with Natural Orbitals for Chemical Valence (ETS-NOCV) analysis was done based on the Amsterdam Density Functional (ADF) package[20] in which this scheme was implemented. In addition, for selected cases CCSD(T) and DFT (BLYP D3, BP D3, PBE D3 and MO6 2X) calculations were also performed.

3. Basic concepts of methods used.

Extended Transition State coupled with Natural Orbitals for Chemical Valence (ETS-NOCV)

The natural orbitals for chemical valence (NOCV)[17b] are eigenvectors that diagonalize the deformation density matrix:

$$\Delta P C_i = v_i C_i \tag{1}$$

$$\Psi_i = \sum_j^N C_{i,j} \lambda_j , \tag{2}$$

where C_i is a vector of coefficients, expanding Ψ_i in the basis of fragment orbitals λ_j; N is a total number of fragment λ_j orbitals. It was shown that the natural orbitals for chemical valence pairs (ψ_{-k}, ψ_k) decompose the differential density $\Delta\rho$ into NOCV-contributions $(\Delta\rho_k)$:

$$\Delta\rho(r) = \sum_{k=1}^{M/2} [-\psi_{-k}^2(r) + \psi_k^2(r)] = \sum_{k=1}^{M/2} \Delta\rho_k(r) , \tag{3}$$

where v_k and M stand for the NOCV eigenvalues and the number of basis functions, respectively. Visual inspection of deformation density plots $(\Delta\rho_k)$ helps to attribute symmetry and the direction

6

of the charge flow. In addition, these pictures are enriched by providing the energetic estimations, $\Delta E_{orb}(k)$, for each $\Delta\rho_k$ within the ETS-NOCV scheme.[17a] The exact formula, which links the ETS and NOCV methods, will be given in the next paragraph, after we briefly present the basic concept of the ETS scheme. In this method the total bonding energy, ΔE_{int}, between interacting fragments, exhibiting the geometry as in the combined complex, is divided into three components: $\Delta E_{total} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb}$. The first term, ΔE_{elstat}, corresponds to the classical electrostatic interaction between the promoted fragments as they are brought to their positions in the final complex. The second term, ΔE_{Pauli}, accounts for the repulsive Pauli interaction between occupied orbitals on the two fragments in the combined molecule – this destabilizing contribution originates from the rise in kinetic energy and consequently it is considered as the source of 'steric' effects. Finally, the last stabilizing term, ΔE_{orb}, represents interactions between the occupied molecular orbitals of one fragment with the unoccupied molecular orbitals of the other fragment as well as mixing of occupied and virtual orbitals within the same fragment (inner-fragment polarization). This energy term may be linked to the electronic bonding effect coming from the formation of a chemical bond. In the combined ETS-NOCV scheme the orbital interaction term (ΔE_{orb}) is expressed in terms of NOCV's eigenvalues (v_k) as:

$$\Delta E_{orb} = \sum_k \Delta E_{orb}(k) = \sum_{k=1}^{M/2} v_k [-F_{-k,-k}^{TS} + F_{k,k}^{TS}], \tag{4}$$

where $F_{i,i}^{TS}$ are diagonal Kohn-Sham matrix elements defined over NOCV with respect to the transition state (TS) density at the midpoint between density of the molecule and the sum of fragment densities. The above components $\Delta E_{orb}(k)$ provide the energetic estimation of $\Delta\rho_k$ that may be related to the importance of a particular electron flow channel for the bonding between the considered molecular fragments.

Fragment Attributed Molecular System Energy Change (FAMSEC)

The idea of FAMSEC stems from a realization that the energy of and made by an intramolecular bond/interaction to a molecule cannot be directly computed or measured. However, one can trace many properties of a molecule when it changes from any suitable for a purpose initial state (or a reference state, *ref*) to the final state (*fin*) under consideration. In the previous implementation of FAMSEC,[7e] diatomic fragments were used to characterize classical intramolecular H-bond and steric clashes. In this work, we generalize this approach to any size of a molecular fragment $\mathcal{G}$, because 2- and 4-atom fragments will serve the purpose of this study best, whereas remaining atoms of a molecule, here 2-butene, will be treated as another poly-

7

atomic fragment $\mathcal{H}$. There are two principle components of molecular energy in the IQA scheme, self-atomic and diatomic interaction energies; hence, on any structural change only these two energy terms can change. This means that, from the perspective of a selected *n*-atom molecular fragment $\mathcal{G}$, there are only three energetic changes that can be <u>attributed to this fragment</u>, namely (i) self-energy of *n* atoms of a fragment $\mathcal{G}$ (self-fragment energy component), (ii) diatomic interactions between atoms of $\mathcal{G}$ (intrafragment interaction energy term) and (iii) diatomic interactions between atoms of $\mathcal{G}$ and atoms of a molecular fragment $\mathcal{H}$ (an interfragment interaction energy term).

Relative to the *ref* state of a molecular system (*e.g.*, the equilibrium structure of *trans*-2-butene, *trans*-eq), a self-fragment energy change, $\Delta E_{\text{self}}^{\mathcal{G}}$, when in the *fin* state (*e.g.*, *cis*-2-butene, *cis*-eq) can be written as

$$\Delta E_{\text{self}}^{\mathcal{G}} = {}^{cis\text{-eq}}E_{\text{self}}^{\mathcal{G}} - {}^{trans\text{-eq}}E_{\text{self}}^{\mathcal{G}} = {}^{cis\text{-eq}}\sum_{X\in\mathcal{G}}E_{\text{self}}^{X} - {}^{trans\text{-eq}}\sum_{X\in\mathcal{G}}E_{\text{self}}^{X} . \tag{5}$$

In case of a fragment made of two atoms involved in a bond/interaction, $\Delta E_{\text{self}}^{\mathcal{G}}$ is typically positive and can be interpreted as deformation energy[16a] of the fragment $\mathcal{G}$, an energy 'penalty' required for atoms to undergo an intra-atomic rearrangement from a non-bonded to bonded state.

Even though atoms of $\mathcal{G}$ might not be involved in any classical (non)bonding intramolecular interaction in *ref* (implying that the interatomic distances are larger than the sum of their van der Waals radii) in the IQA scheme they always interact with each other regardless of their placement within a molecule. To account for the change in the intrafragment interactions, $\Delta E_{\text{int}}^{\mathcal{G}}$, one can use Eq. 6,

$$\Delta E_{\text{int}}^{\mathcal{G}} = {}^{cis\text{-eq}}E_{\text{int}}^{\mathcal{G}} - {}^{trans\text{-eq}}E_{\text{int}}^{\mathcal{G}} = {}^{cis\text{-eq}}\sum_{\substack{X,Y\in\mathcal{G}\\Y\neq X}}E_{\text{int}}^{X,Y} - {}^{trans\text{-eq}}\sum_{\substack{X,Y\in\mathcal{G}\\Y\neq X}}E_{\text{int}}^{X,Y} . \tag{6}$$

Finally, the combined change in the interaction energy between atoms of $\mathcal{G}$ and atoms of $\mathcal{H}$, the interfragment energy change, $\Delta E_{\text{int}}^{\mathcal{G}\mathcal{H}}$, can be expressed as

$$\Delta E_{\text{int}}^{\mathcal{G}\mathcal{H}} = {}^{cis\text{-eq}}E_{\text{int}}^{\mathcal{G}\mathcal{H}} - {}^{trans\text{-eq}}E_{\text{int}}^{\mathcal{G}\mathcal{H}} = {}^{cis\text{-eq}}\sum_{X\in\mathcal{G}}\sum_{Y\in\mathcal{H}}E_{\text{int}}^{XY} - {}^{trans\text{-eq}}\sum_{X\in\mathcal{G}}\sum_{Y\in\mathcal{H}}E_{\text{int}}^{XY} . \tag{7}$$

By combining the three energy terms defined in Eqs. 5-7 we obtain the expression needed to compute energy contribution made by a fragment to a relative stability of a molecule when it changed from the *ref* to *fin* state,

$$E_{\text{attr-mol}}^{\mathcal{G}} = \Delta E_{\text{self}}^{\mathcal{G}} + \Delta E_{\text{int}}^{\mathcal{G}} + \Delta E_{\text{int}}^{\mathcal{G}\mathcal{H}} . \tag{8}$$

Eq. 8 also accounts, although indirectly, for the geometric deformation energy of all atoms. This is because the IQA scheme operates in real space with atoms defined within the Bader's Quantum Theory of Atoms in Molecules. Note, that the geometry of any atom, not necessarily directly involved in an interaction, can change when a molecular system is transformed from the *ref* to *fin* state. As a consequence, density distribution within atomic basins as well as net charge of these atoms must change resulting in different self-atomic and diatomic interaction energies in both states of a molecule.

It is seen in Eq. 8 that first two terms account for bonding and non-bonding interatomic regions within the $\mathcal{G}$ fragment. Hence, their sum can be interpreted as the energy change localized to a space occupied by $\mathcal{G}$, $E_{\text{attr-loc}}^{\mathcal{G}}$ (*loc*-FAMSEC), a molecule experiences when going from the *ref* to *fin* state,

$$E_{\text{attr-loc}}^{\mathcal{G}} = \Delta E_{\text{self}}^{\mathcal{G}} + \Delta E_{\text{int}}^{\mathcal{G}} . \tag{9}$$

This is a useful term that quantifies change of fragment's energy and describes the nature of the change, stabilizing or otherwise. Incorporating Eq. 9 into Eq. 8, we obtain a two-component expression clearly showing a difference between *loc-* and *mol*-FAMSEC terms,

$$E_{\text{attr-mol}}^{\mathcal{G}} = E_{\text{attr-loc}}^{\mathcal{G}} + \Delta E_{\text{int}}^{\mathcal{G}\mathcal{H}} . \tag{10}$$

To conclude this section it is worthwhile to mention that *net* and *effective* energies of an atom as well as a molecular fragment, concepts steaming from McWeeny's ideas,[21] were defined and used within the IQA framework.[16] Note, that IQA partitioning scheme does not require any reference state and the energy of a molecule is recovered by summing up additive energies of fragments. On the other hand, the concept of FAMSEC requires a reference state to compute an energy change of a molecular fragment $\mathcal{G}$ ($E_{\text{attr-loc}}^{\mathcal{G}}$) and this fragment energy contribution to a relative stability of a molecule ($E_{\text{attr-mol}}^{\mathcal{G}}$) on a structural change from the *ref* to *fin* state, *e.g.*, from *trans*-2-butene (*ref* state) to *cis*-2-butene (*fin* state). These energy terms can be expressed as a

difference in the *net* or *effective* energy of $\mathcal{G}$, $E_{\text{attr-loc}}^{\mathcal{G}} = {}^{\text{fin}}E_{net}^{\mathcal{G}} - {}^{\text{ref}}E_{net}^{\mathcal{G}}$ and $E_{\text{attr-mol}}^{\mathcal{G}} = {}^{\text{fin}}E_{\text{eff}}^{\mathcal{G}} - {}^{\text{ref}}E_{\text{eff}}^{\mathcal{G}}$.[7e] From this follows that $E_{\text{attr-loc}}^{\mathcal{G}}$ and $E_{\text{attr-mol}}^{\mathcal{G}}$ do not apply when a molecule has not change structurally whereas $E_{\text{net}}^{\mathcal{G}} < 0$ and $E_{\text{eff}}^{\mathcal{G}} < 0$ holds always. Similar reasoning applies to, *e.g.*, the atomic deformation energy defined[16a] as $E_{\text{def}}^{\text{A}} = E_{\text{net}}^{\text{A}} - E_{\text{vac}}^{\text{A}} = \Delta T^{\text{A}} + \Delta V_{\text{en}}^{\text{AA}} + \Delta V_{\text{ee}}^{\text{AA}}$ which describes a change in atom's energy when it changes its state from being free to that in a molecule. Clearly, for free atoms in vacuum $E_{\text{def}}^{\text{A}}$ does not apply because components of atomic energy (atomic kinetic energy T^{A}, intraatomic electron-nucleus $V_{\text{en}}^{\text{AA}}$ and electron-electron $V_{\text{ee}}^{\text{AA}}$ interaction energies) stay unchanged.

4. Results and Discussions

The relative energy differences across a wide range of *ab initio* and DFT methods are shown in Table 1, and it is clear that the *cis* isomer of 2-butene is consistently less stable than the corresponding trans isomer, by ~0.9 − 1.4 kcal/mol, depending on the level of theory. Most of our calculations were performed at the MP2/6-311++G(d,p) level, and ΔE = +1.36 kcal/mol compares with the CCSD(T)/cc-pvdz data very well. Data in Table 1 also shows that rotational energy barrier of +0.62 kcal/mol in *cis* isomer (on change from *cis*-eq to transitional state, *cis*-TS) is significantly smaller when compared with *trans* isomer, +1.97 kcal/mol, both values at MP2 (see also Figure S2 in the SI for relevant data at CCSD(T)).

Table 1. Relative energies of indicated 2-butene structures based on the DFT and wavefunction methods.

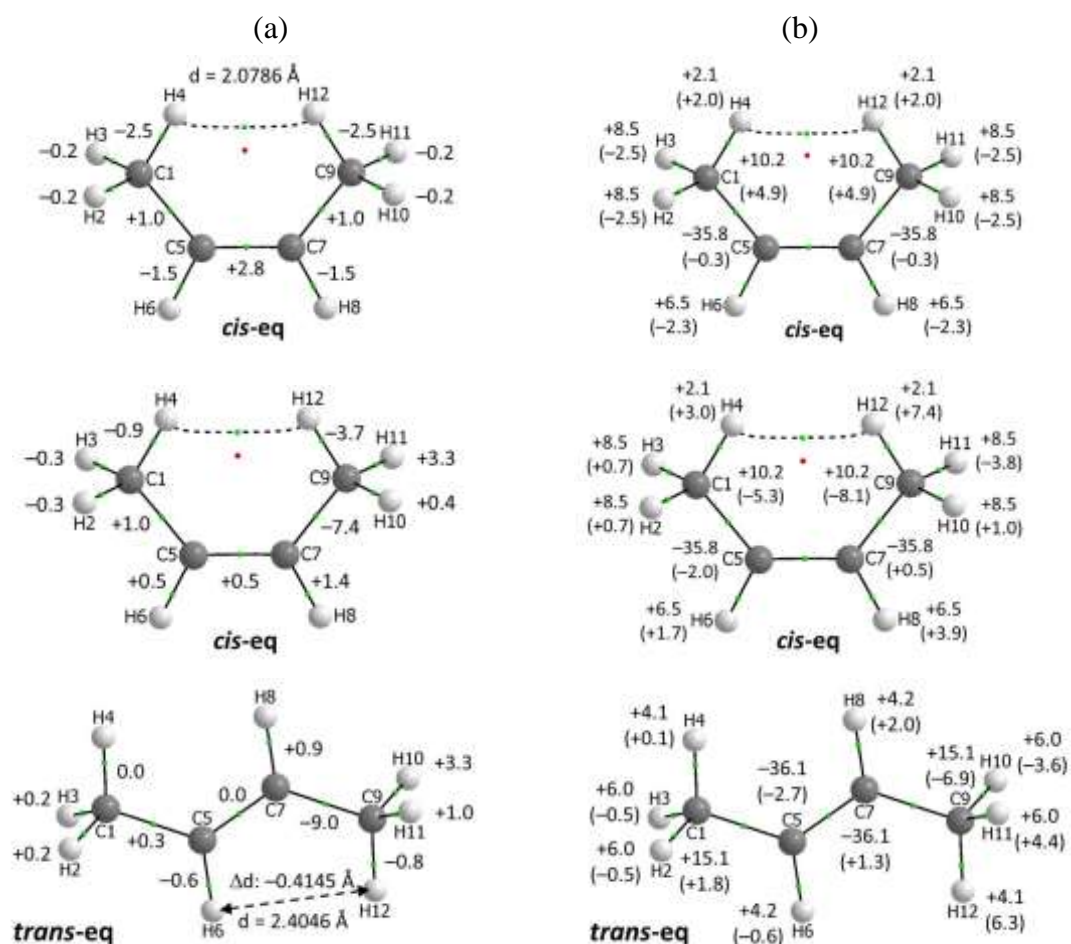| Methods	ΔE^{a}
cis-eq relative to *trans*-eq	
CCSD(T)/cc-pvdz	1.38
MP2/6-311++G(d,p)	1.36
BP86-D3/TZ2P	0.86
BLYP-D3/TZ2P	0.96
PBE-D3/TZ2P	0.92
M06-2X/TZ2P	1.07
cis-eq relative to *cis*-TS	
MP2/6-311++G(d,p)	−0.62
trans-eq relative to *trans*-TS	
MP2/6-311++G(d,p)	−1.97

[a] Values are in kcal/mol.

Figure 2. Molecular graphs of equilibrium structures, with atoms' numbering, showing a change in bond lengths in mÅ (part a) and net atomic charges and a change in electron population (in brackets), both in m*e* (part b) for *trans*-eq→*cis*-eq (top row), *cis*-TS→*cis*-eq (middle row) and *trans*-TS→*trans*-eq (botom row).

QTAIM-defined molecular graphs shown in Figure 2 include the atom numbering which will be used consistently throughout this work as well as selected properties (bond lengths, net atomic charges, changes in the electron population) for all structural changes investigated here, *trans*-eq→*cis*-eq, *cis*-TS→*cis*-eq and *trans*-TS→*trans*-eq. A bond path (BP), with well separated bond and ring critical points (BCP and RCP, respectively) is present between the H4 and H12 atoms in *cis*-2-butene. Based on the results presented in Table 1 and Figure 2, we can ask the following questions:

1. What is the nature of the H4•••H12 interaction, repulsive or attractive and is it affected by a structural change, from *trans*-eq to *cis*-eq and *cis*-TS to *cis*-eq?

2. Does the BP between H4 and H12 represents a bonding interaction or rather is another example where Bader-based interpretation of BP is misleading the chemists' community?

3. Is the molecular fragment $\mathcal{G} = \{H4,H12\}$ stabilized or strained in *cis*-eq relative to *trans*-eq and *cis*-TS?

4. What is the energy contribution made by the molecular fragment $\mathcal{G} = \{H4,H12\}$ to *cis*-eq, stabilizing or destabilizing relative to *trans*-eq and *cis*-TS?

5. Why equilibrium structure of *cis*-2-butene is less stable by 1.36 kcal/mol even though a BP between H4 and H12 is observed?

6. What is the origin of rotational energy barrier in both isomers and why it is so different?

In order to shed some light on answers to these six fundamental questions, we have performed extensive FAMSEC analyses which are supported by results from ETS-NOCV[17] and IQA[16] methods as well as geometric and vibrational analyses. Hence, our results are organized in three sections as: PART I. Relative energies of *cis*-eq and *trans*-eq, PART II. Methyl rotation in *cis*-2-butene and PART III. Methyl rotation in *trans*-2-butene, followed by final conclusions.

PART I. Relative energies of *cis*-2-butene and *trans*-2-butene

Perspective from loc-FAMSEC energy term

Interatomic steric strain is not observable quantity in quantum mechanical sense; accordingly, it is not a well-defined property. However, a general notion suggests that when 'clashing' atoms are strained in a molecular system then they should be involved in a repulsive interaction, $\Delta E_{int}^{X,Y} > 0$, and the molecular energy should increase relative to strain-free isomer implying that $\left| \Delta E_{self}^{\mathcal{G}} \right| < \Delta E_{int}^{X,Y} > 0$. This is indeed observed for, *e.g.*, a classical repulsive interaction between O-atoms of the eclipsed form of glycol (Figure 1). Hence, besides providing information on energy change of a fragment, the *loc*-FAMSEC seems to be ideally suited to identify potentially strained fragments of a molecule as it accounts for (i) these two contributions, $E_{attr-loc}^{\mathcal{G}} = \Delta E_{self}^{\mathcal{G}} + \Delta E_{int}^{X,Y}$; hence $E_{attr-loc}^{\mathcal{G}} > 0$ is expected and (ii) energy changes within two atomic basins as well as interatomic region. Moreover, *loc*-FAMSEC can be useful in quantifying energy contribution attributed to a classical intramolecular hydrogen bond,[7e] *e.g.*, N•••H; in such a case $\Delta E_{int}^{X,Y} < 0$ and $E_{attr-loc}^{\mathcal{G}} < 0$ is observed because the strength of an interaction, as measured by $\Delta E_{int}^{X,Y}$, overrides an increase in self-atomic energies of atoms involved, $\Delta E_{self}^{\mathcal{G}} > 0$.

All possible 66 (de)stabilized 2-atom fragments and 20 most (de)stabilized 4-atom fragments, as measured by the $E_{\text{attr-loc}}^{\mathcal{G}}$ term, are shown in Part S1 of the SI, which also contains additional data related to the *trans*-eq→*cis*-eq structural change. For illustration purposes, most relevant molecular fragments which became stabilized in *cis*-eq, relative to *trans*-eq, are shown in Figure 3. For convenience and consistency, we have used throughout the text the convention where red colored fragments with dotted line and blue ones with dashed line represent, relative to a *ref* state, destabilized and stabilized fragment, respectively. Moreover, to avoid unnecessary repetitions, *loc*- and *mol*-FAMSEC terms as well as changes in all energy terms will apply to a structural change indicated in the heading of a particular section. Hence, all the energy terms computed in the PART I refer to the *trans*-eq→*cis*-eq structural change, unless specified otherwise.
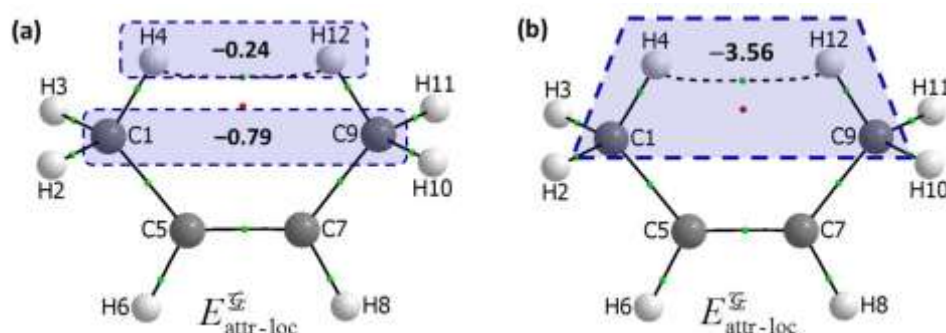

Figure 3. Selected 2-atom (part a) and 4-atom (part b) molecular fragments which became stabilized on the *trans*-eq→*cis*-eq structural change; values are in kcal/mol.

There are only ten 2-atomic fragments which became stabilized on the *trans*-eq→*cis*-eq structural change for which $-0.14 > E_{\text{attr-loc}}^{\mathcal{G}} > -0.96$ kcal/mol. It is clear that $\mathcal{G}=$ {H4,H12} with d(H4,H12) = 2.0786 Å became slightly stabilized, by about –0.2 kcal/mol, and it is not strained in *cis*-eq because (i) $E_{\text{attr-loc}}^{\mathcal{G}} < 0$, (ii) atoms of $\mathcal{G}$ are involved in attractive interaction in *cis*-eq ($E_{\text{int}}^{\text{H4,H12}} = -3.5$ kcal/mol) and (iii) $\Delta E_{\text{int}}^{\text{H4,H12}} < 0$. Moreover, these atoms self-atomic energies increased by +1.6 kcal/mol when *trans*-eq→*cis*-eq. Hence, the H4•••H12 interaction has the same signature ($E_{\text{int}}^{\text{H4,H12}} < 0$, $\Delta E_{\text{int}}^{\text{H4,H12}} < 0$, $\Delta E_{\text{self}}^{\text{H4}} > 0$, $\Delta E_{\text{self}}^{\text{H12}} > 0$ and $E_{\text{attr-loc}}^{\mathcal{G}} < 0$) as observed for strain-free classical intramolecular hydrogen bonds, N•••H and O•••H[7e] (for convenience, this is also depicted in Figure S1 in the SI). It is important to comment that we have also looked at the results from HF/6-311++G(d,p) and have found notably higher (less stabilizing) interaction energy ($E_{\text{int}}^{\text{H4,H12}} = -2.15$ kcal/mol) what demonstrates an important role of dispersion (electron correlation)

13

in intramolecular H•••H interactions. Similar is valid for numerous intermolecular H•••H interactions.[6,7]

The $\mathcal{G}= \{C1,C9\}$ fragment can be seen as a strain-free across-a-molecule non-bonded diatomic fragment as $E_{\text{attr-loc}}^{\mathcal{G}}$ of −0.8 kcal/mol was obtained. One must recall that in the IQA partitioning scheme all atoms are treated on equal footing, regardless whether they are bonded or not. Importantly, both C-atoms are involved in attractive interaction of $E_{\text{int}}^{C1,C9} = -0.6$ kcal/mol in *cis*-eq and it changed in stabilizing manner ($\Delta E_{\text{int}}^{\mathcal{G}} = -0.4$ kcal/mol) on *trans*-eq→*cis*-eq even though their net atomic charges are essentially identical (+0.010*e*), a feature also observed for H4 and H12, which have charge of +0.002*e*.

To gain further insight, it makes perfect sense to expand the FAMSEC analysis to chemically meaningful and relevant to this work 4-atom fragments. There are four such fragments in 2-butene, two terminal –CH$_3$ groups, C1H4•••H12C9 and H6C5=C7H8. Realizing that there are 495 unique 4-atom fragments in 2-butene, it was also of utmost interest and importance to find out relative significance of the selected four fragments in terms of their energetic contributions. Furthermore, working with 4-atom fragments implies that one accounts for wider molecular environment; hence, one would expect that this kind of analysis might provide some 'definite' answers related to the origin of relative stability trend, *E*(*cis*-eq) > *E*(*trans*-eq). We have established that the most stabilized ($E_{\text{attr-loc}}^{\mathcal{G}} = -3.6$ kcal/mol) part of a *cis*-eq molecule, in terms of 4-atom fragments, consists of the {C1,H4} and {C9,H12} fragments involved in the intramolecular H4•••H12 interaction − Figure 3(b). We also found that these four atoms are involved in attractive diatomic intrafragment interactions which have changed most favorably, by $\Delta E_{\text{int}}^{\mathcal{G}} = -6.4$ kcal/mol, among all 4-atom fragments on the *trans*-eq→*cis*-eq structural change. Clearly, the entire C1H4•••H12C9 part of *cis*-eq is not strained and this correlates well with 2-atom based analysis.

Perspective from mol-FAMSEC energy term

The above, *loc*-FAMSEC based analysis was informative as it revealed the origin, relative to *trans*-eq, on why 2- and 4-atom fragments containing a steric clash in question became stabilized in *cis*-eq. In this section our focus is on fragments which contributed to relative instability of *cis*-2-butene, as predicted by relevant mol-FAMSEC terms, when *trans*-eq changed to *cis*-eq.

Starting from 2-atom fragments, *cis*-eq was destabilized the most by {C5,H6} and {C7,H8}, with *mol*-FAMSEC = +1.95 kcal/mol each, followed by across-a-molecule fragments, {C5,H8} and {H6,C7}, for which we found $E_{\text{attr-mol}}^{\mathcal{G}}$ of +1.4 kcal/mol - see Figure 4(a). Moreover, atoms of H6C5=C7H8 feature among fragments with largest positive $E_{\text{attr-mol}}^{\mathcal{G}}$ values and for $\mathcal{G}$ = {C5,C7} it is +0.6 kcal/mol. Clearly, these atoms play a prominent role in destabilizing *cis*-eq and this is also confirmed by 4-atom fragment based analysis. We found that the middle part, H6C5=C7H8, with $E_{\text{attr-mol}}^{\mathcal{G}}$ = +3.9 kcal/mol, is destabilizing *cis*-eq the most among all possible 495 fragments because the interfragment interactions changed most unfavorably among all 4-atom fragments, $\Delta E_{\text{int}}^{\mathcal{G},\mathcal{H}}$ = +5.7 kcal/mol.
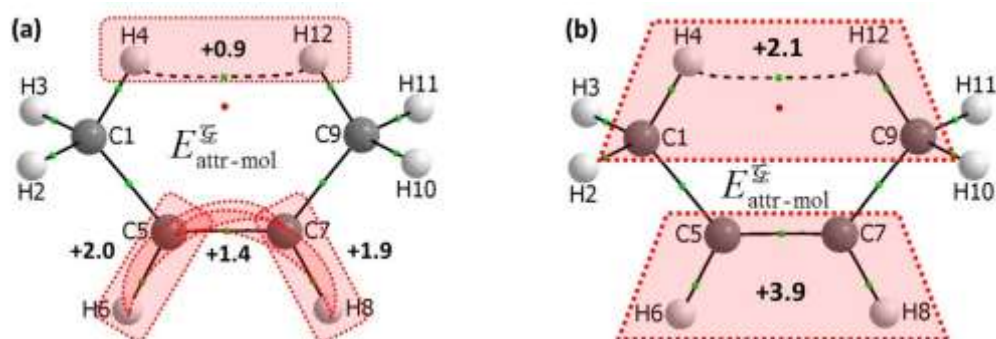

Figure 4. Selected 2-atom (part a) and 4-atom (part b) fragments which contributed, as measured by the *mol*-FAMSEC energy term, to an increase in energy of *cis*-eq when it changed from *trans*-eq; values are in kcal/mol.

It is also clear that the { H4•••H12} and { C1H4•••H12C9} fragments also destabilize *cis*-eq but they are not major 'players' (Figure 4). We have established that the origin of $E_{\text{attr-mol}}^{\mathcal{G}}$ = +0.9 kcal/mol computed for {H4,H12} can be linked with less favorable interactions with remaining atoms in *cis*-eq relative to *trans*-eq as we found $\Delta E_{\text{int}}^{\mathcal{G}\mathcal{H}}$ of +1.1 kcal/mol which compensated over the stabilizing contribution of *loc*-FAMSEC. In search of the origin of $E_{\text{attr-mol}}^{\mathcal{G}}$ of +2.1 kcal/mol obtained for $\mathcal{G}$ = {C1H4•••H12C9} we computed $\Delta E_{\text{int}}^{C1\mathcal{R}}$, $\Delta E_{\text{int}}^{H4\mathcal{R}}$, $\Delta E_{\text{int}}^{C9\mathcal{R}}$, and $\Delta E_{\text{int}}^{H12\mathcal{R}}$, where $\mathcal{R}$ = {all atoms minus atoms of $\mathcal{G}$} and obtained +1.0, +1.8, +1.0, and +1.8 kcal/mol, respectively. This shows that all atoms of {C1H4••H12C9} experienced less favorable molecular environment made of atoms of $\mathcal{R}$ in *cis*-eq.

FAMSEC-based analysis of 2- and 4-atom fragments leads us to the following main conclusions:

15

1) We are in disagreement with common notion and interpretation of the H4--H12 (or CH4--H12C) contact as being strained, involved in repulsive interaction and hence solely responsible for larger energy of *cis*-eq relative to *trans*-eq. Although the {H4,H12} fragment does contribute to the relative instability of *cis*-eq, there are (i) 28 additional fragments with $E_{\text{attr-mol}}^{\mathcal{G}} > 0$ and (ii) 16 fragments which contributed in destabilizing manner more than {H4,H12}. Moreover, there are 41 fragments in *cis*-eq with $E_{\text{attr-mol}}^{\mathcal{G}} > +2.1$ kcal/mol computed for the {C1H4••H12C9} fragment. This contradicts the classical approach when it is focused solely on either H--H or CH--HC contacts.

2) The origin of the $E(cis\text{-eq}) > E(trans\text{-eq})$ trend must be linked mainly with the middle part of 2-butene, the H6C5=C7H8 fragment, as it is destabilizing *cis*-eq the most among all possible 495 4-atom fragments. We must also note that (i) *mol*-FAMSEC of +3.9 kcal/mol computed for the H6C5=C7H8 fragment is nearly three times larger than the second in value destabilizing contribution made by a 4-atom fragment made of covalently bonded atoms, H2C1–C5H6, and (ii) {C5,C7}, {C5,H6} and {C7,H8} are the only fragments made of covalently bonded atoms in 2-butene for which we obtained $E_{\text{attr-mol}}^{\mathcal{G}} > 0$ for the *trans*-eq→*cis*-eq structural change.

We have also performed extensive IQA-based analyses and detailed discussion of results is presented in Part S1 of the SI. This covers changes in (i) additive and self-atomic energies, (ii) the interaction energies of an atom X with all other atoms in the system and (iii) diatomic interaction energies; trends observed fully support the FAMSEC-based analyses.

Clearly, paying entire attention just to the CH--HC contact, in terms of relative stability of the two 2-butene isomers, must lead to questionable interpretations and conclusions. Hence, our results are in direct conflict with an orthodox explanation by WSM[12] and they are fully in line with the recent work by Matta et al.[14]

Perspective from ETS-NOCV analysis of cis-eq vs trans-eq

We have supported the above FAMSEC based results by description of the 'middle' C=C bond in *cis*-2-butene based on the overall deformation density ($\Delta\rho_{\text{total}}$) decomposed into the electronic $\Delta\rho_{\text{orb}}$ and Pauli $\Delta\rho_{\text{Pauli}}$ deformation densities, Figure 5. Furthermore, the red areas (charge depletion) of $\Delta\rho_{\text{total}}$, caused predominantly by the Pauli repulsion component (of kinetic origin) $\Delta\rho_{\text{Pauli}}$, are clearly visible at the bottom and upper parts of the ethylenic fragment
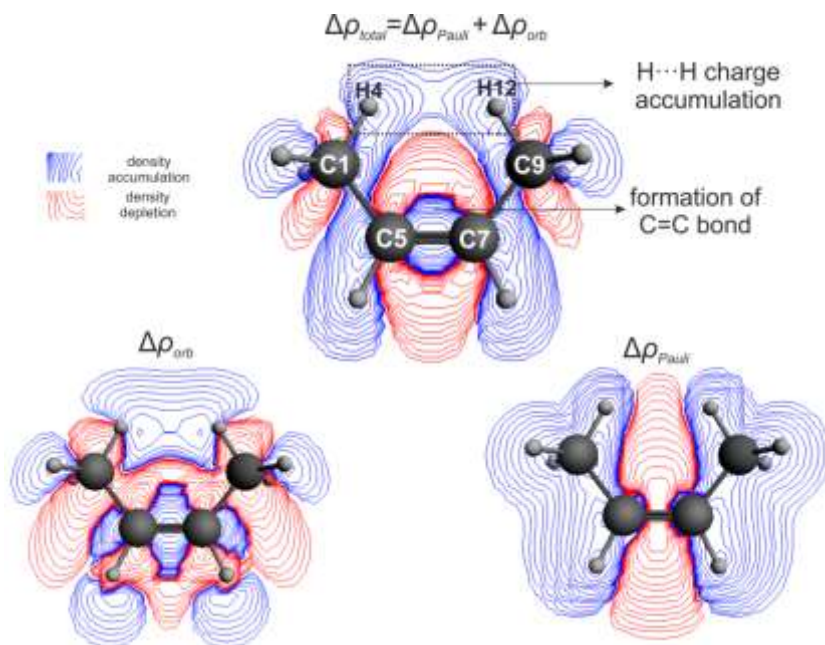
Figure 5. The total deformation density cut-plane isosurface $\Delta\rho_{total}$ decomposed into the electronic $\Delta\rho_{orb}$ and Pauli repulsion contributions, $\Delta\rho_{Pauli}$. The following fragments are considered, $H_3HC\downarrow\downarrow+\uparrow\uparrow CHCH_3$.
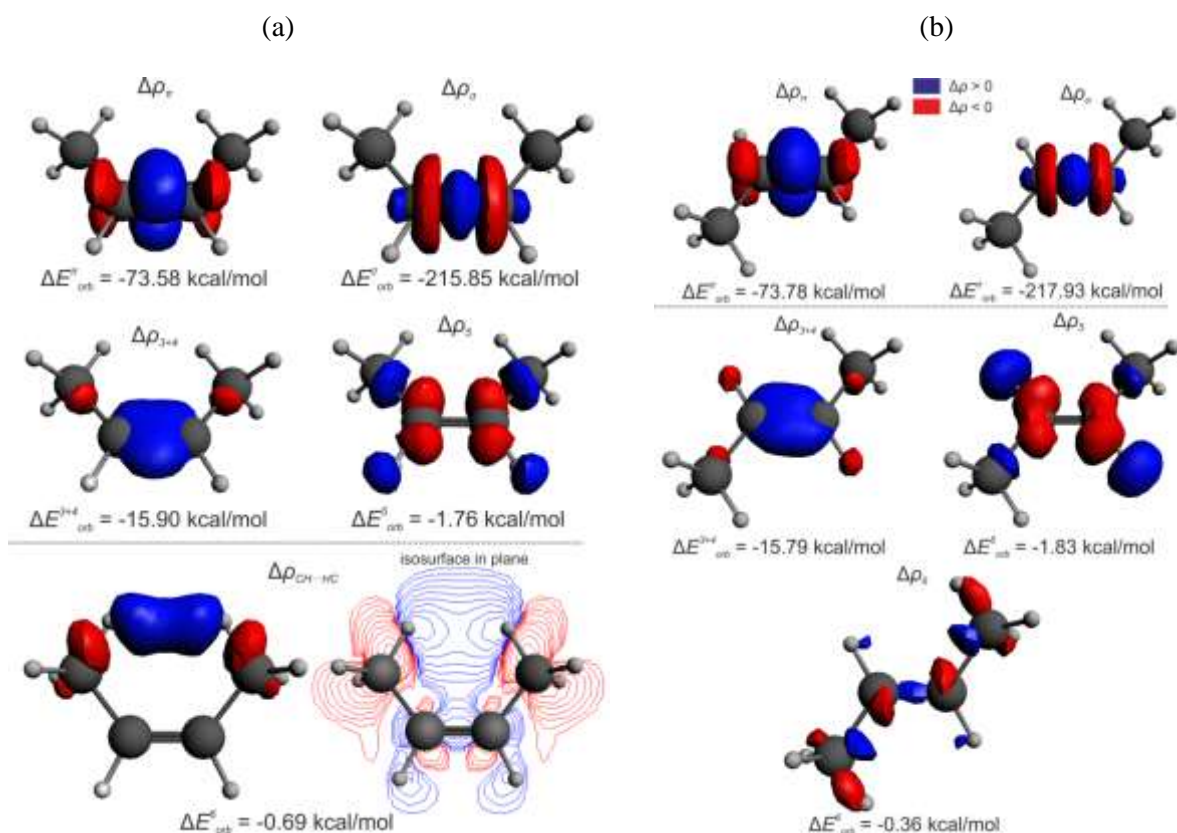

Figure 6. Leading deformation density channels describing C=C bond in *cis*-2-butene (part a) and *trans*-2-butene (part b) together with the corresponding energies from ETS-NOCV scheme.

(H6C5=C7H8), what conform to the knowledge emerging from the FAMSEC method. Similar is suggested by Matta and coworkers upon inspection of atomic energies.[14] As far as the controversial C1H4•••H12C9 region is concerned one can see that the electron density accumulation is definitely noted from $\Delta\rho_{\text{total}}$ – clearly the Pauli repulsion term leading to charge depletion does not fully cancel the accumulation of electron density ($\Delta\rho_{\text{orb}}$). Such picture (*i.e.* H4•••H12 electron accumulation) is in line with the presence of H4•••H12 with BCP from the QTAIM analysis and local stabilization noted from the FAMSEC method.

Additionally, the ETS-NOCV method allowed to extract and quantify the local H4•••H12 stabilization – it is depicted in Figure 5 by the $\Delta\rho_{\text{CH4}\cdots\text{HC12}}$ contour and the corresponding stabilization $\Delta E_{\text{orb}}^{\text{C1H4}\cdot\cdot\text{H24C9}}$ = –0.69 kcal/mol. It is important to emphasize that the existence of charge accumulation in the bay C1H4•••H12C9 region is also visible when considering other fragmentation patterns (Part S1, Figure S8 in the SI).

Comparison of the ETS-NOCV results for *cis*-eq and *trans*-eq leads to the conclusion that the σ(C=C) bond is notably weaker in the former case: $\Delta E_{\text{orb}}^{\sigma}$ = –215.85 kcal/mol (for the *cis* from) and $\Delta E_{\text{orb}}^{\sigma}$ = –217.93 kcal/mol (for *trans*), as shown in Figure 6. It is consistent with the shorter C=C bond in the latter case, by ~0.003Å, Figure 2. The π(C=C) bonds are similarly stable in both cases: $\Delta E_{\text{orb}}^{\pi} \approx$ –74 kcal/mol. These results are again in accord with the destabilization of C5=C7 bond when going from the *trans* to *cis* isomer. It is important to emphasize that the same trend is also visible from the calculated spin-spin coupling constants J(C=C) – namely, they are 95.317 Hz for the *cis* and slightly larger 96.156 Hz for the *trans* isomer (DFT/ADF/GIAO/BLYP-D3/TZP). Consistently, the calculated stretching C=C frequency in the *cis*-isomer, ca. 1657 cm^{-1}, is slightly lower than the corresponding value ca. 1666 cm^{-1} in the *trans*-form. . Similar trend is valid when considering CCSD(T)/cc-pVDZ – namely, 1725 cm^{-1} (*cis*-2-butene) and 1734 cm^{-1} (*trans*-2-butene).

PART II. Methyl rotation in *cis*-2-buthene

At the MP2/6-311++G(d,p) level, a small change in molecular energy ΔE = –0.62 kcal/mol was found when *cis*-TS changed to *cis*-eq. The MP2 energy change compares well with ~–0.8 kcal/mol at HF/6–31G* theory level reported by WSM[12] and –0.8 kcal/mol at MP2(FC)/cc-pVTZ level reported by MSBF.[14] We will explore here numerous properties needed to rationalize the observed small rotational energy barrier. As shown in Part S2 of the SI, where

18

additional data related to *cis*-TS→*cis*-eq is included, significant changes in bond lengths, atomic electron populations and IQA-defined energy terms took place throughout a molecule.

Perspective from loc-FAMSEC energy term

A structural change caused by rotation of the –C9H$_3$ terminal group results in breaking three H--H contacts in *cis*-TS (Figure 7(a)) and formation of new three H--H contacts in *cis*-eq (Figure 7(b)). Considering atoms of the bay, the most striking observation is similarity between resultant *loc*-FAMSEC energy terms computed for *trans*-eq→*cis*-eq and *cis*-TS→*cis*-eq.

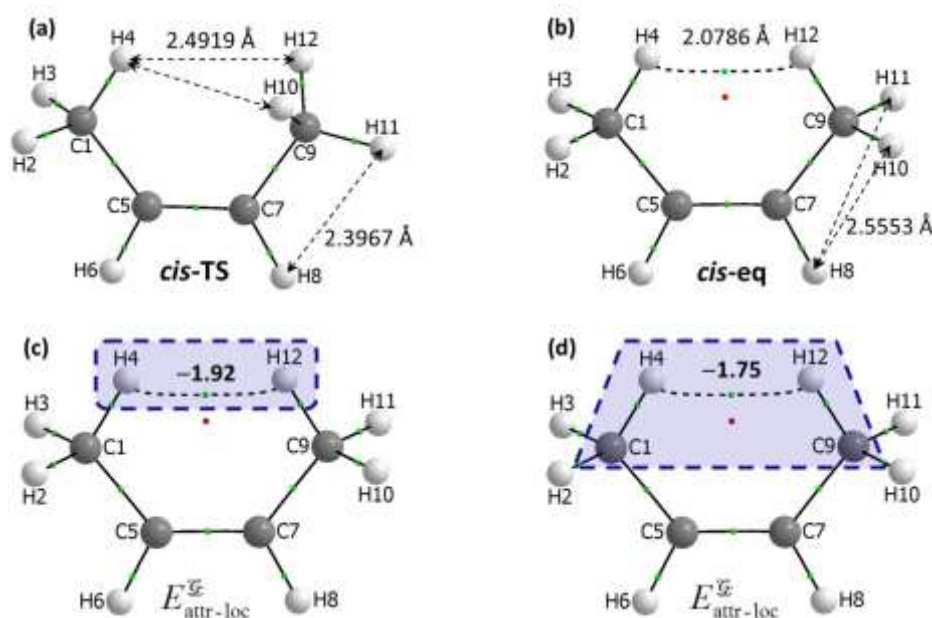**Figure 7.** Structural change from *cis*-TS (part a) to *cis*-eq (part (b) showing also interatomic distances for atoms involved as well as 2-atom (part c) and 4-atom (part d) molecular fragments which became stabilized on *cis*-TS→*cis*-eq; values are in kcal/mol.

Namely, the {H4•••H12} and {C1H4•••H12C9} fragments became stabilized in *cis*-eq and, importantly, the $E_{\text{attr-loc}}^{\text{H4,H12}}$ value (Figure 7(c)) is most significant stabilizing contribution among all 66 *loc*-FAMSEC values. Moreover, we found that the origin of $\Delta E_{\text{self}}^{\mathcal{G}} = +0.6$ kcal/mol and $\Delta E_{\text{int}}^{\mathcal{G}} = -2.6$ kcal/mol, hence also $E_{\text{attr-loc}}^{\mathcal{G}}$ of -1.9 kcal/mol obtained for the {H4,H12} fragment (Figure 7(c)) is exactly the same as discussed for *trans*-eq→*cis*-eq. These findings reveal that the formation of the intramolecular H4•••H12 interaction has the same 'ingredients' of a bonding interaction regardless of the *ref* state used, either *trans*-eq or *cis*-TS.

It is seen in Figure 7(a) that H8 and H11 are aligned in *cis*-TS and we found that they are involved in somewhat attractive interaction which changed to slightly repulsive when in *cis*-eq

with $E_{\text{int}}^{\text{H8,H11}}$ of −0.2 and +0.1 kcal/mol, respectively. This finding is highly informative as it shows that the nature of an intramolecular interaction depends on the overall molecular arrangement. Furthermore, breaking an attractive interaction between H8 and H11 in *cis*-TS also contributed to destabilization of the {H8,H11} fragment with $E_{\text{attr-loc}}^{\mathcal{G}} = +0.6$ kcal/mol.

One can look at these two fragments, {H4,H12} and {H8,H11}, from a different perspective, namely considering a rotation of the –C9H$_3$ group by 60° in the opposite direction such *cis*-eq is changed to *cis*-TS. Then exactly the same *loc*-FAMSEC values would be obtained but with opposite signs implying that (i) by braking the H4•••H12 interaction, $E_{\text{attr-loc}}^{\text{H4,H12}} = +1.9$ kcal/mol would be computed whereas (ii) by aligning H8 with H11 with d(H8,H11) = 2.397 Å (forming an interaction without a BP) would stabilize {H8,H11} with $E_{\text{attr-loc}}^{\text{H8,H11}} = -0.6$ kcal/mol. Moreover, for transition from *cis*-eq to *cis*-TS we would obtain $\Delta E_{\text{int}}^{\text{H4,H12}} / \Delta E_{\text{int}}^{\text{H8,H11}}$ of +2.6/−0.3 kcal/mol with negligible change in the classical component $\Delta V_{\text{cl}}^{\text{H4,H12}} / \Delta V_{\text{cl}}^{\text{H8,H11}}$ of −0.06/+0.04 kcal/mol. This exemplifies the same physics underlying energy contributions made by any two-atom fragment regardless whether BP is formed or not. This also illustrates usefulness of the FAMSEC method as it is not restricted to the presence of BP.

Let us complete the analysis of *loc*-FAMSEC terms by looking at all three {C9,H} fragments of the rotated terminal methyl group – Figure 8(a). This is because H10 features among most stabilized fragments but just opposite applies to H11. Among the {C9,H} fragments, only {C9,H11}, containing H11 which was aligned with H8 in *cis*-TS, became destabilized and,

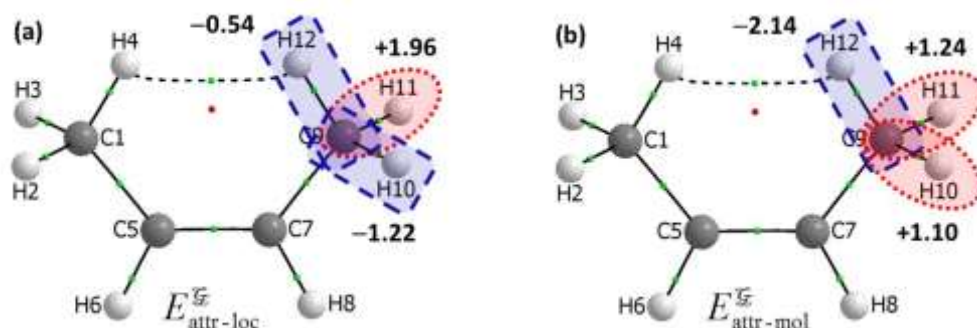**Figure 8.** Computed *loc*-FAMSEC (part a) and *mol*-FAMSEC (part b) energy terms for three {C,H} fragments of rotated terminal –C9H$_3$ functional group when *cis*-TS→*cis*-eq; values are in kcal/mol.

importantly, computed $E_{\text{attr-loc}}^{\mathcal{G}}$ of +2.0 kcal/mol is the largest value among all 66 fragments when *cis*-TS changed to *cis*-eq. The origin of that can be traced to: (i) largest increase in length of the

C9–H11 bond and (ii) largest combined outflow of electrons among all C–H fragments resulting in $\Delta E_{\text{self}}^{\mathcal{G}} = +0.3$ kcal/mol and $\Delta E_{\text{int}}^{\mathcal{G}} = +1.6$ kcal/mol.

Perspective from mol-FAMSEC energy term

Unexpectedly, we discovered that the {H4•••H12} fragment added to the relative molecular stabilizing of *cis*-eq significantly, namely $E_{\text{attr-mol}}^{\mathcal{G}} = -1.1$ kcal/mol - Figure 9(a). This observation is of fundamental significance as it shows that the same two atoms being involved in an intramolecular interaction in the same final structure, here *cis*-eq, can either stabilize or destabilize a molecule depending on the initial structural arrangement used as a *ref* state;
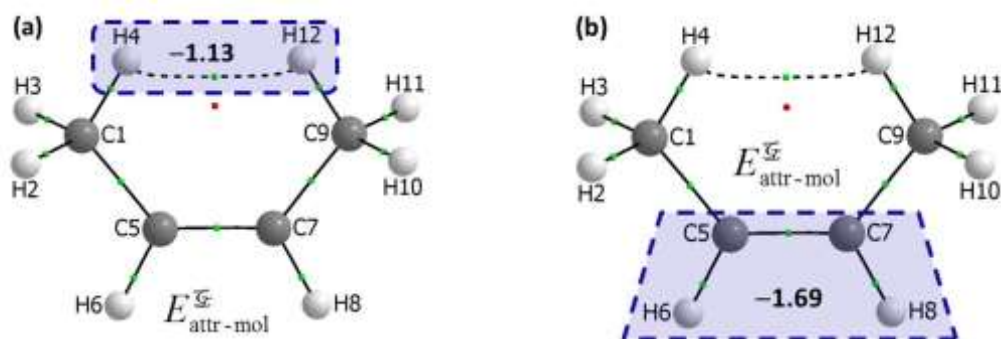

Figure 9. Energy contribution made to *cis*-eq, when it changed from the initial *cis*-TS state, by the {H4•••H12} fragment (part a) and {H6C5=C7H8} fragment (part b); values are in kcal/mol.

recall that $E_{\text{attr-mol}}^{\text{H4,H12}} = +0.9$ kcal/mol was computed for *trans*-eq→*cis*-eq. Importantly, we found analogous phenomenon for several 2- and 4-atom fragments made of covalently bonded atoms. For instance, we found that the middle fragment, {H6C5=C7H8}, made largest stabilizing contribution on *cis*-TS→*cis*-eq ($E_{\text{attr-mol}}^{\mathcal{G}} = -1.7$ kcal/mol) among three 4-atom fragments *cis*-2-butene can be partitioned to, the remaining two fragments being both terminal –CH$_3$ groups. This is a very different picture when compared with the *trans*-eq→*cis*-eq structural change for which we found $E_{\text{attr-mol}}^{\mathcal{G}} = +3.9$ kcal/mol (the largest contribution among all possible 495 4-atom fragments) attributed to {H6C5=C7H8}.

From a classical point of view, quite unexpected $E_{\text{attr-mol}}^{\mathcal{G}}$ values were obtained for three {C9,H} fragments (Figure 8(b)); only {C9,H12}, containing the H12-atom involved in a classical clash, has added to relative molecular stability a staggering value of $E_{\text{attr-mol}}^{\mathcal{G}} = -2.1$ kcal/mol due to highly favorable change in interfragment interactions, $\Delta E_{\text{int}}^{\mathcal{G}\mathcal{H}} = -1.6$ kcal/mol. To learn about

21

the origin, we computed contributions coming from individual atoms of the {C9,H12} fragment and obtained −3.2 and +1.6 kcal/mol for $\Delta E_{\text{int}}^{\text{H12},\mathcal{K}}$ and $\Delta E_{\text{int}}^{\text{C9},\mathcal{K}}$, respectively, where $\mathcal{K}=$ {all atoms of 2-butene except C9 and H12}. This nicely illustrates that (i) this is H12, and not C9, which made the $\Delta E_{\text{int}}^{\mathcal{GH}}$ term of stabilizing nature, (ii) molecular environment in *cis*-eq, in terms of interactions with other atoms, is more attractive for H12 and less attractive for C9 and (iii) the stabilizing contribution made by {C9,H12}, in terms of *mol*-FAMSEC, must be attributed mainly to H12. Further support of these conclusions is provided by (i) the change in additive atomic energies as we found −1.5/+0.2 kcal/mol for H12/C9 and (ii) the fact that H12 belongs to nine {H12,X} fragments that contributed, in terms of $E_{\text{attr-mol}}^{\mathcal{G}}$, to a relative molecular stability most when *cis*-TS changed to *cis*-eq.

The above and additional extensive FAMSEC- and IQA -based analyses included in Part S2 of the SI lead us to the several conclusions related to the small $\Delta E_{\text{rot}}^{\#}=$ +0.62 kcal/mol rotational energy barrier for *cis*-eq→*cis*-TS, namely:

a) Neither {H4,H12} nor {C1H4,H12C9} became strained on *cis*-TS→*cis*-eq.

b) From *mol*-FAMSEC perspective, neither {H4,H12} nor {H6C5=C7H8} can be directly linked with the small $\Delta E_{\text{rot}}^{\#}=$ +0.62 kcal/mol rotational energy barrier for *cis*-eq→*cis*-TS. This is because *mol*-FAMSEC contributions of +1.1 and +1.7 kcal/mol are much larger than the $\Delta E_{\text{rot}}^{\#}$ value; note that these mol-FAMSEC terms are of the same value, but with opposite sign, as computed for cis-TS→*cis*-eq (Figure 9).

c) The rotational energy barrier is simply an overall result of an interplay between many and quite well-balanced stabilizing and destabilizing energy contributions coming from numerous molecular fragments.

However, the origin of such small rotation barrier can be linked with energetically the most unfavorable change in a diatomic interaction and, quite surprisingly when a classical interpretation is concerned, this involves atoms of the {H4,H12} fragment. We found that to account for the overall (or total) change in diatomic interactions, when the –C9H$_3$ is rotated from the *cis*-eq to *cis*-TS state, it is sufficient to consider five most significant changes in diatomic interactions, two largest destabilizing ($\Delta E_{\text{int}}^{\text{H4,H12}}=$ +2.6 and $\Delta E_{\text{int}}^{\text{C7,C9}}=$ +1.7 kcal/mol) and three most significant stabilizing ($\Delta E_{\text{int}}^{\text{H11,C9}}=$ −1.6, $\Delta E_{\text{int}}^{\text{H4,C9}}=$ −1.0 and $\Delta E_{\text{int}}^{\text{H4,H10}}=$ −0.9 kcal/mol) contributions. When these values are summed up, it results in +0.7 kcal/mol and this compares

very well with $\Delta E_{\text{rot}}^{\#}$ of +0.62 kcal/mol. This can be interpreted as local forces of comparable magnitude, attractive and repulsive interactions, which make a rotation of the terminal group in *cis*-2-butene almost energy-free.

ETS-NOCV-based interpretation

In this section we examine changes in the nature of bonds C9–H12, C9–H11 and C7–C9 upon rotation of the *cis*-2-butene transition state, *cis*-TS, into the ground state isomer, *cis*-eq, based on totally different approach; namely, the charge and energy decomposition scheme ETS-NOCV which relies on fragment molecular orbitals as opposed to real-space perspective offered by the FAMSEC/IQA approaches. As far as the C7–C9 bond is concerned we observe, in line with the local FAMSEC outcomes, the strengthening of this connection (the drop in ΔE_{total} value by ca. 0.86 kcal/mol) upon rotation *cis*-TS→*cis*-eq, Figure 10A. It is clear from Figure 10B that the C9–H12 bond becomes evidently stabilized when the *cis*-TS changes into the *cis*-eq as indicated by the lowering of the interaction energy ΔE_{total} by ca. −8.28 kcal/mol, whereas the exactly opposite is true when considering the C9–H11 connection (the ΔE_{total} value appeared to be less stabilizing by ca. +8.43 kcal/mol). This trend is fully in accord with the conclusions drawn from the local FAMSEC results (see Figure 8 and the related discussion). Further decomposition of ΔE_{total} according to ETS-NOCV scheme suggests that the trend setting factor is Pauli repulsion term ΔE_{Pauli} which destabilizes the C9–H11 bond significantly (by 28.58 kcal/mol) in the *cis*-eq (relative to the *cis*-TS). The opposite is valid when considering the C9–H12 bond – namely, as the *cis*-TS rotates into the *cis*-eq one observes the relief (drop) in Pauli term by ca. 26.28 kcal/mol, Figure 10B. This can be explained by the fact that the σ(C9-H11) gets involved in repulsive interaction with the π(C5=C7) bond when rotating *cis*-TS→*cis*-eq, whereas the opposite is true for the C9–H12 connection (where the suggested σ(C9-H12)/π(C5=C7) repulsion shall vanish as they are orthogonal).

It is to be emphasized that the important role of Pauli contribution in determining the strength of C9–H12 and C9–H11 bonds can also be deduced from the FAMSEC/IQA energy decomposition. For instance, as opposed to the C9–H12 bond, the destabilization of C9-H11 bond originates from both unfavorable self-deformation energy (ΔE_{self}=+0.34 kcal/mol) as well as the positive value of ΔE_{int} = +1.61 kcal/mol caused largely by the exchange-correlation term, ΔV_{XC} = +1.68 kcal/mol, a result of charge depletion in the interatomic region which, in the ETS-

NOCV scheme, reflects the Pauli repulsion contribution. Similar interrelation has been found by Pendás and Francisco.[16d].
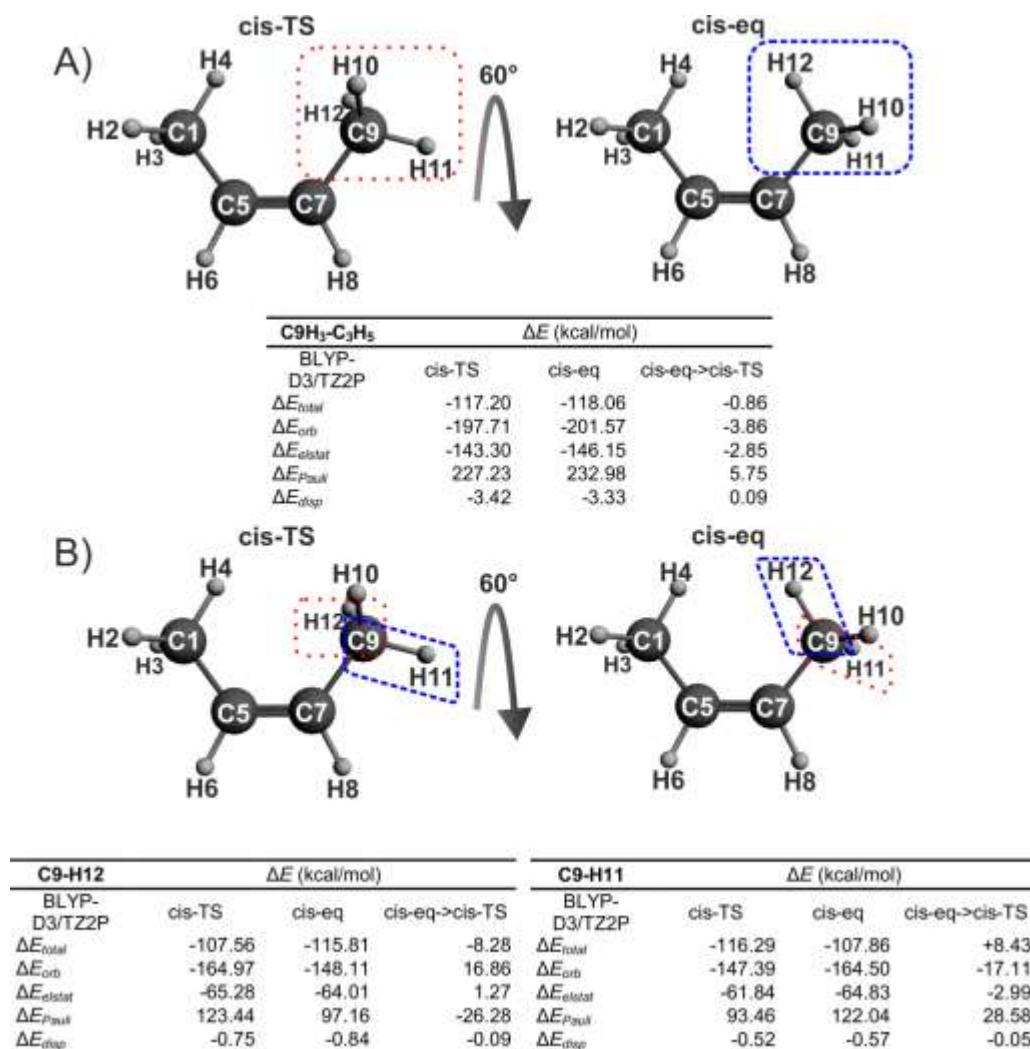

C9H$_3$-C$_3$H$_5$	ΔE (kcal/mol)		
BLYP-D3/TZ2P	cis-TS	cis-eq	cis-eq->cis-TS
ΔE$_{total}$	-117.20	-118.06	-0.86
ΔE$_{orb}$	-197.71	-201.57	-3.86
ΔE$_{elstat}$	-143.30	-146.15	-2.85
ΔE$_{Pauli}$	227.23	232.98	5.75
ΔE$_{disp}$	-3.42	-3.33	0.09

C9-H12	ΔE (kcal/mol)			C9-H11	ΔE (kcal/mol)		
BLYP-D3/TZ2P	cis-TS	cis-eq	cis-eq->cis-TS	BLYP-D3/TZ2P	cis-TS	cis-eq	cis-eq->cis-TS
ΔE$_{total}$	-107.56	-115.81	-8.28	ΔE$_{total}$	-116.29	-107.86	+8.43
ΔE$_{orb}$	-164.97	-148.11	16.86	ΔE$_{orb}$	-147.39	-164.50	-17.11
ΔE$_{elstat}$	-65.28	-64.01	1.27	ΔE$_{elstat}$	-61.84	-64.83	-2.99
ΔE$_{Pauli}$	123.44	97.16	-26.28	ΔE$_{Pauli}$	93.46	122.04	28.58
ΔE$_{disp}$	-0.75	-0.84	-0.09	ΔE$_{disp}$	-0.52	-0.57	-0.05

Figure 10. Changes in the nature of the C7-C9, C9-H11 and C9-H12 bonds upon cis-TS→cis(eq) rotation obtained from the ETS-NOCV energy decomposition scheme. The following fragmentation patterns are considered: A: C9H$_3$|C$_3$H$_5$ B: H11|C$_4$H$_7$. ΔE$_{total}$= ΔE$_{orb}$+ ΔE$_{elstat}$+ ΔE$_{Pauli}$+ ΔE$_{disp}$.

PART III. Methyl rotation in trans-2-buthene

As we found for *cis*-TS→*cis*-eq, significant geometric and energetic changes also took place throughout *trans*-2-butene on *trans*-TS→*trans*-eq. To explain why rotational barrier is larger for *trans*-eq isomer we followed exactly the same approach as applied in the analysis of *cis*-eq - additional and extensively commented data is included in Part S3 of the SI.

Perspective from FAMSEC energy terms

An in depth analysis of numerous *loc*- and *mol*-FAMSEC energy terms attributed to 2- and 4-atomic fragments revealed that values computed for analogues fragments follow very much the

same trends when either *cis*-TS or *trans*-TS changed to the relevant ground state isomer. A set of representative data is included in Table 2 (see Figure 2 for atoms' numbering) where a particular fragment in *trans*-2-butene is always placed first followed by the analogous fragment in *cis*-2-butene.

Table 2. Computed *loc*- and *mol*-FAMSEC energy terms (in kcal/mol) for the indicated molecular fragments and structural changes.

Molecular fragment	*trans*-TS→*trans*-eq		*cis*-TS→*cis*-eq	
	loc-FAMSEC	*mol*-FAMSEC	*loc*-FAMSEC	*mol*-FAMSEC
{H6,H12}-*trans*	−1.7	−1.6		
{H4,H12}-*cis*			−1.9	−1.1
{H8,H10}-*trans*	+0.3	+1.5		
{H8,H11}-*cis*			+0.6	+1.6
{C5,C7}	+0.1	−1.9	+0.1	−1.3
{C7,C9}	−1.6	+0.6	−1.8	+1.2
{C9,H10}-*trans*	+2.4	+0.7		
{C9,H11}-*cis*			+2.0	+1.2
{C9,H11}-*trans*	−0.4	−0.2		
{C9,H10}-*cis*			−1.2	+1.1
{C9,H12}	−0.8	−2.0	−0.5	−2.1
{-C9H$_3$}	+0.5	−2.0	+0.8	−1.1
{H6C5=C7H8}	+0.2	−2.7	−0.1	−1.7

Let us consider, as an example, the first entry in Table 2. Even though H6 and H12 are not linked by BP in *trans*-eq and d(H6,H12) > (sum of vdW radii), the {H6,H12} fragment is stabilized with $E_{\text{attr-loc}}^{\mathcal{G}} = -1.7$ kcal/mol and added to relative molecular stability, $E_{\text{attr-mol}}^{\mathcal{G}} = -1.6$ kcal/mol, when *trans*-TS→*trans*-eq. This fragment can be seen as equivalent to {H4,H12} (the second entry in Table 2) with BP in *cis*-eq and d(H4,H12) << (sum of vdW radii), for which a comparable values were obtained, $E_{\text{attr-loc}}^{\mathcal{G}} = -1.9$ kcal/mol and $E_{\text{attr-mol}}^{\mathcal{G}} = -1.1$ kcal/mol when *cis*-TS→*cis*-eq. In both cases the main contribution to *loc*-FAMSEC came from the stabilizing in nature $\Delta E_{\text{int}}^{\text{X,Y}}$ term which, in turn, is dominated by the XC-term, $\Delta V_{\text{XC}}^{\text{X,Y}}$. This is also supported by NOCV deformation density channel (Part S3 of the SI) demonstrating the charge delocalization due to H6•••H12 interaction in *trans*-2-butene. Combined data obtained for {H6,H12}-*trans* and equivalent {H4,H12}-*cis* plus {H8,H10}-*trans* and equivalent {H8,H11}-*cis* nicely illustrates that rotation of a terminal group results in similar trends and energy contributions related to aligned H-atoms regardless of conformer involved or presence (absence) of a BP. It should be pointed out that the presence of quantitatively important H6•••H12

stabilization in *trans*-2-butene which, in fact, is entirely unintuitive from the geometric point of view, has been consistently identified from both the FAMSEC and ETS-NOCV methods herein for the first time; therefore, we should carefully look at molecules when rationalizing their stability. In this respect, the IQA and the related FAMSEC approaches, which treat every pair of atoms independently and on equal footing, regardless whether they are close or far away from each other, are of great importance.

Focusing now on the three {C9,H} fragments, we note again that trends in *loc*-FAMSEC in *trans*-eq mimic those in *cis*-eq exactly. Importantly, these trends were also reproduced by the results from the ETS-NOCV calculations – Part S3 of the SI. Considering the *mol*-FAMSEC term, we note that the fragments containing (i) H12 contributed to conformer's relative stability the most, –2.0/–2.1 kcal/mol in *trans*-eq/*cis*-eq whereas (ii) H10 in *trans*-eq and H11 in *cis*-eq (they were aligned with H8 in both TSs of *trans* and *cis* isomers) contributed in destabilizing manner to respective ground state conformer's energy the most, +0.7/+1.2 kcal/mol in *trans*-eq/*cis*-eq.

In general, the comparative analysis shows that rotation of the terminal group -C9H$_3$ produced diverse energy contributions made by molecular. However, trends in *mol*-FAMSEC terms computed for the same, or equivalent, fragments in both isomers, can be used in explaining larger rotational energy barriers in *trans*-2-butene. To this effect, we will use *mol*-FAMSEC computed for 4-atom fragments of chemical significance. For *trans*-TS→*trans*-eq and *cis*-TS→*cis*-eq we observe, respectively:

   a) –2.0 and –1.1 kcal/mol for {C9,H10,H11,H12} (the rotated methyl unit)
   b) –2.7 and –1.7 kcal/mol for {C5,H6,C7,H8} (the ethylenic middle fragment)
   c) –1.3 and +0.2 kcal/mol for {C5,H6,C9,H12} (the ethylenic C5H6 and rotated C9H12) in *trans*-eq and equivalent {C1,H4,H12,C9} in *cis*-eq.

Note that *mol*-FAMSEC of –2.0 kcal/mol for *trans*-TS→*trans*-eq becomes +2.0 kcal/mol on rotation in the opposite direction. Hence, rotating the -C9H$_3$ terminal group from equilibrium to TS contributes $\left| {}^{trans-eq}E_{\text{attr-mol}}^{\mathcal{G}} \right| - \left| {}^{cis-eq}E_{\text{attr-mol}}^{\mathcal{G}} \right| = +0.9$ kcal/mol more to the rotational energy barrier in the case of the *trans* isomer. Moreover, the rotation of the terminal group from eq→TS induces structural changes throughout both, *trans* and *cis* isomers and this results in additional energy required which is larger in the case of trans isomer by, *e.g.*, +1.0 kcal/mol attributed to {C5,H6,C7,H8} and +1.5 kcal/mol attributed to {C5,H6,C9,H12} in *trans*-eq and equivalent

{C1,H4,H12,C9} in *cis*-eq. Although it is impossible to recover the exact difference in rotational energy barriers from the *mol*-FAMSEC values, all the above clearly shows that the overall origin has been recovered.

To conclude, let us perform a unique and comparative analysis of rotational barriers for *cis*-eq→*cis*-TS and *trans*-eq→*trans*-TS. To this effect, we will consider a specific for the purpose energy partitioning scheme involving the *mol*-FAMSEC terms computed for each terminal -CH$_3$ group of 2-butene (a $\mathcal{G}$ fragment) whereas the rest of this molecule (an $\mathcal{H}$ fragment) will be considered as contributing the remaining part to the rotational energy barrier. Looking at Eq. 10 it is clear that to make two *mol*-FAMSEC terms additive, it is necessary to eliminate a double inclusion (through the $\Delta E_{int}^{\mathcal{G}\mathcal{H}}$ term) of diatomic interactions between atoms of two molecular fragments, here $\mathcal{G}_1$= {-C1H$_3$} and $\mathcal{G}_2$ = {–C9H$_3$}. In such a way one can obtain directly comparable for the two structural changes, *cis*-eq→*cis*-TS and *trans*-eq→*trans*-TS, energy term ξ $= E_{attr-mol}^{C1,H2,H3,H4} + E_{attr-mol}^{C9,H10,H11,H12} - \Delta E_{int}^{\mathcal{G}1,\mathcal{G}2}$. We computed $\xi = -0.40 + 1.12 - 0.36) = +0.4$ kcal/mol for *cis*-eq→*cis*-TS and $\xi = 0.07 + 2.02 - (-0.01) = +2.1$ kcal/mol for *trans*-eq→*trans*-TS. These values, +0.4 and +2.1 kcal/mol, not only follow the trend but also approximate the rotational energy barriers for *cis* and *trans* isomers well. This strongly points at the terminal groups and associated *mol*-FAMSEC terms as the main, but not exclusive, source of the rotational energy barrier $\Delta E_{rot}^{\#}$ of +0.6 and +2.0 kcal/mol computed respectively for the *cis* and *trans* conformers of 2-butene.

4. Conclusions

On the onset of this investigation we posed 6 questions which we considered as of fundamental significance to explain the trends in (i) relative stability and (ii) energy of rotational barrier computed for *trans*- and *cis*-2-butene. Detailed answers to these questions were provided in dedicated sections above; hence, we would like to point at most important conclusions of general significance first followed by brief summary of specific main findings.

It has been shown conclusively that each conformational change investigated here, either from *trans*-eq to *cis*-eq, *cis*-TS to *cis*-eq or *trans*-TS to *trans*-eq, resulted in throughout-a-molecule significant variations in all fundamental molecular and atomic properties. Hence, it is rather impossible to pin-point at an exact fundamental property change to explain either the difference in electronic energy of the two isomers, ΔE, or rotational energy barrier, $\Delta E_{rot}^{\#}$ of *trans*- and *cis*-

2-butene molecules. However, we have demonstrated that the formation of the intramolecular H4•••H12 interaction has the same 'ingredients' of a bonding interaction (as found for the intramolecular H-bond) regardless of the *ref* state used, either *trans*-eq or *cis*-TS. Moreover, we discovered that qualitative and quantitative changes in many properties were comparable for rotational energy barriers of *cis*- and *trans*-2-butene – it is very important, to some degree unintuitive, and entirely new knowledge in the literature. As an example, H6 and H12 are not linked by BP in *trans*-eq and d(H6,H12) > (sum of vdW radii); however, the {H6,H12} fragment is stabilized with $E_{\text{attr-loc}}^{\mathcal{G}}$ = −1.7 kcal/mol and added to molecular stability, $E_{\text{attr-mol}}^{\mathcal{G}}$ = −1.6 kcal/mol, when *trans*-TS→*trans*-eq. These values compare well with $E_{\text{attr-loc}}^{\mathcal{G}}$ = −1.9 kcal/mol and $E_{\text{attr-mol}}^{\mathcal{G}}$ = −1.1 kcal/mol computed on *cis*-TS→*cis*-eq for an equivalent {H4,H12} fragment with BP in *cis*-eq and d(H4,H12) << (sum of vdW radii). This is important finding as it shows that these changes are not entirely related to the formation of the controversial steric contact H4--H12 in *cis*-eq. Furthermore, it has been shown that the change in fundamental properties as well as energy contributions made by a fragment, *e.g.*, {H4,H12}, depend on the reference state used. To this effect, we have found that the {H4,H12} fragment (i) was stabilized by −0.2/−1.9 kcal/mol when *trans*-eq/*cis*-TS changed to *cis*-eq; notably, the $E_{\text{attr-loc}}^{\text{H4,H12}}$ value of −1.9 kcal/mol is most significant among all 66 *loc*-FAMSEC values, and (ii) destabilized/stabilized the *cis*-eq molecule by +0.9/−1.1 kcal/mol when *trans*-eq/*cis*-TS changed to *cis*-eq. It is important to stress that a change in the value as well as the nature of energy contributions attributed to the {H4,H12} fragment is not unique as similar trends were found for many other fragments of chemical significance in 2-butene molecules. Similar conclusions also apply to the extended 4-atom fragments and, for instance (i) for *trans*-eq→*cis*-eq both terminal –CH$_3$ groups stabilized *cis*-eq whereas for *cis*-TS→*cis*-eq, *cis*-eq was stabilized only by the –C9H$_3$ terminal which was rotated, and (ii) the middle fragment, H6C5=C7H8, destabilized *cis*-eq most among all possible 495 4-atom fragments on *trans*-eq→*cis*-eq, but it added to stability a lot when *trans*-TS changed to *trans*-eq. Our results demonstrate that any attempt to explain a difference in energies between or rotational barriers of *cis*- and *trans*-2-butene will provide an incomplete and indeed a misleading picture when an explanation is based on exploring properties related just to a single molecular fragment, such as the H4--H12 steric contact. We are convinced that the latter statement is of general nature and should be applicable to any set of conformers (*e.g.*, planar and bent biphenyl) or structurally similar molecular systems.

Our main specific findings, we arrived at from the FAMSEC-/IQA-/ETS-NOCV-based energy partitioning schemes, for conformational change from *trans*-eq to *cis*-eq are summarized below:

- The {H4,H12} fragment in *cis*-2-butene is stabilized regardless whether *trans*-eq or *cis*-TS changes to *cis*-eq; this has been discovered from the FAMSEC, IQA and ETS-NOCV energy partitioning schemes. Importantly, we have demonstrated herein, for the first time, consistent conclusions emerging from totally different approaches based on the real space and molecular orbitals models of chemical bonding. Moreover, the {C1,H4•••H12,C9} fragment (i) is stabilized most (by -3.6 kcal/mol) and (ii) intrafragment interaction energies changed most favorably (by -6.4 kcal/mol) among all possible 4-atom fragments when *trans*-eq→*cis*-eq. Our results showed that neither {H4•••H12} nor {C1H4•••H12,C9} are strained in *cis*-eq.

- Although the {H4,H12} fragment does contribute $E_{\text{attr-mol}}^{\mathcal{G}}= +0.9$ kcal/mol to the relative instability of *cis*-eq vs. *trans*-eq, there are (i) 28 additional fragments with $E_{\text{attr-mol}}^{\mathcal{G}} > 0$ and (ii) 16 fragments which contributed in destabilizing manner more than {H4,H12}.

- It is of paramount importance to stress that the origin of the $E(cis\text{-eq}) > E(trans\text{-eq})$ trend can be linked mainly with contributions made by the atoms of the middle part of 2-butene, H6C5=C7H8. This is because these atoms form four diatomic fragments which (i) have most positive $E_{\text{attr-mol}}^{\mathcal{G}}$ values among all 2-atom fragments (+2.0 and +1.9 kcal/mol for {C5,H6} and {C7,H8}, respectively, +1.4 kcal/mol for {C5,H8} and {C7,H6}, +0.6 kcal/mol for {C5, C7}), (ii) feature among 22 largest positive values of *mol*-FAMSEC, and (iii) {C5,C7}, {C5,H6} and {C7,H8} are the only fragments made of covalently bonded atoms in 2-butene for which we obtained $E_{\text{attr-mol}}^{\mathcal{G}} > 0$ in *cis*-eq when it changed from *trans*-eq. Moreover, the entire {H6C5=C7H8} fragment, on transition from *trans*-eq to *cis*-eq, (i) destabilized *cis*-eq the most as measured by $E_{\text{attr-mol}}^{\mathcal{G}}= +3.9$ kcal/mol which is nearly three times larger than the second destabilizing contribution, (ii) the interfragment interactions changed most unfavorably among all 4-atom fragments, by +5.70 kcal/mol, and (ii) the C1–H4 (or C9–H12) do not feature at all among all 4-atom fragments with *mol*-FAMSEC > 0.

- As far as the chemically significant fragments which stabilize the *cis*- relative to *trans*-2-butene are concerned one must recognize {C1,H4} and {C9,H12}; they both contribute with the same values of $E_{\text{attr-mol}}^{\mathcal{G}} = -2$ kcal/mol.

Considering the difference in the rotational barrier, we would like to conclude that:

a) The origin of such small rotation barrier in cis-2-butene can be linked with energetically most favorable change in the H4•••H12 interaction on *cis*-TS→*cis*-eq. We found that two most stabilizing ($\Delta E_{int}^{H4,H12} = -2.56$ and $\Delta E_{int}^{C7,C9} = -1.68$ kcal/mol) and three destabilizing ($\Delta E_{int}^{H11,C9} = +1.62$, $\Delta E_{int}^{H4,C9} = +0.97$ and $\Delta E_{int}^{H4,H10} = +0.93$ kcal/mol) interactions sum up to -0.72 kcal/mol (it compares well with ΔE of -0.62 kcal/mol). Clearly forces of the same magnitude, attractive and repulsive interactions, make rotation of the terminal group almost energy-free.

b) A reasonable approximation of the rotational energy barrier one can make from $E_{attr-mol}^{\mathcal{G}}$ computed just for two terminal $-CH_3$ groups: (i) $-0.4(-C1H_3) + 1.1(-C9H_3) = +0.7$ kcal/mol for the *cis*-eq→*cis*-TS transition, and (ii) $+0.1(-C1H_3) + 2.0(-C9H_3) = +2.1$ kcal/mol for the *trans*-eq→*trans*-TS transition which reproduced $\Delta E_{rot}^{\#}$ $+0.62$ and $+1.97$ kcal/mol for *trans* and *cis* conformers, respectively, quite well.

Table 3. Summary of the most important changes in $E_{attr-mol}^{\mathcal{G}}$ values that describe the rotational barriers [*cis*-eq→*cis*-TS] and [*trans*-eq→*trans*-TS].

[*cis*-eq→*cis*-TS]		[*trans*-eq→*trans*-TS]		*trans–cis*
2-atom molecular fragments $\mathcal{G}$				
H4•••H12	+1.13	H6•••H12	+1.64	+0.51
H8•••H11	−1.55	H8•••H10	−1.51	+0.04
C7–C9	−1.18	C7–C9	−0.62	+0.56
C5–C7	+1.26	C5–C7	+1.64	+0.38
C1–C5	−0.87	C1–C5	+0.14	+1.01
C9–H12	+2.14	C9–H12	+2.00	−0.14
C9–H11	−1.24	C9–H11	−0.72	+0.52
C9–H10	−1.10	C9–H10	+0.22	+1.32
4-atom molecular fragments $\mathcal{G}$				
C1–H4•••H12–C9	−0.20	C5–H6•••H12–C9	+1.34	+1.54
−C1H_3	−0.40	−C1H_3	+0.49	+0.89
−C9H_3	+1.12	−C9H_3	+2.02	+0.90
C1–C5–C7–C9	−0.90	C1–C5–C7–C9	−0.04	+0.86
H6–C5=7–H8	+1.69	H6–C5=7–H8	+2.67	+0.98

c) However, to explain the higher (by ~1.5 kcal/mol) rotational barrier of the methyl group in trans with respect to cis-2-butene isomers one must take into consideration changes in

interactions between various atoms – for illustration purposes, the selected ones are collected in Table 3.

Our qualitative and quantitative results stemming mostly from the real space FAMSEC approach (supported also by the ETS-NOCV energy decomposition scheme) are in disagreement with common notion and interpretation of the H4--H12 contact as being strained and solely responsible for larger energy of *cis*-eq relative to *trans*-eq, hence, our interpretation is in direct conflict with an orthodox explanation provided by WSM[12] but is largely in line with the recent work by MSBF.[14]

ASSOCIATED CONTENT

Supporting Information

FAMSEC-based interpretation of classical H-bonds and steric clash; selected CCSD(T)/cc-pvtz data; extensively commented full or extended sets of geometric, IQA (additive, self-atomic and interaction energies), QTAIM (net atomic charges and electron populations, atomic areas and volumes) as well as *loc*- and mol-FAMSEC data for equilibrium and TS structures of 2-butene; NOCV deformation density channels corresponding to CH4•••12HC interaction in *cis*-2-butene, C5H6•••H12C9 in trans-2-butene and ETS-NOCV-based energy decomposition of *trans*-TS→*trans*-eq rotation.

AUTHOR INFORMATION
Corresponding Authors
*E-mail: ignacy.cukrowski@up.ac.za
*E-mail: mitoraj@chemia.uj.edu.pl

Notes
The authors declare no competing financial interest.

REFERENCES

1. R. Custelcean, J. E. Jackson, *Chem. Rev.* **2001**, *101*, 1963-1980 (and references therein).
2. V. I. Bakhmutov, Dihydrogen Bonds: Principles, Experiments and Applications, Wiley-Interscience, New-Jersey, **2008**, ISBN 978-0-470-18096-9 (and references therein).
3. X. Chen,J. C. Zhao, S. G. Shore, *Acc. Chem. Res.* **2013**, *46*, 2666-2675 (and references therein).
4. (a) A. Staubitz, A. P. M. Robertson, I. Manners, *Chem. Rev.* **2010**, *110*, 4079-4124 (b) F. Sagan, Ł. Piękoś, M. Andrzejak, M. P. Mitoraj, *Chem. Eur. J.* **2015**, 21*, 15299-15307 (c) M. P. Mitoraj, *J. Phys. Chem. A* **2011**, *115*, 14708-14716 (d) M. Parafiniuk, M. P. Mitoraj, *Organometallics* **2013**, *32*, 4103-4113 (e) M. Parafiniuk, M. P. Mitoraj, *J. Mol. Model.* **2014**, *20,* 2272 (article number).
5. D. J. Wolstenholme, J. L. Dobson, G. S. McGrady, *Dalton Trans.* **2015**, *44*, 9718-9731 (and references therein).
6. J. P. Wagner, P. R. Schreiner, *Angew. Chem. Int. Ed.* **2015**, *54*, 12274-12296 (and references therein).
7. (a) C. F. Matta, J. Hernández-Trujillo, T. H. Tang, R. F. W. Bader, *Chem. Eur. J.* **2003**, *9*, 1940-1951 (b) J. Hernández-Trujillo, C. F. Matta, *Struct. Chem.* **2007**, *18*, 849–857 (c) R. F. W. Bader, *Chem. Eur. J.* **2006**, *12*, 2896-2901 (d) D. A. Safin, M. G. Babashkina, K. Robeyns, M. P. Mitoraj, P. Kubisiak, Y. Garcia *Chem. Eur. J.* **2015**, *21*, 16679-16687 (e) I. Cukrowski, *Comput. Theor. Chem.* **2015**, *1066,* 62-75 (f) I. Cukrowski, K. K. Govender, M. P. Mitoraj, M. Srebro, *J. Phys. Chem. A* **2011**, *115*, 12746–12757 (g) I. Cukrowski, J. H. de Lange, M. P. Mitoraj, *J Phys. Chem. A* **2014**, *118*, 623–637 (h) I. Cukrowski, J. H. de Lange, A. S. Adeyinka, P. Mangondo, *Comput. Theor. Chem.* **2015**, *1053*, 60-76 (i) D. A. Safin, M. G. Babashkina, P. Kubisiak, M. P. Mitoraj, C. S. Le Duff, K. Robeyns, Y. Garcia, *Eur. J. Inorg. Chem.* **2014**, 5522–5529 (j) E. Lyngvi, I. A. Sanhueza, F. Schoenebeck, *Organometallics* **2015**, *34*, 805–812 (k) L. P. Wolters, R. Koekkoek, F. M. Bickelhaupt, *ACS Catalysis* **2015**, *5*, 5766-5775 (l) J. Echeverría, G. Aullón, D. Danovich, S. Shaik, S. Alvarez, *Nat. Chem.* **2011**, *3*, 323-330 (m) S. Grimme, P. R. Schreiner, *Angew. Chem. Int. Ed.* **2011**, *50*, 12639-12642 (n) A. Fokin, L. V. Chernish, P. A. Gunchenko, E. Y. Tikhonchuk, H. Hausmann, M. Serafin, J. E. P. Dahl, R. M. K. Carlson, P. R. Schreiner, *J. Am. Chem. Soc.* **2012**, *134*, 13641-13650 (o) J. Zhang, M. Dolg, *Chem. Eur. J.* **2014**, *20*, 13909-13912 (p) A. Krapp, G. Frenking, E. Uggerud, *Chem. Eur. J.* **2008**, *14*, 4028-4038.
8. (a) J. Poater, M. Solà, F. M. Bickelhaupt, *Chem. Eur. J.* **2006**, *12*, 2889-2895 (b) S. Grimme, C. Mück-Lichtenfeld, G. Erker, G. Kehr, H. Wang, H. Beckers, H. Willner, *Angew. Chem. Int. Ed.* **2009**, *48*, 2592-2595 (c) H. Jacobsen, *Dalton Trans.* **2010**, *39*, 5426-5428 (e) R. D. Hancock, I. V. Nikolayenko, *J. Phys. Chem. A* **2012**, *116*, 8572-8583.
9. K. Eskandari, C. V. Alsenoy, *J. Comp. Chem.* **2014**, *35*, 1883-1889.
10. F. Sagan, R. Filas, M. P. Mitoraj, *Crystals* **2016**, *6*(3), 28 (article number).
11. (a) P. Schouwink, H. Hagemann, J. P. Embs, V. D. Anna, R. Černý, *J. Phys. Condens. Matter* **2015**, *27*, 265403 (article number) (b) P. Ravindran, P. Vajeeston, R. Vidya, A. Kjekshus, H. Fjellvåg, *Phys. Rev. Lett.* **2002**, *89*, 106403 (article number) (c) D. J.

Wolstenholme, J. Flogeras, F. N. Che, A. Decken, A.; G. S. McGrady, *J. Am. Chem. Soc.* **2013**, *135*, 2439-2442 (d) D. J. Wolstenholme, K. T. Traboulsee, Y. Hua, L. A. Calhoun, G. S. McGrady, *Chem. Commun.* **2012**, *48*, 2597-2599.

12. F. Weinhold, P. R. Schleyer, W. C. McKee, *J. Comp. Chem.* **2014**, *35*, 1499-1508.

13. (a) F. Weinhold, C. R. Landis, Discovering Chemistry with Natural Bond Orbitals; Wiley: New York, **2012** (b) J. K. Badenhoop, F. Weinhold, *J. Chem. Phys.* **1997**, *107*, 5406-5421.

14. C. F. Matta, S. A. Sadjadi, D. A. Braden, G. Frenking, *J. Comp. Chem.* **2016**, *37*, 143-154.

15. (a) G. Frenking, N. Fröhlich *Chem. Rev.* **2000**, *100,* 717-774 (b) The Chemical Bond. Fundamental Aspects of Chemical Bonding. G. Frenking and S. Shaik (Eds), Wiley-VCH, Weinheim, **2014** (c) The Chemical Bond. Chemical Bonding Across the Periodic Table.G. Frenking and S. Shaik (Eds), Wiley-VCH, Weinheim, **2014** (d) G. Frenking, A. Krapp *J. Comp. Chem.* **2007**, *28*, 15-24 (e) R. G. Parr, P.W. Ayers, R.F. Nalewajski *J. Phys. Chem. A*, **2005**, *109,* 3957-3959.

16. (a) M. A. Blanco, A. M. Pendás, E. Francisco, *J. Chem. Theory Comput.* **2005**, *1*, 1096-1109 (b) E. Francisco, A. M. Pendás, M. A. A. Blanco, *J. Chem. Theory Comput.* **2006**, *2*, 90−102 (c) A. M. Pendás, M. A. Blanco, E. Francisco, *J. Comp. Chem.* **2006**, *28*, 161−184 (d) A. M. Pendás, E. Francisco *J. Comp. Chem.* **2006**, *30*, 98−109.

17. (a) M. P. Mitoraj, A. Michalak, T. Ziegler, *J. Chem. Theory Comput.* **2009**, *5*, 962-975 (b) M. P. Mitoraj, A. Michalak, *J. Mol. Model.* **2007**, *13*, 347-355 (c) M. P. Mitoraj, A. Michalak, *J. Mol. Model.* **2013**, *19*, 4681-4688 (d) M. P. Mitoraj, G. V. Janjic, V. B. Medakovic, D. Z. Veljkovic, A. Michalak, S. D. Zaric, M. K. Milcic, *J. Comp. Chem.* **2015**, *36*, 171-180.

18 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision D.1, Gaussian, Inc., Wallingford CT, **2009**.

19 A. Keith, AIMAll (Version 14.06.21), TK Gristmill Software, Overland Parks KS, USA, **2014** (aim.tkgristmill.com).

20 ADF2012.01: (a) G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders and T. Ziegler, J. Comput. Chem., 2001, 22, 931 and references therein; (b) E. J. Baerends, J. Autschbach, D. Bashford, A. Bérces, F. M. Bickelhaupt, C. Bo, P. M. Boerrigter, L. Cavallo, D. P. Chong, L. Deng, R. M. Dickson, D. E. Ellis, M. van Faassen, L. Fan, T. H. Fischer, C. Fonseca Guerra, A. Ghysels, A. Giammona, S. J. A. van Gisbergen, A. W. Götz, J. A. Groeneveld, O. V. Gritsenko, M. Grüning, F. E. Harris, P. van den Hoek, C. R. Jacob, H. Jacobsen, L. Jensen, G. van Kessel, F. Kootstra, M. V. Krykunov, E. van Lenthe, D. A. McCormack, A. Michalak, M. Mitoraj, J. Neugebauer, V. P. Nicu, L. Noodleman, V. P. Osinga, S. Patchkovskii, P. H. T. Philipsen, D. Post, C. C. Pye, W. Ravenek, J. I. Rodríguez, P. Ros, P. R. T. Schipper, G.

Schreckenbach, M. Seth, J. G. Snijders, M. Solà, M. Swart, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, L. Visscher, O. Visser, F. Wang, T. A. Wesolowski, E. M. van Wezenbeek, G. Wiesenekker, S. K. Wolff, T. K. Woo, A. L. Yakovlev and T. Ziegler, Theoretical Chemistry, Vrije Universiteit, Amsterdam.

21   R. McWeeny, Methods of Molecular Quantum Mechanics, 2nd ed., Academic Press, London, 1992.

TOC
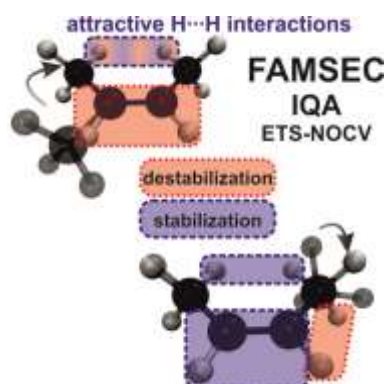
To describe 2-buthene isomers, the real space Fragment Attributed Molecular System Energy Change (FAMSEC) method is applied for the first time together with the Extended Transition State (ETS) method coupled with the Natural Orbitals for Chemical Valence (NOCV). It has been shown that (i) a molecular fragment made of H•••H in *cis*-eq and *cis*-TS is stabilized (not strained), diatomic interaction is attractive, has several features typical for a classical H-bond and can be linked with smaller, relative to trans-2-butene, rotational energy barrier, and (ii) higher energy of *cis*- relative to *trans* isomer must be linked with the middle part of the molecule, HC=CH.