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

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Supplementary Information

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Comprehensive summary of relevant findings from the first paper on FAMSEC[1]

In the first implementation of FAMSEC, the common notion of classical stabilizing H•••N and H•••O interactions, treated as diatomic molecular fragments $\mathscr{G}$, in the protonated forms of ethylenediamine (**Hen**) and ethanolamine (**Hea**), respectively, was fully recovered. These fragments' energy decreased ($E_{\text{attr-loc}}^{\mathscr{G}} < 0$) and they stabilized **Hen** and **Hea** molecules ($E_{\text{attr-mol}}^{\mathscr{G}} < 0$); just opposite was found for the destabilizing O--O steric contact in the eclipsed form of glycol (**gc**) – see Figure S1.

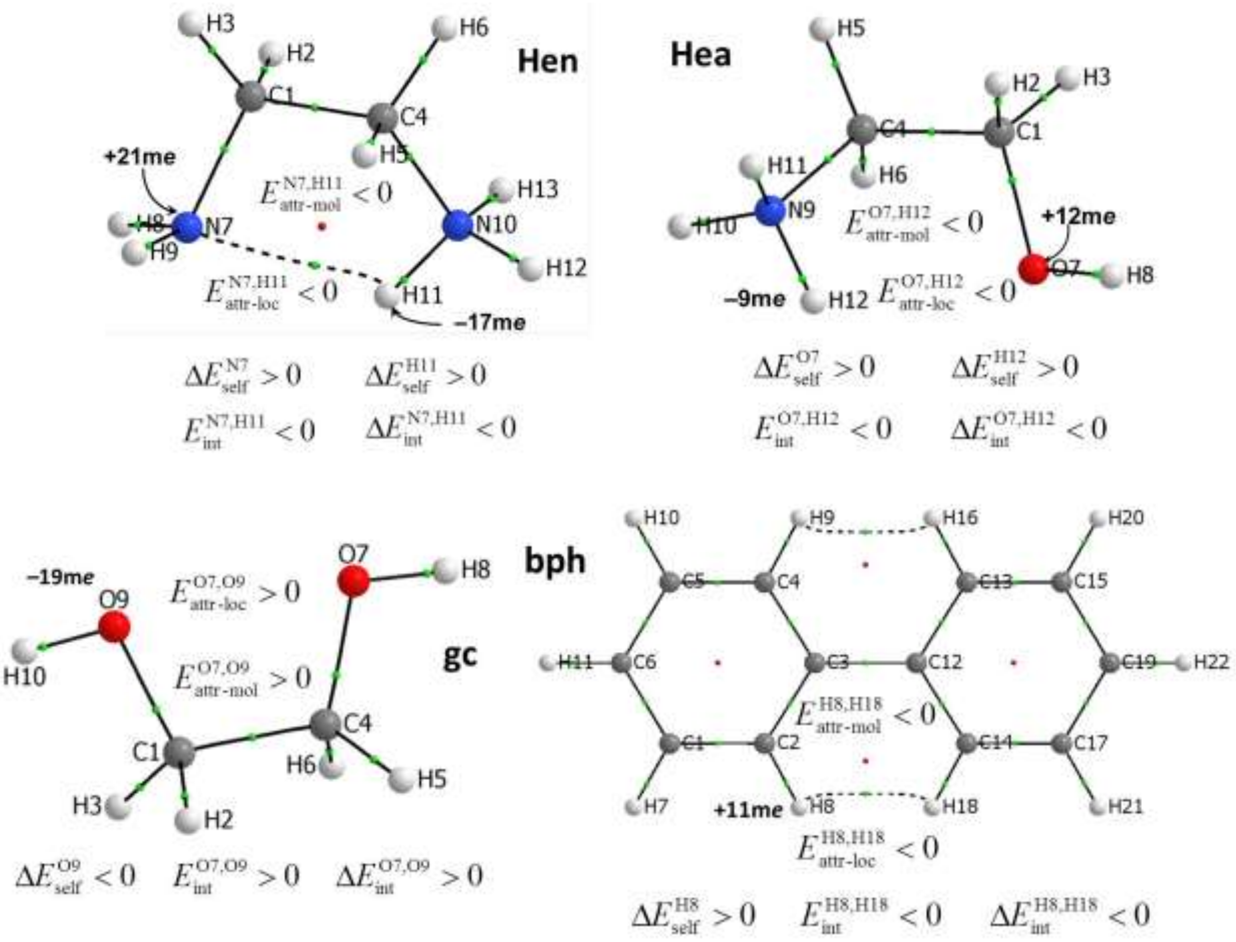


Figure S1. Molecular graphs of protonated forms of lowest energy ethylenediamine (**Hen**) and ethanolamine (**Hea**), higher energy forms of eclipsed glycol (**gc**) and planar biphenyl (**bph**) – all used as the final state of a molecular system. A change in electron population for atoms involved in an interaction as well as sets of FAMSEC/IQA-defined energy terms, used as signatures for stabilizing intramolecular interactions in **Hen**, **Hea** and **bph** and destabilizing steric clash in **gc**, were calculated relative to a relevant initial state of a molecule: linear **Hen** and **Hea**, staggered **gc** and twisted **bph**.[7e]

Exploring the origin of these interactions showed that additive atomic energy of each individual atom in N•••H and O•••H has decreased, $\Delta E_{\text{add}}^{\text{X}} < 0$, due to favorable interactions with remaining atoms of a molecular system and, as expected for atoms involved in attractive and highly stabilizing intramolecular H-bonding, their self-atomic energies increased, $\Delta E_{\text{self}}^{\text{X}} > 0$; just opposite trends were found for the O-atoms in **gc**. Data obtained also showed that leading interactions drive a molecule to the lowest energy state; H•••N in **Hen** and H•••O in **Hea,** from the linear to bent state where the attractive intramolecular interaction is present, $E_{\text{int}}^{\text{XY}} < 0$, and this interaction becomes more attractive in the final state, $\Delta E_{\text{int}}^{\text{XY}} < 0$, whereas O--O in **gc** drives the molecule from the eclipsed to staggered state, where steric clash disappears. Using the same methodology, the origin of the higher energy of the planar biphenyl, **bph**, relative to its twisted conformer, was investigated. Firstly, it was concluded that the H--H contacts do not drive a structural change from the planar to lower energy, twisted form of **bph**. This is because the sum of these atoms interactions with remaining atoms of planar **bph** was slightly attractive. Moreover, the H•••H interactions in both forms of **bph** were attractive and significantly stronger, by –3.8 kcal mol^{-1}, in the higher energy conformer. The higher energy of the planar **bph** was attributed to all C-atoms of a bay; the energy contribution $E_{\text{attr-mol}}^{\mathcal{G}}$ of +3.2 and +2.5 kcal mol^{-1} was obtained for C-atoms linking the rings (C3 and C12) and each pair of remaining atoms of two bays (C4/C13 and C2/C14 – Figure S1), respectively. Considering 'clashing' H-atoms, energy of each pair treated as a molecular fragment $\mathcal{G}$, $E_{\text{attr-loc}}^{\mathcal{G}}$, decreased by –0.5 kcal mol^{-1}, and each pair stabilized planar **bph,** by $E_{\text{attr-mol}}^{\mathcal{G}} = –0.7$ kcal/mol^{-1}.

[1] I. Cukrowski, *Computational and Theoretical Chemistry* **2015**, *1066*, 62.

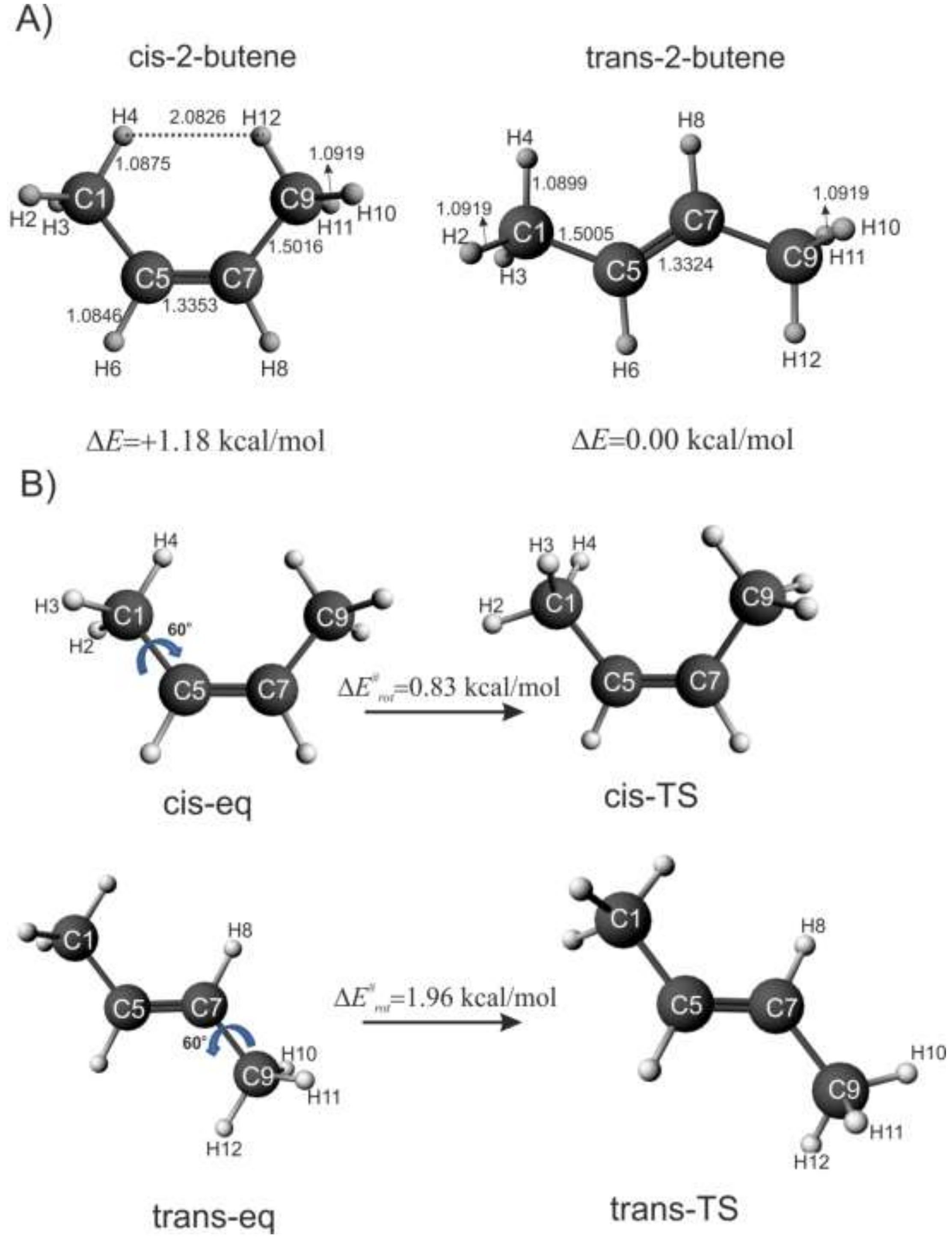


Figure S2. The structures and selected distances (in Å) in *cis*- and *trans*-2-buthene isomers based on the CCSD(T)/cc-pvtz calculations (part A). In part B the barriers to methyl rotations are presented.

Part S1

Data computed for transition from *trans*- to *cis*-2-butene

FAMSEC data obtained for 2-atom molecular fragments $\mathfrak{G}$

Table S1. The $E_{\text{attr-loc}}^{\mathfrak{G}}$ energy term (in kcal/mol at MP2) computed for all possible 66 diatomic fragments for the *trans*-eq to *cis*-eq change.

Stabilizing contribution			**Destabilizing contribution**					
Atom	**Atom**	$E_{\text{attr-loc}}^{\mathfrak{G}}$	**Atom**	**Atom**	$E_{\text{attr-loc}}^{\mathfrak{G}}$	**Atom**	**Atom**	$E_{\text{attr-loc}}^{\mathfrak{G}}$
H6	C5	-0.96	C5	H2	0.00	H11	H6	0.44
H8	C7	-0.89	C5	H3	0.01	H10	H6	0.44
C9	C1	-0.79	H11	C1	0.02	H8	H2	0.45
H8	C5	-0.39	H10	C1	0.03	H8	H3	0.45
C7	H6	-0.33	C9	C5	0.04	H11	H2	0.54
H12	H4	-0.24	H11	C5	0.05	H10	H3	0.54
H6	C1	-0.22	H10	C5	0.05	H11	H3	0.57
C5	C1	-0.22	C9	H2	0.06	H10	H2	0.57
C9	H8	-0.19	C9	H3	0.06	H11	H10	0.58
C9	C7	-0.14	H11	C7	0.07	H3	H2	0.58
			H10	C7	0.07	H4	C1	1.23
			C7	C1	0.08	H12	C9	1.26
			C7	H2	0.12	C5	H4	1.66
			C7	H3	0.12	H12	C7	1.73
			H2	C1	0.18	H6	H4	1.79
			H3	C1	0.19	H12	H8	1.81
			C7	C5	0.20	H11	H4	1.84
			H10	C9	0.20	H10	H4	1.84
			H11	C9	0.21	H12	H2	1.84
			H8	C1	0.35	H12	H3	1.84
			H12	C1	0.35	H4	H3	1.88
			C9	H6	0.36	H4	H2	1.88
			H8	H6	0.36	H12	H11	1.89
			C9	H4	0.39	H12	H10	1.89
			H6	H2	0.41	H12	C5	1.98
			H6	H3	0.41	C7	H4	2.04
			H11	H8	0.42	H12	H6	2.98
			H10	H8	0.42	H8	H4	2.98

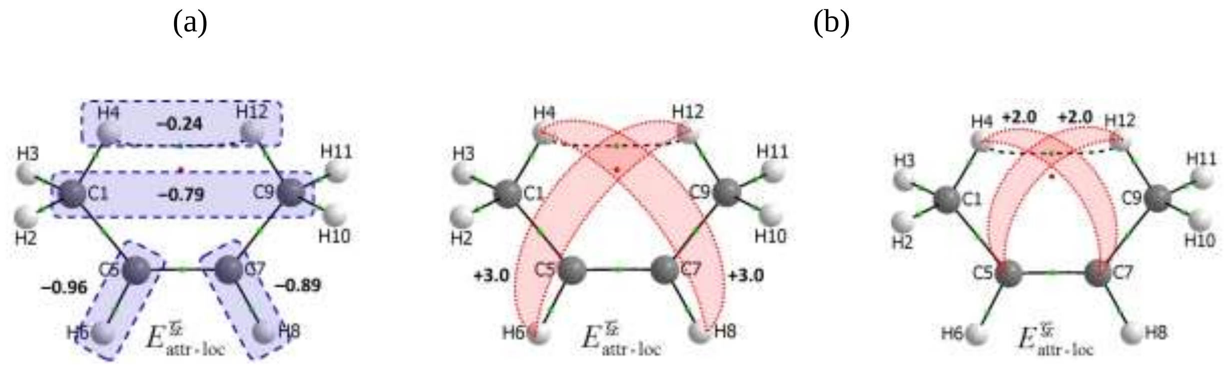


Figure S3. Selected most stabilizing (part a) and destabilizing (part b) contributions, *loc*-FAMSEC, made by selected 2-atom fragments $\mathscr{G}$ when *trans*-eq changed to *cis*-eq; values in kcal/mol.

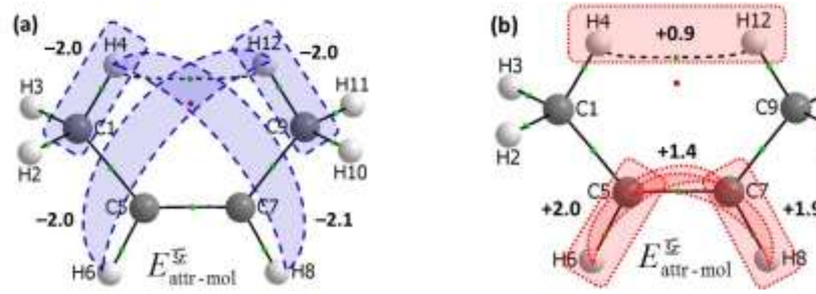


Figure S4. Selected 2-atom fragments $\mathscr{G}$, which made most significant stabilizing (part a) and destabilizing (part b) *mol*-FAMSEC contribution when *trans*-eq changed to *cis*-eq: values are in kcal/mol.

We have also looked at a set of $E_{\text{attr-loc}}^{\mathcal{G}}$ energy terms, and its components, computed for fragments made of covalently bonded atoms in 2-butene plus BP-linked H4 and H12 atoms – see Table S2. It reveals that {C1,H4} and {C9,H12} became most destabilized but this is less than 50% of energy increase found for {H4,H8} and {H12,H6}. The self-atomic energies of C1/C9 have decreased but these atoms interactions with H4/H12 became stronger when in *cis*-eq. Hence, the origin of the observed increase in the {C1,H4} and {C9,H12} fragments *loc*-FAMSEC values is related to an increase in self-atomic energies of H4/H12 atoms due to their involvement in a bonding-like interaction in *cis*-eq. There are other five fragments which experienced an increase in their energy, all by about +0.2 kcal/mol. Among them, C5=C7 of the backbone of 2-butene and two {C,H} fragments from each terminal CH_3 group; note that the remaining two fragments of the backbone, {C1,C5} and {C7,C9}, are stabilized in *cis*-eq.

Table S2. The $E_{\text{attr-loc}}^{\mathcal{G}}$ energy term and its components (in kcal/mol at MP2) computed for fragments made of covalently bonded atoms in 2-butene plus BP-linked H4and H12 atoms when *trans*-eq changed to *cis*-eq. Fragments are arranged from most negative to most positive *loc*-FAMSEC value.

Atom	**Atom**	$\Delta E_{\text{int}}^{\mathcal{G}}$	$\Delta E_{\text{self}}^{\mathcal{G}}$	$E_{\text{attr-loc}}^{\mathcal{G}}$
C5	H6	-0.88	-0.08	-0.96
C7	H8	-0.88	-0.01	-0.89
H4	H12	-3.54	3.30	-0.24
C1	C5	0.24	-0.46	-0.22
C7	C9	0.23	-0.37	-0.14
C1	H2	0.13	0.04	0.18
C1	H3	0.14	0.04	0.19
C5	C7	0.61	-0.41	0.20
C9	H10	0.14	0.06	0.20
C9	H11	0.14	0.06	0.21
C1	H4	-0.20	1.43	1.23
C9	H12	-0.19	1.45	1.26

Table S3. Ten most stabilizing and destabilizing a molecule diatomic fragments, as measured by the $E_{\text{attr-mol}}^{\mathcal{G}}$ energy term (in kcal/mol at MP2) when *trans*-eq changed to *cis*-eq.

Stabilizing contribution			**Destabilizing contribution**		
Atom	**Atom**	$E_{\text{attr-mol}}^{\mathcal{G}}$	**Atom**	**Atom**	$E_{\text{attr-mol}}^{\mathcal{G}}$
H8	H4	-2.05	H10	C5	1.04
H12	H6	-2.05	H11	C5	1.05
H4	C1	-1.98	H10	C7	1.05
H12	C9	-1.95	H11	C7	1.05
C7	H4	-1.31	C5	H3	1.09
C9	C1	-1.29	C5	H2	1.09
H12	C5	-1.26	C7	H6	1.37
H12	C1	-1.10	H8	C5	1.41
C9	H4	-1.09	H8	C7	1.93
H12	C7	-0.99	H6	C5	1.98

Table S4. The $E_{\text{attr-mol}}^{\mathcal{G}}$ and $E_{\text{attr-loc}}^{\mathcal{G}}$ energy terms (in kcal/mol at MP2) computed for fragments made of covalently bonded atoms in 2-butene plus BP-linked H4and H12 atoms when *trans*-eq changed to *cis*-eq. Fragments are arranged from most negative to most positive *mol*-FAMSEC value.

Atom	**Atom**	$E_{\text{attr-loc}}^{\mathcal{G}}$	$E_{\text{attr-mol}}^{\mathcal{G}}$
C1	H4	1.23	-1.98
C9	H12	1.26	-1.95
C1	H3	0.19	-0.56
C1	H2	0.18	-0.55
C9	H11	0.21	-0.53
C9	H10	0.20	-0.52
C7	C9	-0.14	-0.45
C1	C5	-0.22	-0.44
C5	C7	0.20	0.63
H4	H12	-0.24	0.87
C7	H8	-0.89	1.93
C5	H6	-0.96	1.98

FAMSEC data obtained for 4-atom molecular fragments $\mathfrak{G}$

Table S5. Most (de)stabilized, as measured by $E_{\text{attr-loc}}^{\mathfrak{G}}$ (in kcal/mol at MP2), 4-atom fragments $\mathfrak{G}$. when 2-butene changed from *trans*-eq to *cis*-eq.

Stabilizing contributions					**Destabilizing contributions**				
Atoms of a $\mathfrak{G}$ fragment				$E_{\text{attr-loc}}^{\mathfrak{G}}$	**Atoms of a $\mathfrak{G}$ fragment**				$E_{\text{attr-loc}}^{\mathfrak{G}}$
C1	H4	C9	H12	-3.56	H2	H6	H8	H12	3.37
C5	H6	C7	H8	-1.82	H3	H6	H8	H12	3.37
C1	H4	H11	H12	-1.60	H6	C9	H10	H12	3.38
C1	H4	H10	H12	-1.59	H2	H3	H6	H12	3.38
H3	H4	C9	H12	-1.53	H6	C9	H11	H12	3.38
H2	H4	C9	H12	-1.53	H4	H8	H10	H11	3.39
C1	H2	H4	H12	-1.45	H2	H4	H6	H8	3.42
C1	H3	H4	H12	-1.44	H3	H4	H6	H8	3.42
H4	C9	H10	H12	-1.39	H6	H8	H11	H12	3.42
H4	C9	H11	H12	-1.38	H2	H6	H11	H12	3.42
C1	H4	C5	H12	-0.92	H6	H8	H10	H12	3.42
H2	C5	H6	H8	-0.81	H3	H6	H10	H12	3.42
C1	C5	H6	H11	-0.81	H2	H4	H8	H11	3.43
H3	C5	H6	H8	-0.81	H3	H4	H8	H10	3.43
C1	C5	H6	H10	-0.81	H3	H6	H11	H12	3.45
H4	C7	C9	H12	-0.81	H2	H6	H10	H12	3.45
C1	C5	H6	H8	-0.81	H3	H4	H8	H11	3.45
C1	C5	H6	C9	-0.79	H2	H4	H8	H10	3.46
C5	H6	H8	H11	-0.77	H6	H10	H11	H12	3.54
C5	H6	H8	H10	-0.77	H2	H3	H4	H8	3.54

Table S6. Most (de)stabilizing $E_{\text{attr-mol}}^{\mathfrak{G}}$ contributions to molecular energy (kcal/mol at MP2) made by 4-atom fragments $\mathfrak{G}$ when 2-butene changed from *trans*-eq to *cis*-eq.

Stabilizing contributions					**Destabilizing contributions**				
Atoms of a $\mathfrak{G}$ fragment				$E_{\text{attr-mol}}^{\mathfrak{G}}$	**Atoms of a $\mathfrak{G}$ fragment**				$E_{\text{attr-mol}}^{\mathfrak{G}}$
C1	H4	C5	C7	-2.88	C5	C7	H8	H11	2.71
C5	C7	C9	H12	-2.85	H2	C7	H8	H10	2.73
C1	H3	H4	H8	-2.81	H3	C7	H8	H11	2.74
C1	H2	H4	H8	-2.80	H3	C7	H8	H10	2.76
H6	C9	H11	H12	-2.78	H2	C7	H8	H11	2.76
H6	C9	H10	H12	-2.77	H2	C5	H6	H10	2.77
C1	H4	C7	H8	-2.67	H3	C5	H6	H11	2.78
H6	C7	C9	H12	-2.64	H3	C5	H6	H10	2.80
C1	H4	C5	H8	-2.64	H2	C5	H6	H11	2.80
C5	H6	C9	H12	-2.60	C7	H8	H10	H11	2.81
C1	H4	H8	H10	-2.58	H2	H3	C5	H6	2.84
C1	H4	H8	H11	-2.57	H3	H6	C7	H8	3.05
H3	H6	C9	H12	-2.56	H2	H6	C7	H8	3.05
H2	H6	C9	H12	-2.55	C5	H6	H8	H10	3.08
C1	H4	H6	H8	-2.53	C5	H6	H8	H11	3.09
H6	H8	C9	H12	-2.50	H6	C7	H8	H10	3.09
C1	H4	H8	C9	-2.33	H6	C7	H8	H11	3.10
C1	H6	C9	H12	-2.31	H3	C5	H6	H8	3.13
C1	H3	H4	C7	-2.14	H2	C5	H6	H8	3.13
C1	H2	H4	C7	-2.13	C5	H6	C7	H8	3.88

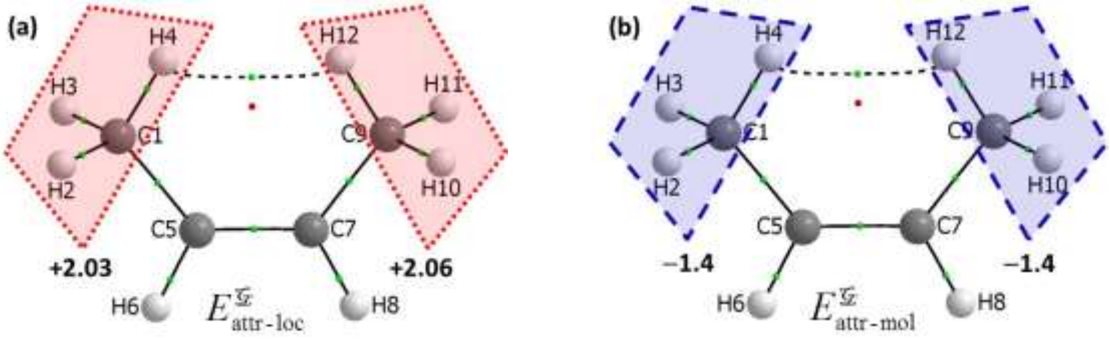


Figure S5. An example showing a change in the nature of energy contribution made by the same 4-atom fragments. Terminal –CH_3 groups became destabilized in *cis*-eq in terms of *loc*-FAMSEC (part a) but added to molecular stability, in terms of mol-FAMSEC (part b) on the *trans*-eq→*cis*-eq structural change; values are in kcal/mol.

Table S7. The $E^{\mathcal{G}}_{\text{attr-mol}}$ terms (kcal/mol at MP2) computed for 4-atom fragments $\mathcal{G}$ made of covalently bonded atoms. Due to molecular symmetry, only specific fragments are included.

Atoms of a $\mathcal{G}$ fragment				$E^{\mathcal{G}}_{\text{attr-mol}}$
C1	**H4**	C5	C7	-2.9
C1	C5	C7	**C9**	-2.1
C1	H3	**H4**	C5	-1.5
C1	H2	**H4**	C5	-1.5
C1	H2	H3	**H4**	-1.4
C1	H3	C5	C7	-0.6
C1	H2	C5	C7	-0.6
C1	H4	C5	H6	-0.3
C1	H2	H3	C5	0.1
C1	C5	C7	H8	0.3
C1	C5	H6	C7	0.9
C1	H3	C5	H6	1.4
C1	H2	C5	H6	1.4
C5	H6	C7	H8	3.9

IQA-based analysis

Additive and self atomic energies.

Within the IQA-framework, molecular energy is recovered by summing up additive energies of atoms, $\Delta E_{\mathrm{add}}^{\mathrm{X}}$. Because of that, an increase or decrease in $\Delta E_{\mathrm{add}}^{\mathrm{X}}$ can be interpreted as a destabilizing or stabilizing energy contribution made by an atom to a molecule when it changes from any arbitrarily chosen reference (*ref*) state to the final (*fin*) state. One must recall that $\Delta E_{\mathrm{add}}^{\mathrm{X}}$ is made of energy of an atom (self-atomic energy) and halved interaction energies between this atom and remaining atoms of a molecule. From that follows, that even when atom itself is destabilized (its self energy increased) it might add to molecule's electronic energy an overall stabilizing contribution, as $\Delta E_{\mathrm{add}}^{\mathrm{X}}$, due to favorable change in all diatomic interactions. Computed $\Delta E_{\mathrm{add}}^{\mathrm{X}}$ and $\Delta E_{\mathrm{self}}^{\mathrm{X}}$ values for transition from *trans*-eq to *cis*-eq are included in Table S8.

Table S8. Change in additive and self-atomic energies (in kcal/mol at MP2) when 2-butene changed from *trans*-eq to *cis*-eq conformation.

Atom X	$\Delta E_{\mathrm{add}}^{\mathrm{X}}$	$\Delta E_{\mathrm{self}}^{\mathrm{X}}$
C1	-0.53	-0.22
H2	0.35	0.26
H3	0.35	0.27
H4	0.16	1.65
C5	0.20	-0.24
H6	0.31	0.15
C7	0.21	-0.17
H8	0.31	0.16
C9	-0.51	-0.20
H10	0.35	0.26
H11	0.35	0.26
H12	0.16	1.65

Analysis of the $\Delta E_{\mathrm{add}}^{\mathrm{X}}$ data leads to the following conclusions:

a) Only two atoms, **C1** and **C9** to which 'clashing' H-atoms are bonded to, add by about –0.52 kcal/mol to stability of *cis*-eq.

b) All H-atoms of 2-butene decreased stability of *cis*-eq, but the 'clashing' **H4** and **H12** contributed the least, +0.16 kcal/mol, among atoms with $\Delta E_{\mathrm{add}}^{\mathrm{X}} > 0$.

c) The largest positive $\Delta E_{\text{add}}^{\text{X}}$ values are observed for H-atoms of both terminal –CH$_3$ groups, <u>atoms which are not involved in the steric clash</u>; their contributions of +0.35 kcal/mol is over twice as much as computed for 'clashing' H-atoms.

d) Atoms of the –H6C5=C7H8– fragment experienced a significant increase in $\Delta E_{\text{add}}^{\text{X}}$. Also, this is the only fragment made of covalently bonded atoms for which a consistent change in the $\Delta E_{\text{add}}^{\text{X}}$ values was discovered; $\Delta E_{\text{add}}^{\text{X}} > 0$ is observed for each atom and this correlates well with our conclusion that the main source of increased energy of *cis*-eq relative to *trans*-eq should be linked mainly with this molecular fragment.

It is clear that destabilization of *cis*-eq is caused by many (most) atoms but the **H4**/**H12**-atoms contributed to the sum of all $\Delta E_{\text{add}}^{\text{X}} > 0$ only 11.6%, contradicting the classical interpretation.

Analysis of the $\Delta E_{\text{self}}^{\text{X}}$ data leads to the following conclusions:

a) Only self-atomic energies of all C-atoms decreased, by about –0.2 kcal/mol, when *trans*-eq changes to *cis*-eq.

b) Except H4 and H12, self-energies of H-atoms have increased by 0.16 to 0.26 kcal/mol.

c) H4 and H12 experienced by far the largest increase in self energies, by about 1.65 kcal/mol. As discussed in the main body of the text, this is a result of highly attractive interaction between them, when in *cis*-eq, which lead to a 'bonding-like' interaction with a bond path and this interaction has numerous descriptors found among classical intramolecular H-bonds.

Interaction energy between an atom X and all other atoms in the molecular system.

It is important to realize that on transformation from *trans*-eq to *cis*-eq interactions between atoms must have changed. We investigate here a combined effect, *i.e.*, the change in the interactions energy between a selected atom X and remaining atoms of 2-butene. To this effect, it is convenient to use a fragment notation by placing all but the selected atom in a molecular fragment $\mathcal{H}$. The computed $\Delta E_{\text{int}}^{\text{X},\mathcal{H}}$ values and their components, classical $\Delta V_{\text{cl}}^{\text{X},\mathcal{H}}$ and exchange-correlation $\Delta V_{\text{XC}}^{\text{X},\mathcal{H}}$ contributions, are included in Table S9.

Table S9. Change in interaction energy between an atom X and the remaining atoms in 2-butene, as molecular fragment $\mathcal{H}$ (in kcal/mol at MP2) when *trans*-eq changed to *cis*-eq conformation.

Atom X	$\Delta E_{\text{int}}^{\text{X},\mathcal{H}}$	$\Delta V_{\text{cl}}^{\text{X},\mathcal{H}}$	$\Delta V_{\text{XC}}^{\text{X},\mathcal{H}}$
H12	-2.99	-0.10	-2.89
H4	-2.98	-0.09	-2.89
C1	-0.62	-0.38	-0.24
C9	-0.61	-0.51	-0.10
H3	0.16	0.15	0.01
H10	0.16	0.11	0.05
H2	0.16	0.11	0.05
H11	0.17	0.12	0.05
H8	0.29	0.21	0.08
H6	0.30	0.20	0.10
C7	0.77	-0.21	0.98
C5	0.88	-0.08	0.96

From the $\Delta E_{\text{int}}^{\text{X},\mathcal{H}}$ data it follows that:

a) Atoms of the H4--H12 contact experienced most stabilizing and significant change in their interactions with remaining atoms of the molecule, about –3.0 kcal/mol (which is almost entirely of the XC origin) when going from the *trans*-eq to *cis*-eq; one might say that they found themselves in more favorable molecular environment when sum of all diatomic interactions is considered.

b) Atoms of the H4--H12 contact experienced more attractive molecular environment as we obtained $\Delta V_{\text{cl}}^{\text{X},\mathcal{H}} = –0.1$ kcal/mol.

c) Only atoms of the C1—H4 and C9—H12 fragments (i) experienced an overall stabilizing change in interactions with remaining atoms and (ii) have both interaction energy components, $\Delta V_{\text{cl}}^{\text{X},\mathcal{H}}$ and $\Delta V_{\text{XC}}^{\text{X},\mathcal{H}}$, being negative, a change in a stabilizing manner.

d) The largest destabilizing change in $\Delta E_{\text{int}}^{\text{X},\mathcal{H}}$ of +0.8 kcal/mol is observed for the atoms of the link, –C5=C7–. Furthermore, these atoms show the largest (about +1 kcal/mol) unfavorable change in the $\Delta V_{\text{XC}}^{\text{X},\mathcal{H}}$ component, just opposite to what we found for 'clashing' H-atoms.

Diatomic interaction energies, the $\Delta E_{\text{int}}^{\text{X,Y}}$ term.

The analysis of the $\Delta E_{\text{int}}^{\text{X},\mathcal{H}}$ energy terms provided an overall picture pointing at H4 and H12 as being placed in more favorable molecular environment when in *cis*-eq and just opposite we discovered for the –C5=C7– molecular fragment. We decided to explore all 66 unique diatomic interactions (ten most significant positive and negative $\Delta E_{\text{int}}^{\text{X,Y}}$ values are provided in Table S10) as this should provide an insight on the origin of that phenomenon; fragments with most significant (de)stabilizing $\Delta E_{\text{int}}^{\text{X,Y}}$ contributions are shown in Figure S6.

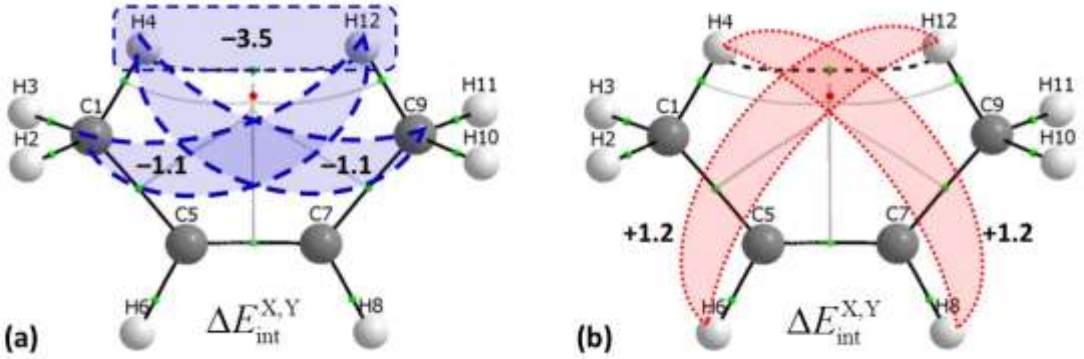


Figure S6. Pictorial representation of 2-atom fragments $\mathcal{G}$, which experienced most significant change in diatomic interactions when *trans*-eq changed to *cis*-eq: stabilized (part a) and destabilized (part b). All values in kcal/mol at MP2.

Firstly, we want to note that the sum of all 34 stabilizing contributions, with $\Delta E_{\text{int}}^{\text{X,Y}} < 0$, gave –9.75 kcal/mol whereas for 32 destabilizing we obtained +7.81 kcal/mol. Hence the total change in all 66 unique diatomic interaction energies (when going from *trans*-eq to *cis*-eq conformer) is –1.94 kcal/mol. This is an important finding as it points at the origin of higher energy of *cis*-eq, namely the overall increase in self-atomic energies, which is more significant than the stabilizing in nature change in all diatomic interactions. From the $\Delta E_{\text{int}}^{\text{X,Y}}$ data the following observations can be made:

a) The most stabilizing contribution of –3.5 kcal/mol is made by the H4•••H12 interaction which is –2.4 kcal/mol more significant when compared with second largest computed these H-atoms with C-atoms of the bay. Hence, atoms of the C1—H4 and C9—H12 molecular fragments provided most stabilizing contributions in terms of $\Delta E_{\text{int}}^{\text{X,Y}}$.

b) H4 and H12 are involved in many interactions with $\Delta E_{\text{int}}^{\text{X,Y}}$ being of (de)stabilizing nature. Importantly, however, the sum $\Delta E_{\text{int}}^{\text{H4,X}} + \Delta E_{\text{int}}^{\text{H12,X}}$ computed for 10 most stabilizing and destabilizing contribution amounted to –6.1 and +3.7 kcal/mol, respectively – Table S10; this explains $\Delta E_{\mathrm{int}}^{\mathrm{H4},\mathcal{H}} < 0$ (and $\Delta E_{\mathrm{int}}^{\mathrm{H12},\mathcal{H}} < 0$) very well.

c) We note that atoms of the C5—H6 and C7—H8 molecular fragments are involved in all 10 most destabilizing $\Delta E_{\mathrm{int}}^{\mathrm{X,Y}}$ contributions; this explains $\Delta E_{\mathrm{int}}^{\mathrm{X},\mathcal{H}} > 0$ obtained for these four atoms.

Importantly, data shown in Table S10 also uncovered the origin of all most significant (de)stabilizing contributions; all of them are dominated by the V_{XC} energy term. This must be due to the formation of a new interaction between H4 and H12 which required some inflow of density from other parts of 2-butene. Furthermore, the Coulombic-type of contribution is negligible, on average about ±0.1 kcal/mol for all atoms of *cis*-eq. This finding clearly shows that, from the perspective of the $\Delta V_{\mathrm{cl}}^{\mathrm{X,Y}}$ term, the H4•••H12 interaction (i) does not stand-up among all others, (ii) is not involved in a classical highly repulsive contact and (iii) cannot be made responsible for larger energy of *cis*-eq based on an orthodox interpretation.

Table S10. Most significant changes in diatomic interaction energies (in kcal/mol at MP2) when *trans*-eq changed to *cis*-eq conformation.

Stabilizing interaction					**Destabilizing interactions**				
Atom X	Atom Y	$\Delta E_{\mathrm{int}}^{\mathrm{X,Y}}$	$\Delta V_{\mathrm{cl}}^{\mathrm{X,Y}}$	$\Delta V_{\mathrm{XC}}^{\mathrm{X,Y}}$	Atom X	Atom Y	$\Delta E_{\mathrm{int}}^{\mathrm{X,Y}}$	$\Delta V_{\mathrm{cl}}^{\mathrm{X,Y}}$	$\Delta V_{\mathrm{XC}}^{\mathrm{X,Y}}$
H12	H4	-3.54	0.11	-3.64	H12	C7	0.25	-0.01	0.26
H12	C1	-1.08	-0.01	-1.07	C9	H6	0.40	-0.06	0.46
C9	H4	-1.06	0.01	-1.07	H8	C1	0.40	-0.06	0.46
H8	C7	-0.88	0.05	-0.93	C7	C1	0.47	-0.13	0.60
H6	C5	-0.88	0.05	-0.93	C9	C5	0.48	-0.12	0.60
C9	C1	-0.37	0.08	-0.45	H12	C5	0.57	-0.04	0.61
H8	C5	-0.31	0.09	-0.40	C7	H4	0.57	-0.04	0.61
C7	H6	-0.31	0.09	-0.40	C7	C5	0.61	-0.05	0.66
H4	C1	-0.20	0.09	-0.29	H8	H4	1.17	-0.13	1.30
H12	C9	-0.19	0.08	-0.28	H12	H6	1.17	-0.13	1.30
Total:		–8.83			Total:		+6.10		
Sum for H4+H12		–6.07			Sum for H4+H12		+3.73		

For convenience, a pictorial representation of two energy terms, $\Delta E_{\mathrm{add}}^{\mathrm{X}}$ and $\Delta E_{\mathrm{int}}^{\mathrm{X},\mathcal{H}}$, is shown in Figure S7. Trend observed fully support the FAMSEC-based analyses:

a) The smallest increase in additive atomic energy is observed for H4 and H12, Figure S7(a), and they experienced most favorable change in interactions with remaining atoms of 2-butene when in *cis* isomer - Figure S7(b).

b) There is only one 4-atom fragment of chemical significance, namely C1H4•••H12C9, where interactions with remaining atoms of 2-butene changed favorable for each atom – Figure S7(b).

c) Except H4 and H12, the largest increase in additive atomic energy is observed for H-atoms - Figure S7(a).

d) There is only one 4-atom fragment of chemical significance, namely H6C5=C7H8, where an increase in additive energy of all atoms was uncovered, Figure S7(a), and these atoms interactions with remaining atoms of 2-butene changed in most unfavorable fashion on transition from *trans*-eq *to* cis-eq - Figure S7(b).

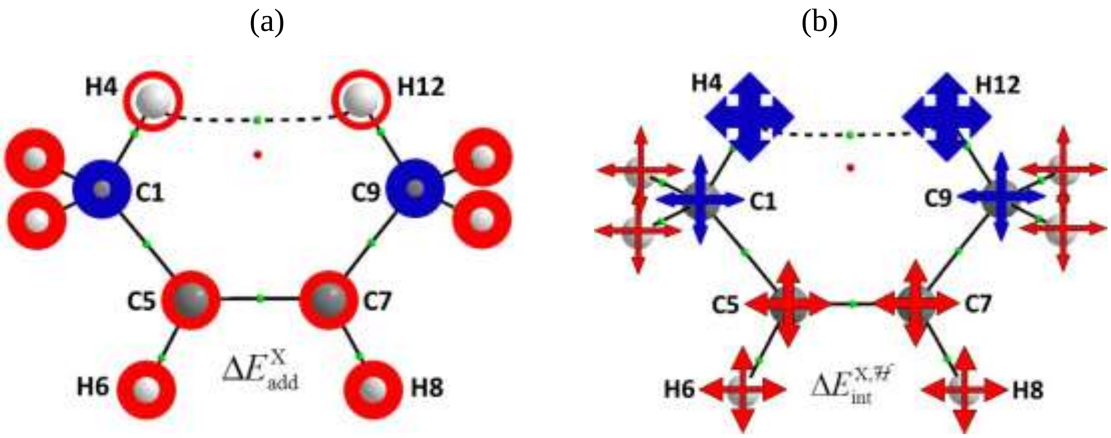


Figure S7. Pictorial representation of changes in additive atomic energies (part a) and the $\Delta E_{\text{int}}^{\text{X},\mathcal{H}}$ energy terms (part b) when *trans*-eq changed to *cis-eq*.; the thicker discs/arrows the larger contribution and blue/red colours correspond to stabilizing/destabilizing nature.

ETS-NOCV description of C1H4•••H12C9 interaction

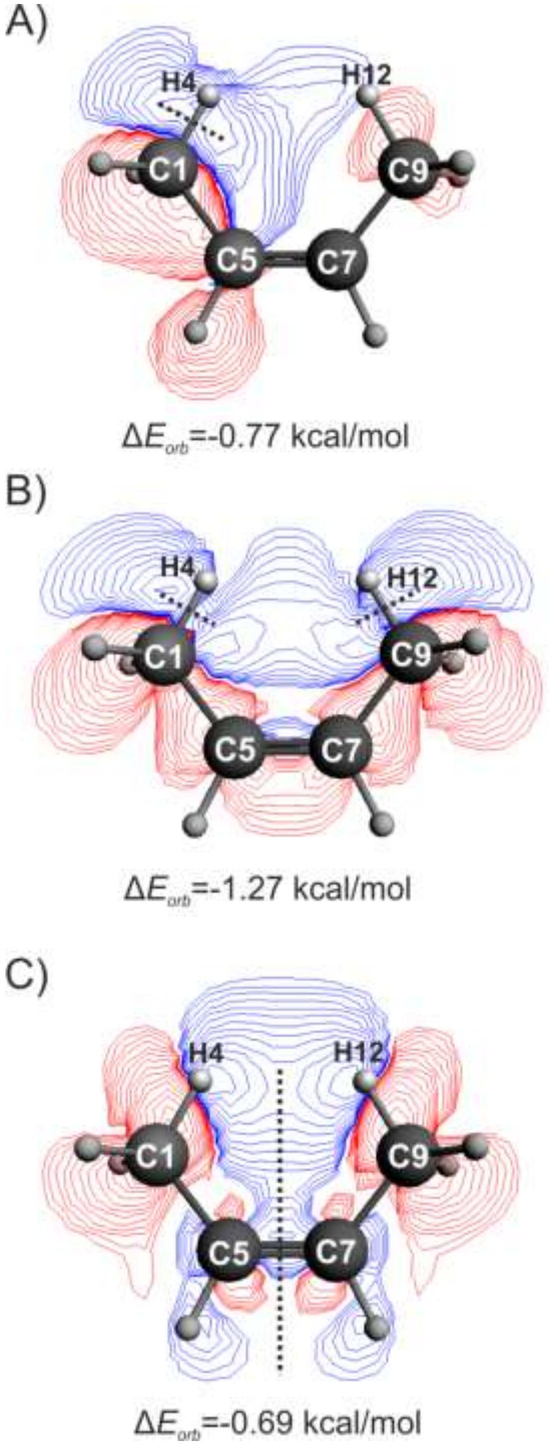


Figure S8. Deformation density channels corresponding to CH•••HC interaction in *cis*-2-butene based on various fragmentation: C_4H_6-H12|H4 (part A); H4|C_4H_6|H12 (part B) and C_2H_3-H4|H12-C_2H_3.

Part S2

Data computed for a structural change from transitional to equilibrium state of *cis*-2-butene (rotation of the terminal –C9H_3 group by 60°)

Geometric changes resulting from the methyl rotation in cis-2-butene

Rotation of the –C9H_3 functional group in *cis*-TS by 60° resulted in bond length changes throughout entire molecule, as shown in Figure S9, as well as a short contact between H4 and H12 with d = 2.0786 Å. Rather unexpectedly, the largest decrease is observed in the backbone of the molecule where Δd(C7,C9) = $d(C7,C9)_{eq}$ – $d(C7,C9)_{TS}$ of –0.0074 Å was found. As one would predict, both d(C1,H4) and d(C9,H12) decreased but not evenly, as we found Δd(C1,H4) = –0.0009 Å and Δd(C9,H12) = –0.0037 Å. Classically, these changes, together with elongation of the interatomic distance between C5 and C7, could be interpreted as the response of a molecule to accommodate clashing H-atoms.

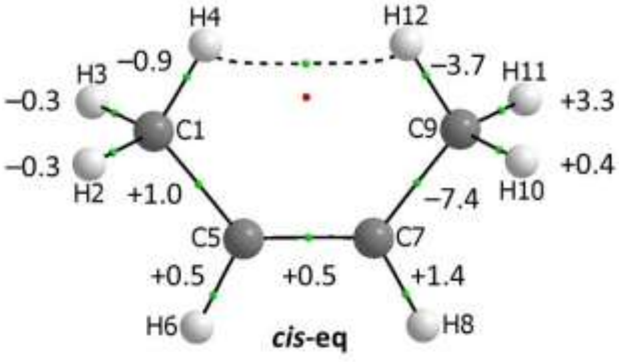


Figure S9. Changes in bond length (in mÅ) when *cis*-TS changed to *cis*-eq.

However, the overall changes observed do not seem to follow the same reasoning as it is rather difficult to explain why (i) all bonds in the –C1H_3 fragment became shorter whereas (ii) d(C9,H10) and d(C9,H11) became longer, or why (iii) d(C1,C5) increased but d(C7,C9) decreased. A full set of 66 interatomic distances in *cis*-TS and *cis*-eq as well as changes in distances when –C9H_3 in *cis*-TS was rotated by 60° is shown in Table S11.

Table S11. All possible (66) interatomic distances, d(A,B), in *cis*-TS and *cis*-eq of 2-buthene and changes $\Delta d(A,B) = d(A,B)_{eq} - d(A,B)_{TS}$. All values in Å.

***cis*-TS**		***cis*-eq**		**Δd(X,Y)**
Atoms	**Distance**	**Atoms**	**Distance**	
C1 - H2	1.09567	C1 - H2	1.09538	-0.00029
C1 - H3	1.09567	C1 - H3	1.09538	-0.00029
C1 - H4	1.09222	C1 - H4	1.09129	-0.00093
C1 - C5	1.50234	C1 - C5	1.50325	0.00092
C1 - H6	2.21438	C1 - H6	2.20404	-0.01034
C1 - C7	2.53171	C1 - C7	2.55450	0.02279
C1 - H8	3.49222	C1 - H8	3.50355	0.01134
C1 - C9	3.08431	C1 - C9	3.16983	0.08553
C1 - H10	3.09767	C1 - H10	3.92060	0.82293
C1 - H11	4.15062	C1 - H11	3.92060	-0.23002
C1 - H12	3.09767	C1 - H12	2.78922	-0.30845
H2 - H3	1.76260	H2 - H3	1.76240	-0.00020
H2 - H4	1.77094	H2 - H4	1.76928	-0.00166
H2 - C5	2.14983	H2 - C5	2.14671	-0.00312
H2 - H6	2.57392	H2 - H6	2.55522	-0.01871
H2 - C7	3.24430	H2 - C7	3.25955	0.01525
H2 - H8	4.12241	H2 - H8	4.12190	-0.00051
H2 - C9	3.83773	H2 - C9	3.92063	0.08290
H2 - H10	3.60561	H2 - H10	4.47071	0.86510
H2 - H11	4.88132	H2 - H11	4.80554	-0.07577
H2 - H12	4.01403	H2 - H12	3.52467	-0.48937
H3 - H4	1.77094	H3 - H4	1.76928	-0.00166
H3 - C5	2.14983	H3 - C5	2.14671	-0.00312
H3 - H6	2.57392	H3 - H6	2.55522	-0.01871
H3 - C7	3.24430	H3 - C7	3.25955	0.01525
H3 - H8	4.12241	H3 - H8	4.12190	-0.00051
H3 - C9	3.83773	H3 - C9	3.92063	0.08290
H3 - H10	4.01403	H3 - H10	4.80554	0.79151
H3 - H11	4.88132	H3 - H11	4.47071	-0.41061
H3 - H12	3.60561	H3 - H12	3.52467	-0.08094
H4 - C5	2.16297	H4 - C5	2.17123	0.00826
H4 - H6	3.11396	H4 - H6	3.11249	-0.00147

cis-TS		*cis*-eq		Δd(X,Y)
Atoms	**distance**	**Atoms**	**distance**	
H4 - C7	2.69224	H4 - C7	2.74073	0.04848
H4 - H8	3.76992	H4 - H8	3.81467	0.04475
H4 - C9	2.65607	H4 - C9	2.78925	0.13318
H4 - H10	2.49189	H4 - H10	3.52468	1.03278
H4 - H11	3.74436	H4 - H11	3.52468	-0.21968
H4 - H12	2.49189	H4 - H12	2.07862	-0.41327
C5 - H6	1.08917	C5 - H6	1.08965	0.00049
C5 - C7	1.34522	C5 - C7	1.34570	0.00048
C5 - H8	2.08693	C5 - H8	2.08234	-0.00460
C5 - C9	2.53528	C5 - C9	2.55452	0.01924
C5 - H10	2.88982	C5 - H10	3.25954	0.36972
C5 - H11	3.41162	C5 - H11	3.25954	-0.15208
C5 - H12	2.88982	C5 - H12	2.74071	-0.14911
H6 - C7	2.09164	H6 - C7	2.08232	-0.00932
H6 - H8	2.36375	H6 - H8	2.33983	-0.02393
H6 - C9	3.50130	H6 - C9	3.50356	0.00226
H6 - H10	3.89728	H6 - H10	4.12188	0.22460
H6 - H11	4.24706	H6 - H11	4.12188	-0.12518
H6 - H12	3.89728	H6 - H12	3.81463	-0.08265
C7 - H8	1.08832	C7 - H8	1.08969	0.00137
C7 - C9	1.51065	C7 - C9	1.50330	-0.00735
C7 - H10	2.16771	C7 - H10	2.14672	-0.02100
C7 - H11	2.15550	C7 - H11	2.14672	-0.00878
C7 - H12	2.16771	C7 - H12	2.17128	0.00356
H8 - C9	2.22941	H8 - C9	2.20415	-0.02526
H8 - H10	2.96146	H8 - H10	2.55529	-0.40617
H8 - H11	2.39667	H8 - H11	2.55529	0.15862
H8 - H12	2.96146	H8 - H12	3.11260	0.15114
C9 - H10	1.09503	C9 - H10	1.09536	0.00033
C9 - H11	1.09212	C9 - H11	1.09536	0.00324
C9 - H12	1.09503	C9 - H12	1.09132	-0.00371
H10 - H11	1.76493	H10 - H11	1.76240	-0.00253
H10 - H12	1.76560	H10 - H12	1.76931	0.00371
H11 - H12	1.76493	H11 - H12	1.76931	0.00438

Redistribution of atomic charges

One can make several striking observation from the analysis of atomic charges and changes in electron population Δ*N* shown in Figure S10:

- At the TS, significant differences are observed between charges of relevant atoms and functional groups; clearly, structural properties (bond lengths and angles) as well as charge distribution is such as to obtain lowest energy possible for this configuration. At the equilibrium, however, the half of *cis*-eq is a perfect mirror image, with the same bond lengths and angles, of the other half along the plane perpendicular to the –C5=C7– bond and exactly the same pattern is observed among atomic charge distribution. This observation can be used to explain (i) different changes in bond lengths throughout, as shown in Figure S9 and (ii) different Δ*N* values among all atoms when this isomer of 2-butene changed from asymmetric to fully symmetric configuration.
- The charges on H4 and H12 involved in the clash have decreased (an increase in the electron population is observed) and this can be rationalized in terms of minimizing repulsion between them.

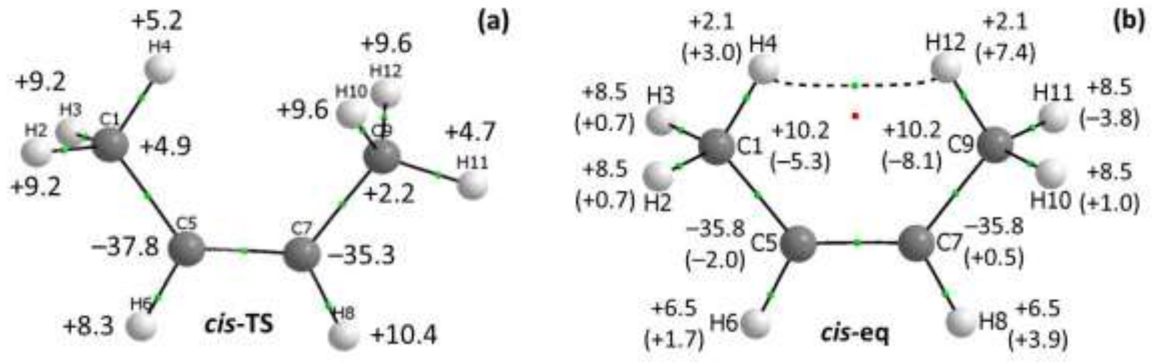


Figure S10. Molecular graphs of energy optimized structures of: *cis*-TS showing net atomic charges in m*e* (part a), and *cis*-eq showing net atomic charges and change in electron population in brackets, both in m*e* (part b).

- Formation of a new bond path between H4 and H12 requires placing additional density in the interatomic region and it is clear that this is a co-operative event as many atoms have made contributions (their population has decreased) with the largest made by three C-atoms (the largest Δ*N* = –8.1 m*e* was found for C9) and H11 with Δ*N* = –3.8 m*e*.

A full set of net atomic charges, *q*, and electron populations, *N*, for each atom as well as Δ*q* and Δ*N* values for transition from *cis*-TS to *cis*-eq are provided in Table S12.

Table S12. A full set of: part (a) - net atomic charges and Δ*q* values and part (b) - electron atomic populations and Δ*N* values for transition from *cis*-TS to *cis*-eq – all values in *e*. Δvalue = *cis*-eq – *cis*-TS.

Part (a)

Atom	***cis*-TS**	***cis*-eq**	**Δ*q***
C1	0.00487	0.01020	0.00532
H2	0.00924	0.00852	-0.00073
H3	0.00924	0.00851	-0.00073
H4	0.00516	0.00213	-0.00303
C5	-0.03783	-0.03582	0.00201
H6	0.00827	0.00653	-0.00174
C7	-0.03528	-0.03580	-0.00052
H8	0.01042	0.00656	-0.00386
C9	0.00220	0.01026	0.00805
H10	0.00956	0.00851	-0.00104
H11	0.00470	0.00852	0.00382
H12	0.00956	0.00215	-0.00741

Part (b)

Atom	***cis*-TS**	***cis*-eq**	**Δ*N***
C1	5.99513	5.9898	-0.00532
H2	0.99076	0.9915	0.00073
H3	0.99076	0.9915	0.00073
H4	0.99484	0.9979	0.00303
C5	6.03783	6.0358	-0.00201
H6	0.99173	0.9935	0.00174
C7	6.03528	6.0358	0.00052
H8	0.98958	0.9934	0.00386
C9	5.99780	5.9897	-0.00805
H10	0.99044	0.9915	0.00104
H11	0.99530	0.9915	-0.00382
H12	0.99044	0.9979	0.00741

IQA-based analysis

Change in atomic additive energies

In the IQA scheme, the molecular energy can be recovered by summing up additive energies of atoms, $E_{\text{add}}^{\text{X}}$. Hence, monitoring changes in atomic energies, $\Delta E_{\text{add}}^{\text{X}}$, should provide an insight on which atom contributed to the change in electronic energy the most in (de)stabilizing manner (Figure S11). Importantly, we found that the sum of all $\Delta E_{\text{add}}^{\text{X}}$ values differed from ΔE by –0.023 kcal/mol, hence it reproduced electronic energy change very well.

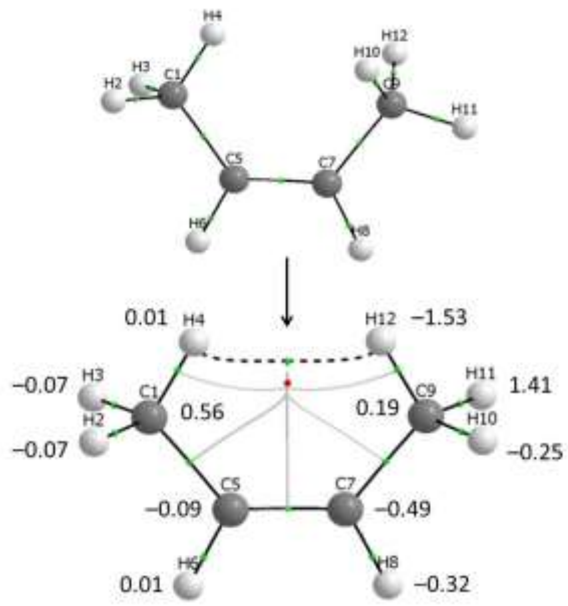


Figure S11. Changes in additive atomic energies when TS changed to eq-structure. All values in kcal/mol.

The most surprising observation, from classical point of view, is related to $\Delta E_{\text{add}}^{\text{H12}} = -1.53$ kcal/mol which clearly shows that on-coming H12 provided most to stability of *cis*-eq after becoming involved in steric clash. As a matter of fact, this single atom contributed about 54% to stability of *cis*-eq as the remaining atoms with $\Delta E_{\text{add}}^{\text{X}} < 0$ contributed –1.29 kcal/mol (data for all additive atomic energy changes is included in the Table S13). One can trace the origin of such significant contribution made by H12. We found that the term describing the overall change in interactions with remaining atoms of a molecule was most significant and of stabilizing nature for H12, $\Delta E_{\text{int}}^{\text{H12},\mathcal{H}} = -3.74$ kcal/mol. Also and importantly, the classical contribution to the combined interactions, $\Delta V_{\mathrm{cl}}^{\mathrm{X},\mathcal{H}}$ = –0.25 kcal/mol, shows that H12 experienced overall more favorable Coulomb-type interactions between all atoms of 2-buthene when in *cis*-eq – see Table S13.

Furthermore, two terminal C-atoms (to which clashing H-atoms are bonded to) became destabilized in terms of their $\Delta E_{\mathrm{add}}^{\mathrm{C}}$ values. In contrast, the atoms of the link, C5 and C7, became stabilized with the latter having second most important stabilizing contribution of –0.49 kcal/mol. Interestingly, most destabilized was found to be H11 ($\Delta E_{\mathrm{add}}^{\mathrm{H11}}$= +1.4 kcal/mol) which was in plane with H8 in *cis*-TS. In general, many changes took place throughout a molecule and we are not able to rationalize them using a classical approach.

Table S13. Changes, as *cis*-eq – *cis*-TS, in the additive atomic energy, $\Delta E_{\mathrm{add}}^{\mathrm{X}}$, self-atomic energy, $\Delta E_{\mathrm{self}}^{\mathrm{X}}$, the total diatomic interaction energy between an atom X and all remaining atoms in a molecule, $\Delta E_{\mathrm{int}}^{\mathrm{X},\mathcal{H}}$, and the classical component of the latter when TS changed to the eq-structure (all values in kcal/mol).

Atom	$\Delta E_{\mathrm{add}}^{\mathrm{X}}$	$\Delta E_{\mathrm{self}}^{\mathrm{X}}$	$\Delta E_{\mathrm{int}}^{\mathrm{X},\mathcal{H}}$	$\Delta V_{\mathrm{cl}}^{\mathrm{X},\mathcal{H}}$
C1	0.56	0.28	0.56	0.64
H2	-0.07	0.02	-0.17	-0.02
H3	-0.07	0.02	-0.17	-0.02
H4	0.01	0.31	-0.60	-0.03
C5	-0.09	-0.44	0.69	0.22
H6	0.01	0.13	-0.24	-0.17
C7	-0.49	0.21	-1.40	0.27
H8	-0.32	-0.33	0.04	-0.30
C9	0.19	-0.31	1.00	1.26
H10	-0.25	-0.73	0.96	0.02
H11	1.41	0.65	1.51	0.00
H12	-1.53	0.34	-3.74	-0.25

Change in self-atomic energies, atomic surface areas and atomic volumes

The primary energy terms in the IQA scheme, self-atomic $E_{\mathrm{self}}^{\mathrm{X}}$ and diatomic interaction $E_{\mathrm{int}}^{\mathrm{X,Y}}$, are also additive and we will start our analysis by examining $\Delta E_{\mathrm{self}}^{\mathrm{X}}$ (see Table S13) caused by the rotation of the –C9H$_3$ functional group by 60°. The largest positive/negative $\Delta E_{\mathrm{self}}^{\mathrm{X}}$ values were obtained for H11/H10 with 0.65 and –0.73 kcal/mol, respectively. Regarding H4 and H12, we found 0.31 and 0.34 kcal/mol, respectively. An increase in $E_{\mathrm{self}}^{\mathrm{X}}$ can, but does not have to, indicate involvement in bonding and the observed $\Delta E_{\mathrm{self}}^{\mathrm{X}}$ values for clashing H-atoms could be rationalized as being involved in bonding interaction when in *cis*-eq. However, it is important to recall that $E_{\mathrm{self}}^{\mathrm{X}}$ accounts for intra-atomic (within QTAIM-defined atomic basin) nucleus-electrons and electron-electron interactions. It is then expected that the change in atomic volumes and atomic surfaces (Table S14), in combination with change in the atomic electron population, must result in the change in self-atomic energies making a direct interpretation for each atom difficult. Because the individual changes in $E_{\mathrm{self}}^{\mathrm{X}}$ are small and spreaded out throughout a molecule, we decided to look at the overall change and found that $\Delta\sum_{\mathrm{X}} E_{\mathrm{self}}^{\mathrm{X}}$ = –0.13 kcal/mol which is much smaller than ΔE. From that follows that major contribution to ΔE must have come from changes in diatomic interaction energies.

Table S14. Changes, as *cis*-eq – *cis*-TS, in atomic surface area and atomic volume (in Bohr) when *cis*-TS changed to *cis*-eq.

Atom A	***cis*-TS**		***cis*-eq**		**ΔArea(A)**	**ΔVol(A)**
	Area(A)	**Vol(A)**	**Area(A)**	**Vol(A)**		
C1	185.025	99.815	158.928	99.813	-26.10	0.00
H2	75.377	97.558	75.106	97.565	-0.27	0.01
H3	75.447	97.555	75.452	97.570	0.00	0.01
H4	74.296	98.281	74.653	98.249	0.36	-0.03
C5	179.838	99.685	153.900	99.680	-25.94	0.00
H6	75.875	97.613	75.658	97.631	-0.22	0.02
C7	181.634	99.667	153.975	99.683	-27.66	0.02
H8	75.556	97.636	75.751	97.630	0.19	-0.01
C9	180.160	99.831	159.042	99.812	-21.12	-0.02
H10	74.541	97.831	75.595	97.566	1.05	-0.26
H11	75.052	97.629	75.248	97.566	0.20	-0.06
H12	74.831	97.834	74.639	98.243	-0.19	0.41

Change in diatomic interaction energies

When going from *cis*-TS (our *ref* state) to *cis*-eq (our *fin* state), we found $\Delta\sum_{Y\neq X} 0.5E_{\text{int}}^{\text{XY}}$ = –0.71 kcal/mol. Adding this to the overall change in self-atomic energies gave ΔE_{IQA} = –0.57 kcal/mol which differs from ΔE just by 0.05 kcal/mol.

There are 66 unique diatomic interactions in the molecule and changes in these interaction energies on *cis*-TS→*cis*-eq are shown in Table S15. There are 36 stabilizing in nature changes which account for –7.61 kcal/mol and 30 destabilizing contribution giving +6.94 kcal/mol, the sum being –0.71 kcal/mol which compares well with ΔE = –0.62 kcal/mol. The question arises: how to analyze these 66 unique diatomic interaction changes? An approach taken here is based on a simple assumption that most of them cancel out their contributions. We decided to test that approach with an aim of identifying the main contributors. The smaller negative and positive contributions were summed up such almost equal, in absolute terms, values were obtained, namely –3.41 and +3.42 kcal/mol (they are highlighted in Table S15). This left us with two largest stabilizing ($\Delta E_{\text{int}}^{\text{H4,H12}}$ = –2.56 and $\Delta E_{\text{int}}^{\text{C7,C9}}$ = –1.68 kcal/mol; in total –4.24 kcal/mol) and three most significant destabilizing ($\Delta E_{\text{int}}^{\text{H11,C9}}$ = +1.62, $\Delta E_{\text{int}}^{\text{H4,C9}}$ = +0.97 and $\Delta E_{\text{int}}^{\text{H10,H4}}$ = +0.93 kcal/mol; in total +3.52 kcal/mol) contributions, which, when summed up, gave –0.72 kcal/mol (it compares well with ΔE of –0.62 kcal/mol). Analysis of the most important five contributions provides already some important hints:

1. Following classical interpretation, one would expect that when going from no clash, in *cis*-TS, to clashing placement of H4 and H12 in *cis*-eq, the interaction between them should become less favorable. In other words, assuming that H4•••H12 results in the repulsive and overall destabilizing interaction in *cis*-eq, than the expected change in their interaction should be of destabilizing nature, $\Delta E_{\text{int}}^{\text{H4,H12}} > 0$. Just opposite is observed and, in addition and importantly, this is the most favorable change among them all.
2. The change in the interaction energy between H4 and H12, $\Delta E_{\text{int}}^{\text{H4,H12}}$ = –2.56 kcal/mol has a very small contribution coming from a classical term, $\Delta V_{\text{cl}}^{\text{H4,H12}}$ = +0.06 kcal/mol (a result of +0.06 and +0.12 kcal/mol in *cis*-TS and *cis*-eq, respectively) and very significant one coming from the exchange-correlation term, $\Delta V_{\text{XC}}^{\text{H4,H12}}$ = –2.63 kcal/mol (–1.03 and –3.66 kcal/mol in *cis*-TS and *cis*-eq, respectively).

Table S15. Full set of changes in diatomic interaction energies, from most stabilizing $\Delta E_{\text{int}}^{\text{XY}}$ to most destabilizing change in kcal/mol, for transition from *cis*-TS to *cis*-eq.

No	**Atom X**	**Atom Y**	$\Delta E_{\text{int}}^{\text{XY}}$	**No**	**Atom A**	**Atom B**	$\Delta E_{\text{int}}^{\text{XY}}$
1	**H12**	**H4**	-2.565	37	H11	H2	0.001
2	C9	C7	-1.678	38	H10	H8	0.011
3	H12	C1	-0.737	39	H8	C1	0.011
4	H12	C9	-0.575	40	H12	H11	0.017
5	H11	C5	-0.345	41	H11	H3	0.021
6	H12	H8	-0.298	42	H10	H2	0.026
7	H10	C7	-0.182	43	C9	H6	0.028
8	H10	C9	-0.178	44	H10	H3	0.038
9	C7	H6	-0.145	45	H8	C5	0.042
10	H11	C7	-0.126	46	H4	C1	0.045
11	C9	H8	-0.080	47	H11	C1	0.054
12	H12	H3	-0.073	48	C9	H3	0.056
13	H8	H6	-0.068	49	C9	H2	0.056
14	H2	C1	-0.063	50	H10	C5	0.065
15	H3	C1	-0.053	51	H6	C5	0.067
16	H12	H10	-0.044	52	H11	H4	0.067
17	H12	H2	-0.041	53	C7	H4	0.072
18	C5	H2	-0.036	54	H8	C7	0.127
19	C5	H3	-0.035	55	C7	C1	0.137
20	H4	H2	-0.033	56	C9	C5	0.201
21	H6	C1	-0.033	57	C5	C1	0.223
22	H4	H3	-0.033	58	H12	C7	0.282
23	C5	H4	-0.027	59	H11	H8	0.312
24	H11	H10	-0.026	60	C7	C5	0.315
25	H6	H4	-0.024	61	H12	C5	0.316
26	H6	H3	-0.020	62	H10	C1	0.341
27	H6	H2	-0.020	63	C9	C1	0.492
28	H3	H2	-0.019	64	H10	H4	0.934
29	C7	H3	-0.017	65	C9	H4	0.972
30	C7	H2	-0.017	66	**H11**	**C9**	1.615
31	H12	H6	-0.016				
32	H8	H4	-0.015				
33	H10	H6	-0.009				
34	H11	H6	-0.007				
35	H8	H3	-0.007				
36	H8	H2	-0.007				
		Sum all:	-7.65			Sum all:	+6.94
		Sum blue:	-3.41			Sum blue:	+3.42

Hence, strictly speaking H4 and H12 are indeed involved in the repulsive (but very weak) interaction in both states, TS and eq, which must be seen as insignificant when its contribution to the energy of rotational barrier is considered. Note that the largest destabilizing contribution comes from $\Delta E_{\text{int}}^{\text{C9,H11}}$= +1.61 kcal/mol and this involves H11 whose additive energy increased the most among all atoms.

3. Realizing that (i) the total change in self-atomic energies is negligible, (ii) $\Delta V_{\text{cl}}^{\text{H4,H12}}$= +0.06 kcal/mol is an order of magnitude smaller (in absolute terms) than ΔE = –0.62 kcal/mol, (iii) $\Delta E_{\text{int}}^{\text{H4,H12}}$ is of stabilizing nature and four times most significant than ΔE, and (iv) the sum $\Delta E_{\text{int}}^{\text{H4,H12}} + \Delta E_{\text{int}}^{\text{C7,C9}}$= –4.24 kcal/mol almost compensated over the three most unfavorable diatomic interactions (+3.52 kcal/mol), leads us to the conclusion that the origin of such small rotation barrier is linked with energetically most favorable change in the H4•••H12 interaction. This is because forces of the same magnitude, attractive and repulsive interactions, make it almost energy-free (about 0.72 kcal/mol) to rotate the terminal group.
4. We also noted that the interaction between covalently bonded C7 and C9 has changed favorably, $\Delta E_{\text{int}}^{\text{C7,C9}}$= –1.68 kcal/mol, when TS changed to the equilibrium structure. This again is not what one would expect; if H4 and H12 were indeed involved in a steric hindrance in *cis*-eq than one would also expect some destabilizing effect on the C7–C9 bond caused by accommodating clashing atoms due to pushing C9 (and C1) further apart, but this is not what we found; the d(C7,C9) value has decreased the most among all bonds, by 7.4 mÅ. We further note that summing up (i) $\Delta E_{\text{self}}^{\text{C7}}$ and $\Delta E_{\text{self}}^{\text{C9}}$ gave –0.10 kcal/mol and (ii) $\Delta E_{\text{add}}^{\text{C7}}$ and $\Delta E_{\text{add}}^{\text{C9}}$ gave –0.30 kcal/mol, additional stabilizing contributions one would not expect when classical reasoning is followed.

An additional insight from diatomic interactions

Initially, we took highly simplified approach by looking at interactions/contacts between closely placed H-atoms due to rotation of the terminal -C9H$_3$ group. In the *cis*-TS, both H10 and H12 are separated from H4 by 2.492 Å (Figure S12) which is more than the sum of the H-atoms vdW radii (2.4 Å). Hence, these two pairs of atoms are not regarded as involved in a classical steric clash. However, H10 and H12 are involved in the same in value and nature interaction with H4 of –1.0 kcal/mol with negligible classical component $\Delta V_{\text{cl}}^{\text{H,H}}$ = +0.05 kcal/mol. Regardless which way the –

$C9H_3$ fragment rotates, these two interactions must be disturbed. The sum of three BP-free H--H contacts in *cis*-TS shown in Figure S12, $E_{\text{int}}^{\text{H4,H10}}$, $E_{\text{int}}^{\text{H4,H12}}$ and $E_{\text{int}}^{\text{H8,H11}}$, results in –2.2 kcal/mol. Recall that in the IQA scheme the vdW criterion is not applicable and interestingly, the $E_{\text{int}}^{\text{H4,H10}}$ value of –1.0 kcal/mol with d(H4,H10) > (the sum of vdW radii) is several times more attractive than $E_{\text{int}}^{\text{H8,H11}}$ of –0.2 kcal/mol involving atoms with d(H8,H11) close to the sum of vdW radii. Focusing on three H--H contacts (one with BP) in *cis*-eq (Figure S12), we obtained –3.5, +0.1 and +0.1 kcal/mol for $E_{\text{int}}^{\text{H4,H12}}$, $E_{\text{int}}^{\text{H8,H10}}$ and $E_{\text{int}}^{\text{H8,H11}}$, respectively, which sums up to –3.4 kcal/mol. Considering the rotation of the -$C9H_3$ functional group as a localized event makes sense as only three H•••H interactions in *cis*-TS must be replaced by three new H•••H interactions involving exactly the same five H-atoms in *cis*-eq. The overall change in these interaction energies amounts to –1.2 kcal/mol. This can be interpreted as a local driving force, due to favorable H4•••H12 interaction, facilitating the conformational change from *cis*-TS to *cis*-eq. Moreover, this simplified approach approximates the rotational energy barrier associated with the -$C9H_3$ terminal group quite well.

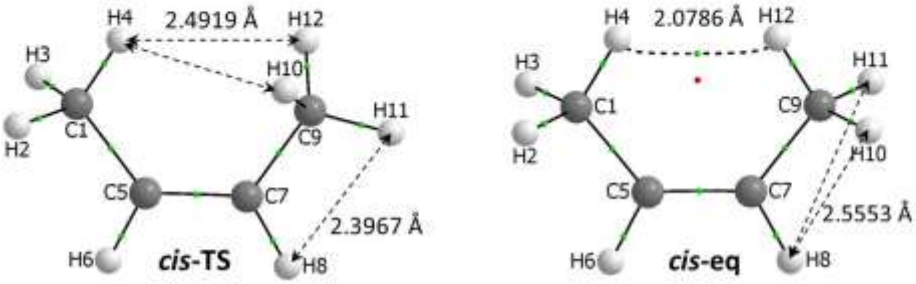


Figure S12. Diatomic distances between selected H-atoms involved in different sets of three H•••H interactions in *cis*-TS and *cis*-eq.

As showed in Tables S11-S15, however, rotation of the -$C9H_3$ functional group results in changes throughout a molecule. Hence, it is clear that some other interactions must have partly compensated the local driving force and we decided to explore all diatomic interactions also because their energies are additive. Let us first recall that the self-atomic $E_{\text{self}}^{\text{X}}$ and diatomic interaction $E_{\text{int}}^{\text{X,Y}}$ are the primary energy terms in the IQA scheme; we found that the sum of all changes in $E_{\text{self}}^{\text{X}}$ gave –0.1 kcal/mol which is much smaller than ΔE, the change in the electronic energy for *cis*-TS→*cis*-eq. From that follows that major contribution to ΔE must have come from changes in diatomic interaction energies and indeed we found $\Delta\sum_{\mathrm{Y}\neq\mathrm{X}} E_{\mathrm{int}}^{\mathrm{X,Y}}$ = –0.7 kcal/mol. Adding this value to the overall change in self-atomic energies gave –0.6 kcal/mol validating our FAMSEC/IQA-based analyses. Using a simple approach (see commented Table S15) left us with two largest stabilizing ($\Delta E_{\mathrm{int}}^{\mathrm{H4,H12}}$ = –2.6 and $\Delta E_{\mathrm{int}}^{\mathrm{C7,C9}}$ = –1.7 kcal/mol) and three most significant destabilizing ($\Delta E_{\mathrm{int}}^{\mathrm{H11,C9}}$ = +1.6, $\Delta E_{\mathrm{int}}^{\mathrm{H4,C9}}$ = +1.0 and $\Delta E_{\mathrm{int}}^{\mathrm{H4,H10}}$ = +0.9 kcal/mol) contributions, which, when summed up, gave –0.7 kcal/mol (it compares well with Δ*E* of –0.62 kcal/mol). Realizing that (i) the total change in self-atomic energies is negligible, (ii) $\Delta V_{\mathrm{cl}}^{\mathrm{H4,H12}}$ = +0.06 kcal/mol is an order of magnitude smaller (in absolute terms) than Δ*E* = –0.62 kcal/mol, (iii) $\Delta E_{\mathrm{int}}^{\mathrm{H4,H12}}$ is of stabilizing nature and four times most significant than Δ*E*, and (iv) the sum $\Delta E_{\mathrm{int}}^{\mathrm{H4,H12}} + \Delta E_{\mathrm{int}}^{\mathrm{C7,C9}}$ = –4.2 kcal/mol barely compensated over the three most unfavorable diatomic interactions (+3.5 kcal/mol), leads us to the conclusion that the origin of such small rotation barrier is linked mainly with energetically most favorable change in the H4•••H12 interaction. This is because forces of the same magnitude, attractive and repulsive interactions, make rotation of the terminal group almost energy-free.

FAMSEC data obtained for 2-atom molecular fragments $\mathfrak{G}$

Table S16. Ten most stabilized and destabilized fragments as measured by the $E_{\text{attr-loc}}^{\mathfrak{G}}$ energy term (in kcal/mol at MP2) when *cis*-TS changed to *cis*-eq.

Stabilized fragments			**Destabilized fragments**		
Atom	**Atom**	$E_{\text{attr-loc}}^{\mathfrak{G}}$	**Atom**	**Atom**	$E_{\text{attr-loc}}^{\mathfrak{G}}$
H12	H4	-1.92	**H11**	H2	0.67
C9	C7	-1.78	**H11**	H3	0.69
H10	C9	-1.22	**H11**	C7	0.73
H10	C5	-1.10	**H11**	H6	0.77
H10	H8	-1.05	H12	C7	0.83
H8	C5	-0.73	C9	H4	0.98
C9	H8	-0.72	**H11**	C1	0.98
H10	C7	-0.71	H12	**H11**	1.00
H10	H2	-0.69	**H11**	H4	1.03
H10	H3	-0.68	**H11**	C9	1.96

Table S17. Twenty most stabilizing and destabilizing contributions to molecular energy made by the $E_{\text{attr-mol}}^{\mathscr{G}}$ energy term (in kcal/mol at MP2) when *cis*-TS changed to *cis*-eq.

Stabilizing contribution			**Destabilizing contribution**		
Atom	**Atom**	$E_{\text{attr-mol}}^{\mathscr{G}}$	**Atom**	**Atom**	$E_{\text{attr-mol}}^{\mathscr{G}}$
H12	C7	-4.88	C9	H6	0.55
H12	H2	-3.52	H10	C1	0.73
H12	H6	-3.50	C9	C5	0.74
H12	H3	-3.49	H3	C1	0.74
H12	C5	-3.47	H2	C1	0.75
H12	H8	-3.40	H6	C1	0.76
H12	H10	-3.12	C5	C1	0.87
H12	C9	-2.14	C9	C1	1.04
H12	C1	-1.83	H10	C9	1.10
H8	C7	-1.61	H11	C7	1.10
C7	H4	-1.55	C9	C7	1.18
C7	H2	-1.33	**H11**	C9	1.24
C7	H3	-1.33	**H11**	H8	1.55
C7	C5	-1.26	**H11**	H4	1.81
H12	H11	-1.26	**H11**	H3	1.99
C7	H6	-1.16	**H11**	H2	2.01
H12	H4	-1.13	**H11**	H6	2.06
H10	H4	-0.99	**H11**	H10	2.42
H10	C7	-0.77	**H11**	C5	2.76
C9	H4	-0.57	**H11**	C1	2.95

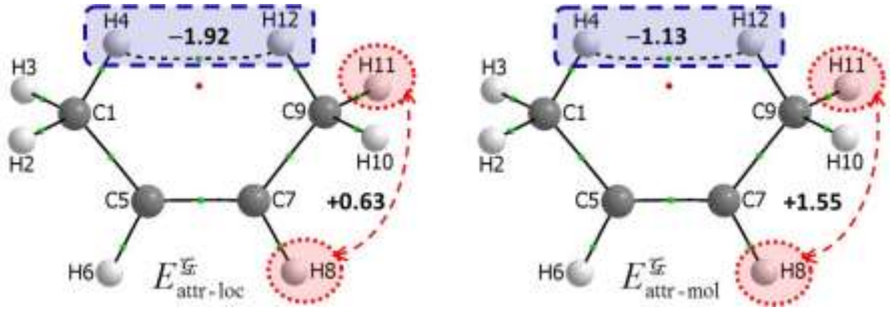


Figure 13. Schematic representation of two-atom fragment attributed *loc*-FAMSEC and *mol*-FAMSEC contributions when *cis*-TS changed to *cis*-eq; values are in kcal/mol.

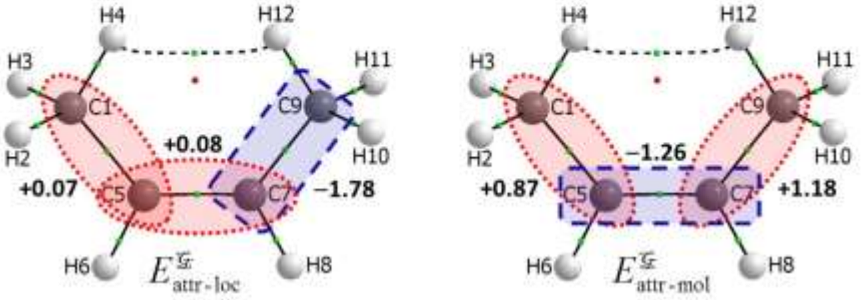


Figure 14. Schematic representation of two-atom fragment attributed *loc*-FAMSEC and *mol*-FAMSEC energy contributions made by carbon atoms when *cis*-TS changed to *cis*-eq; values are in kcal/mol.

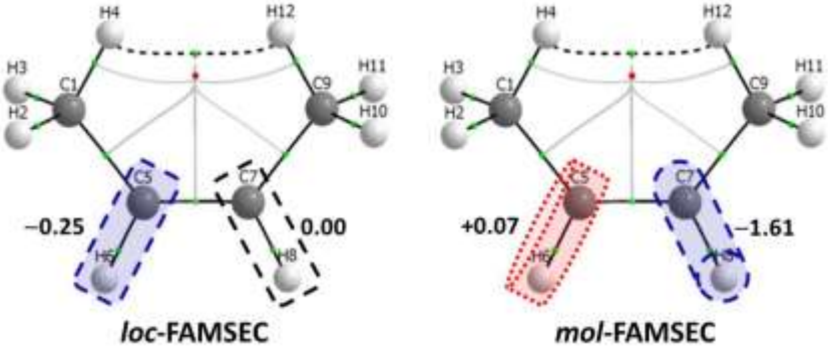


Figure S15. Schematic representation of two-atom fragment attributed *loc*-FAMSEC and *mol*-FAMSEC energy contribution made by the indicated fragments when *cis*-TS changed to *cis*-eq; values are in kcal/mol.

FAMSEC data obtained for 4-atom molecular fragments $\mathfrak{G}$

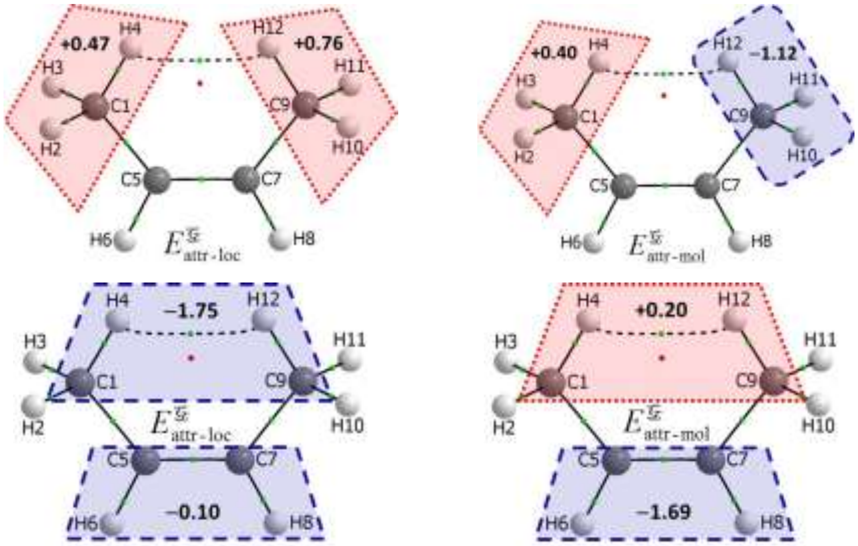


Figure 16. Schematic representation of indicated four-atom fragment attributed *loc*-FAMSEC and mol-FAMSEC energy contributions made when *cis*-TS changed to *cis*-eq; values are in kcal/mol.

Part S3

Data computed for a structural change from transitional to equilibrium state of *trans*-2-butene (rotation of the terminal –CH_3 group by 60°)

Geometric changes

Rotation of the –$C9H_3$ functional group in *trans*-TS by 60° resulted in bond length changes throughout entire molecule, as shown in Figure S17, but there is no H--H contact with interatomic distance smaller than the sum of the vdW radii in both structures. Interestingly, there are some striking similarities in trends of the Δd(A,B) values between two transitions, from *cis*-TS to *cis*-eq and *trans*-TS to *trans*-eq. Rather unexpectedly, the largest decrease in a bond length is observed again for d(C7,C9) with $\Delta d(C7,C9) = d(C7,C9)_{eq} - d(C7,C9)_{TS} = –0.0091$ Å (–0.0075Å was found for *cis* conformer). Also changes in d(C9,H) for all H-atoms of the –$C9H_3$ terminal group are of the same direction as found for *cis* conformer: considering (i) H12 which is facing H6 in *trans*-eq, its d(C9,H12) decreased by –0.0007 Å (a decrease of –0.0037 Å is observed in cis-eq) and (ii) two H-atoms not involved in a contact (H10 and H11), their d(C9,H) increased as also observed in *cis*-eq. It appears that the trends in Δd(C9,H) of the terminal –$C9H_3$ group for both conformers, when they changed from TS to equilibrium state, are similar and do not depend on whether H-atoms are or are not involved in a steric clash.

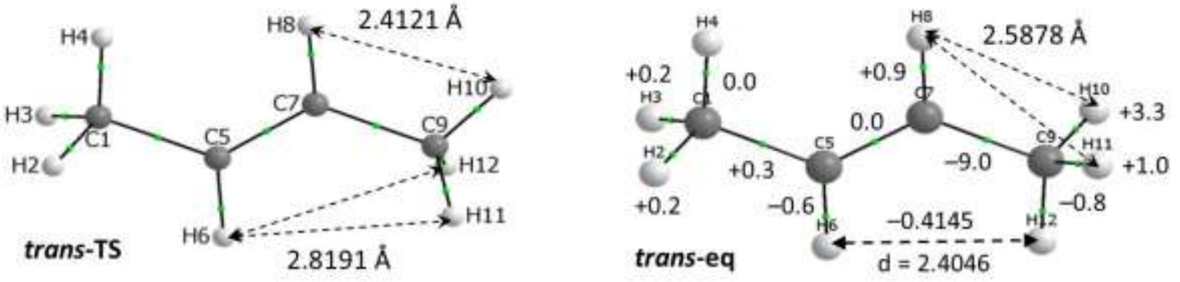


Figure S17. Changes in bond length (in mÅ) on transition from *trans*-TS to *trans*-eq.

One can make another striking observation. Even though d(H6,H12) > 2.4 Å in *trans*-eq (a steric clash criterion based on the sum of the van der Waals radii of H-atoms is not met), a decrease in d(C5,H6) by –0.0005 Å and d(C9,H12) by –0.0007 Å is observed when H6 and H12 face each other. Note that exactly the same trend is observed for H-atoms (H4 and H12) which are indeed involved in the steric clash in *cis*-eq. A full set of 66 interatomic distances in *trans*-TS and *trans*-eq as well as changes in distances when –$C9H_3$ in *trans*-TS was rotated by 60° is shown in Table S18.

Table S18. All possible (66) interatomic distances, d(A,B), in *trans*-TS and *trans*-eq of 2-buthene and changes $\Delta d(A,B) = d(A,B)_{eq} - d(A,B)_{TS}$. All values in Å.

***trans*-TS**		***trans*-eq**		**Δd(A,B)**
Atoms	**Distance**	**Atoms**	**Distance**	
C1 - H2	1.09541	C1 - H2	1.09555	0.00014
C1 - H3	1.09541	C1 - H3	1.09555	0.00014
C1 - H4	1.09379	C1 - H4	1.09381	0.00002
C1 - C5	1.50199	C1 - C5	1.50229	0.00030
C1 - H6	2.22010	C1 - H6	2.22092	0.00081
C1 - C7	2.51823	C1 - C7	2.51931	0.00109
C1 - H8	2.72196	C1 - H8	2.73012	0.00816
C1 - C9	3.93017	C1 - C9	3.92483	-0.00534
C1 - H10	4.67876	C1 - H10	4.55115	-0.12761
C1 - H11	4.30119	C1 - H11	4.55115	0.24995
C1 - H12	4.30119	C1 - H12	4.15689	-0.14430
H2 - H3	1.76340	H2 - H3	1.76360	0.00020
H2 - H4	1.77392	H2 - H4	1.77401	0.00009
H2 - C5	2.15392	H2 - C5	2.15389	-0.00003
H2 - H6	2.58716	H2 - H6	2.58779	0.00063
H2 - C7	3.23551	H2 - C7	3.23627	0.00076
H2 - H8	3.48465	H2 - H8	3.49260	0.00795
H2 - C9	4.55596	H2 - C9	4.55115	-0.00481
H2 - H10	5.34485	H2 - H10	5.33123	-0.01361
H2 - H11	4.69418	H2 - H11	5.03108	0.33690
H2 - H12	5.01518	H2 - H12	4.67310	-0.34207
H3 - H4	1.77392	H3 - H4	1.77401	0.00009
H3 - C5	2.15392	H3 - C5	2.15389	-0.00003
H3 - H6	2.58716	H3 - H6	2.58779	0.00063
H3 - C7	3.23551	H3 - C7	3.23627	0.00076
H3 - H8	3.48465	H3 - H8	3.49260	0.00795
H3 - C9	4.55596	H3 - C9	4.55115	-0.00481
H3 - H10	5.34485	H3 - H10	5.03108	-0.31377
H3 - H11	5.01518	H3 - H11	5.33123	0.31606
H3 - H12	4.69418	H3 - H12	4.67310	-0.02108
H4 - C5	2.14967	H4 - C5	2.15086	0.00118
H4 - H6	3.10955	H4 - H6	3.11060	0.00106

***trans*-TS**		***trans*-eq**		**Δd(A,B)**
Atoms	**distance**	**Atoms**	**distance**	
H4 - C7	2.65212	H4 - C7	2.65509	0.00297
H4 - H8	2.39406	H4 - H8	2.40459	0.01053
H4 - C9	4.16281	H4 - C9	4.15689	-0.00592
H4 - H10	4.69104	H4 - H10	4.67310	-0.01794
H4 - H11	4.66210	H4 - H11	4.67310	0.01101
H4 - H12	4.66210	H4 - H12	4.64198	-0.02011
C5 - H6	1.09179	C5 - H6	1.09124	-0.00056
C5 - C7	1.34291	C5 - C7	1.34288	-0.00002
C5 - H8	2.09186	C5 - H8	2.09637	0.00451
C5 - C9	2.52352	C5 - C9	2.51931	-0.00420
C5 - H10	3.40775	C5 - H10	3.23627	-0.17148
C5 - H11	2.86979	C5 - H11	3.23627	0.36648
C5 - H12	2.86979	C5 - H12	2.65509	-0.21470
H6 - C7	2.09855	H6 - C7	2.09637	-0.00218
H6 - H8	3.05894	H6 - H8	3.06068	0.00175
H6 - C9	2.73216	H6 - C9	2.73012	-0.00204
H6 - H10	3.78104	H6 - H10	3.49260	-0.28844
H6 - H11	2.81909	H6 - H11	3.49260	0.67351
H6 - H12	2.81909	H6 - H12	2.40459	-0.41450
C7 - H8	1.09033	C7 - H8	1.09124	0.00091
C7 - C9	1.51135	C7 - C9	1.50229	-0.00906
C7 - H10	2.16108	C7 - H10	2.15389	-0.00719
C7 - H11	2.16410	C7 - H11	2.15389	-0.01021
C7 - H12	2.16410	C7 - H12	2.15086	-0.01325
H8 - C9	2.23628	H8 - C9	2.22092	-0.01537
H8 - H10	2.41210	H8 - H10	2.58779	0.17569
H8 - H11	2.96406	H8 - H11	2.58779	-0.37627
H8 - H12	2.96406	H8 - H12	3.11060	0.14655
C9 - H10	1.09230	C9 - H10	1.09555	0.00325
C9 - H11	1.09456	C9 - H11	1.09555	0.00099
C9 - H12	1.09456	C9 - H12	1.09381	-0.00074
H10 - H11	1.76483	H10 - H11	1.76360	-0.00123
H10 - H12	1.76483	H10 - H12	1.77401	0.00918
H11 - H12	1.76740	H11 - H12	1.77401	0.00661

Redistribution of atomic charges

As found for interatomic distances, charges on all atoms have changed on the transition from *trans*-TS to *trans*-eq – Figure S18. To make meaningful observations, we will focus mainly on the –C9H_3 terminal group and its closest molecular environment (a full set of net atomic charges, *q*, atomic electron populations, *N*, for each atom as well as Δ*q* and Δ*N* values for transition from *trans*-TS to *trans*-eq is provided in Table S19):

- The largest change in the electron population is observed for C9 with Δ*N*(C9) = –6.9 m*e* (exactly the same trend was found in *cis*-eq with Δ*N*(C9) = –8.1 m*e*).
- Considering H-atoms of this terminal group, the largest increase in the electron population is again observed for H12 even though it is not involved in a classical steric clash; we found Δ*N*(H12) of +6.3 and +7.4 m*e* for *trans*-eq and *cis*-eq, respectively.
- H10 is aligned with H8 in *trans*-TS and its population has decreased in equilibrium structure, Δ*N*(H10) = –3.6 me. Exactly the same trend is observed for H11 in *cis* conformer; H11 is aligned with H8 in *cis*-TS and Δ*N*(H11) = –3.8 m*e* was found.
- Atoms H11 in *trans* and H10 in *cis* conformers are not aligned with another H-atom in both, TS and equilibrium states; they have experienced an increase in *N* when in equilibrium structures with Δ*N* of +4.4 (in *trans*) and +1.0 me in *cis*.

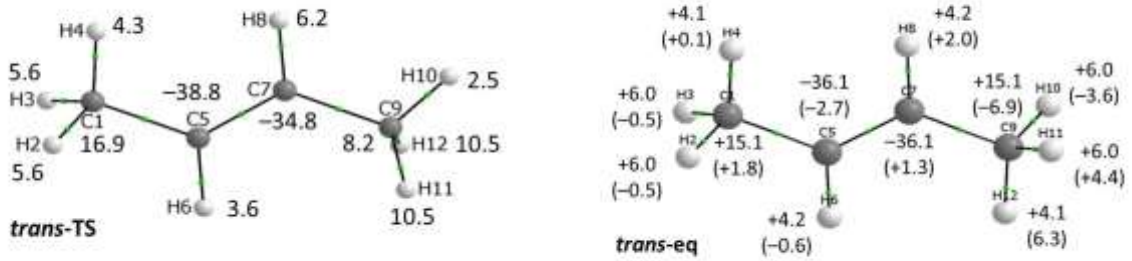


Figure S18. Atomic charges and change in the electron population (values in brackets) on transition from *trans*-TS to *trans*-eq; all values in m*e*.

It is also obvious that net atomic charges of all atoms had to change when a molecule was transformed from the TS to equilibrium state and this applies equally to the *cis* and *trans* conformers. This is because both equilibrium structures can be seen as symmetrical. It appears that the rotation of the terminal –CH_3 group (from TS to eq-state) has determined the variation in the C9–H bond lengths as well as charge redistribution throughout this functional group and the trends are exactly the same for both conformers. These changes (in the –CH_3 group) also determined variations in bond lengths and charge redistribution in remaining parts of the two conformers in such a way as to achieve required structural and net atomic charges symmetry. It is also evident that when two H-atoms become aligned, this results in the increase of their atomic population regardless (i) whether they are or are not linked by an AIL and (ii) of conformational state.

Table S19. A full set of net atomic charges and Δq values (part a) and atomic electron populations and ΔN values (part b) for transition from *trans*-TS to *trans*-eq. All values in *e* and Δvalue = *trans*-eq – *trans*-TS.

Part (a)

Atom	***trans*-TS**	***trans*-eq**	**Δq**
C1	0.01689	0.01513	-0.00176
H2	0.00558	0.00604	0.00046
H3	0.00558	0.00604	0.00046
H4	0.00426	0.00412	-0.00014
C5	-0.03883	-0.03608	0.00275
H6	0.00364	0.00421	0.00058
C7	-0.03479	-0.03608	-0.00129
H8	0.00618	0.00421	-0.00197
C9	0.00820	0.01512	0.00692
H10	0.00249	0.00605	0.00356
H11	0.01045	0.00604	-0.00441
H12	0.01045	0.00412	-0.00633

Part (b)

Atom	***trans*-TS**	***trans*-eq**	**ΔN**
C1	5.98311	5.98487	0.00176
H2	0.99442	0.99396	-0.00046
H3	0.99442	0.99396	-0.00046
H4	0.99574	0.99588	0.00014
C5	6.03883	6.03608	-0.00275
H6	0.99636	0.99579	-0.00058
C7	6.03479	6.03608	0.00129
H8	0.99382	0.99579	0.00197
C9	5.99180	5.98488	-0.00692
H10	0.99751	0.99395	-0.00356
H11	0.98955	0.99396	0.00441
H12	0.98955	0.99588	0.00633

IQA-based analysis

Variation in additive atomic energies

Unexpectedly, the largest change among all atoms (Table S20) is observed for H12 which added to the energy of *trans*-eq –1.69 kcal/mol and this single atom contributed 43.6% of all stabilizing in nature contributions. Even though there is no AIL between H6 and H12 in *trans*-eq, these values compare very well with contributions made by the same atom in *cis*-eq; $\Delta E_{\mathrm{add}}^{\mathrm{H12}}$ = –1.53 kcal/mol which constitutes ~54% of all stabilizing contributions. There is also similarity in contributions made by remaining H-atoms of the –CH_3 terminal group.

Considering H10, the $E_{\mathrm{add}}^{\mathrm{H10}}$ value has increased by 1.25 kcal/mol because H10 is no longer aligned with H8 in *trans*-eq. In case of H11, its $E_{\mathrm{add}}^{\mathrm{H11}}$ decreased by –0.59 kcal/mol when in *trans*-eq; similar trends and quite comparable values were obtained for H11 and H10 in *cis*-eq because they experienced analogous structural change in terms of alignment with another H-atom. Furthermore, additive energy of (i) C9 has increased by 0.29 kcal/mol whereas (ii) C7 and H8 decreased by –0.80 and –0.34 kcal/mol, respectively and all of them resemble the trends in *cis*-eq. Energies of remaining H-atoms (H2, H3, H4 and H6) changed marginally (they overall contribution is about +0.06 kcal/mol) but C1, C5 and C7 added to stability of *trans*-eq –1.23 kcal/mol (~32% of stabilizing contributions) whereas in *cis*-eq these atoms contribution was only –0.03 kcal/mol (0.90% of stabilizing contributions). The overall energy contribution of –$C9H_3$ (in terms of a change in additive atomic energies) was found to be –0.74 and –0.18 kcal/mol in *trans*-eq and *cis*-eq, respectively. This clearly shows that the lower energy of *trans*-eq relative to *cis*-eq is mainly due to more favorable change in additive atomic energy of carbon atoms in *trans*-eq and one is not able to relate it directly to the presence of steric clash in *cis*-eq.

The largest unfavorable change in additive atomic energy was found for H10 and this is paralleled by the change in this atom's interactions with remaining atoms of *trans*-eq, +1.48 kcal/mol. Just opposite is observed for H12 which experienced second most favorable change in this energy term, –1.34 kcal/mol (Table S20) with the change in the classical component of –0.26 kcal/mol (–0.25 kcal/mol we found in *cis*-eq). This means that this atom experienced overall more favorable Coulomb-type interactions between all atoms of 2-buthene in both, *cis* and *trans*, equilibrium structures.

Table S20. Changes, as energy term = *trans*-eq – *trans*-TS, in the additive atomic energy, $\Delta E_{\text{add}}^{\text{X}}$, self-atomic energy, $\Delta E_{\text{self}}^{\text{X}}$, the total diatomic interaction energy between an atom X and all remaining atoms in a molecule, $\Delta E_{\text{int}}^{\text{X},\mathcal{H}}$, and the classical component of the latter when TS changed to the eq-structure (all values in kcal/mol).

Atom	$\Delta E_{\text{add}}^{\text{X}}$	$\Delta E_{\text{self}}^{\text{X}}$	$\Delta E_{\text{int}}^{\text{X},\mathcal{H}}$	$\Delta V_{\text{cl}}^{\text{X},\mathcal{H}}$
C1	-0.323	-0.436	0.226	0.307
H2	0.034	0.015	0.039	-0.007
H3	0.034	0.015	0.039	-0.012
H4	-0.024	-0.009	-0.030	-0.007
C5	-0.111	-0.350	0.479	0.450
H6	0.018	0.306	-0.575	0.056
C7	-0.797	0.069	-1.732	0.393
H8	-0.336	-0.502	0.332	-0.132
C9	0.287	0.338	-0.102	1.240
H10	1.252	0.514	1.477	-0.010
H11	-0.594	-0.697	0.206	-0.268
H12	-1.690	-1.020	-1.339	-0.258

Change in self-atomic energies

When going from *tran*-TS (our *ref* state) to *trans*-eq (our *fin* state), we found $\Delta\sum_{\text{X}} E_{\text{self}}^{\text{X}}$ = –1.76 kcal/mol and $\Delta\sum_{\text{Y}\neq\text{X}} 0.5E_{\text{int}}^{\text{XY}}$ = –0.49 kcal/mol. Here the change in self-atomic energies contributed over three times more when compared with the change in additive contribution made by all diatomic interaction energies and this is very different when compared with the *cis* conformer where the change in self-energies was only –0.13 kcal/mol. The sum of these two energy components for *trans*-2-butene amounts to –2.25 kcal/mol which differs from Δ*E* just by –0.28 kcal/mol; this gives us sufficient confidence when analysis if the IQA-defined terms is considered.

A full set of changes in self-atomic energies is shown in Table S20 where the largest positive/negative $\Delta E_{\text{self}}^{\text{X}}$ values were obtained for H10/H12 with 0.51 and –1.02 kcal/mol, respectively. As a matter of fact, the most significant stabilizing (H12 and H11) and destabilizing (H10 and C9) changes are observed for the atoms of the –C9H$_3$ group and when summed up they produced the –0.87 kcal/mol value. This appears to be reasonable finding as the –C9H$_3$ group was rotated, hence the computed $\Delta E_{\mathrm{self}}^{\mathrm{X}}$ values can be attributed to most significant change in their molecular environment (when *trans*-TS changed to *trans*-eq) and particularly so when H-atoms are concerned. We also noticed that when self-atomic energies of all atoms (except most two stabilizing contribution made by H12 and H11) are summed up the result obtained was –0.04 kcal/mol. Hence, one might conclude that the total change can be attributed mainly to H12 and H11 for which $\Delta E_{\mathrm{self}}^{\mathrm{X}}$ of –1.02 and –0.70 kcal/mol was found and this compares very well with the total change in self-atomic energies of –1.76 kcal/mol.

From the perspective of self-atomic energy changes, H-atoms of the –C9H$_3$ group in combination with H8 contributed most to stability of *trans*-eq, –1.71 kcal/mol (60% of stabilizing contributions) whereas in case of *cis*-eq, these four H-atoms atoms contributed –0.08 kcal/mol (4% of stabilizing contributions). Considering just H-atoms of the –C9H$_3$ groups we obtained –1.20 and +0.26 kcal/mol for *trans* and *cis* conformers, respectively; note that the difference, 0.26 – (–1.20) = +1.46 kcal/mol is quite close to the energy difference $E_{\mathrm{cis}} - E_{\mathrm{trans}}$ with *cis*-eq being higher in energy by +1.36 kcal/mol. The difference in contributions made by H-atoms of the –C9H$_3$ groups in *cis* and *trans* conformers can be rationalized by significantly different molecular environments which resulted in specific changes in atomic volumes, atomic surfaces and atomic populations, hence different intramolecular charge distributions.

Change in diatomic interaction energies

Changes in all 66 unique diatomic interactions on transition from *trans*-TS to *trans*-eq are shown in Table S21. The largest stabilizing $\Delta E_{\mathrm{int}}^{\mathrm{X,Y}}$ values were found for (C7,C9) and (H6,H12) with –2.04 and –0.99 kcal/mol, respectively. In case of the former, this can be attributed to the most significant change in d(C9,C7) which decreased the most among all covalent bonds. Considering the latter pair of atoms, we explain the more stabilizing interaction in *trans*-eq as being due to the largest decrease in the interatomic distance (Δd(H6,H12) = –0.4145 Å) among all 66 possible combinations. This is not exactly what classical interpretation would foresee but our interpretation is strongly supported but data shown in Figure S19 which clearly reveals (i) marginal and positive change in the classical component of the –CH•••HC–interactions, $\Delta V_{\mathrm{cl}}^{\mathrm{X,Y}} > 0$ (typically on the second decimal place of kcal/mol) and (ii) significant contribution coming

Table S21. Full set of changes in diatomic interaction energies (in kcal/mol), from most stabilizing $\Delta E_{\mathrm{int}}^{\mathrm{X,Y}}$ to most destabilizing contribution, for transition from *trans*-TS to *trans*-eq.

No	Atom X	Atom Y	$\Delta E_{\mathrm{int}}^{\mathrm{X,Y}}$	No	Atom X	Atom Y	$\Delta E_{\mathrm{int}}^{\mathrm{X,Y}}$
1	**C9**	**C7**	-2.048	30	H4	H3	0.000
2	**H12**	**H6**	-0.992	31	H10	H3	0.001
3	H10	C5	-0.320	32	H8	H6	0.003
4	H12	H8	-0.281	33	H6	H3	0.004
5	H12	C5	-0.136	34	H6	H2	0.004
6	H12	C9	-0.125	35	H12	H3	0.005
7	H4	C1	-0.089	36	H6	H4	0.006
8	H10	C7	-0.083	37	H12	H2	0.006
9	C7	C1	-0.039	38	H3	C1	0.007
10	H11	C7	-0.037	39	H3	H2	0.009
11	H11	C9	-0.036	40	C9	H4	0.010
12	C7	H6	-0.031	41	C9	H2	0.013
13	H12	C1	-0.030	42	C9	H3	0.013
14	H12	H4	-0.023	43	H8	C1	0.013
15	H11	H10	-0.023	44	H11	H4	0.014
16	C9	H8	-0.017	45	H10	C1	0.017
17	H11	C1	-0.016	46	C5	H2	0.023
18	H12	H11	-0.014	47	C5	H3	0.023
19	H11	H3	-0.013	48	H10	H6	0.024
20	H11	H2	-0.009	49	H6	C1	0.025
21	C7	H4	-0.007	50	C5	H4	0.026
22	H10	H4	-0.004	51	C9	C1	0.027
23	H10	H2	-0.003	52	H11	H8	0.030
24	H2	C1	-0.003	53	H8	H4	0.038
25	C7	H3	-0.002	54	C5	C1	0.055
26	C7	H2	-0.002	55	C9	H6	0.062
27	H8	H2	-0.002	56	H12	H10	0.094
28	H8	H3	-0.002	57	H8	C7	0.102
29	H4	H2	0.000	58	C9	C5	0.118
				59	H8	C5	0.138
				60	H6	C5	0.149
				61	H12	C7	0.151
				62	H11	C5	0.152
				63	H11	H6	0.166
				64	H10	H8	0.310
				65	C7	C5	0.340
				66	**H10**	**C9**	1.504
		Sum all:	-4.39			Sum all:	+3.68
		Sum blue:	-1.35			Sum blue:	+1.36

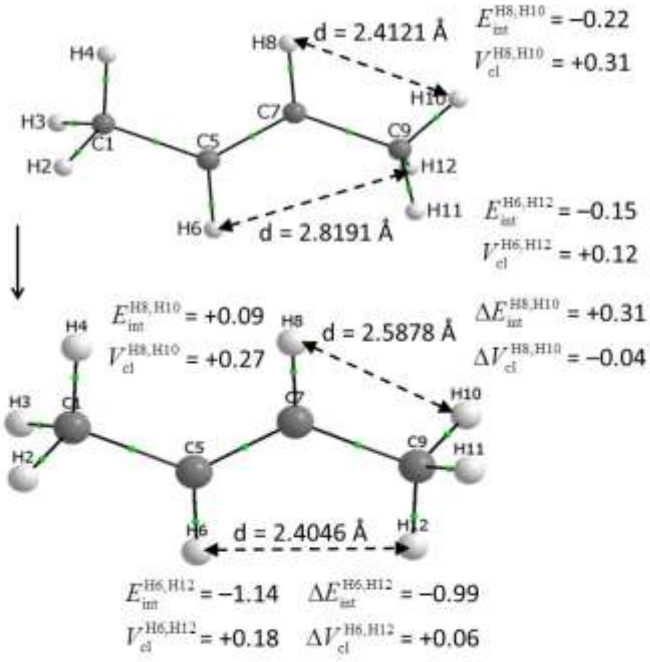


Figure S19. Interatomic distances, d(H8,H10) and d(H6,H12), in *trans*-TS and *trans*-eq and associated changes in the diatomic interaction energy, ΔE_{int}, and its classical component ΔV_{cl} when TS changed to eq-structure. Values in kcal/mol.

from the exchange-correlation term, $\Delta V_{\mathrm{XC}}^{\mathrm{X,Y}} < 0$ which overwrites $\Delta V_{\mathrm{cl}}^{\mathrm{X,Y}}$ when two H-atom approach each other. We note that the most destabilizing contribution was made by {C9,H10} with +1.50 kcal/mol. This is fully understandable because d(C9,H10) increased the most among all covalent bonds when in *trans*-eq.

Considering the sum of three changes, $\Delta E_{\mathrm{int}}^{\mathrm{X,Y}}$, related to the C–H bonds of the –CH$_3$ terminal groups we found (i) +1.34 and –0.09 kcal/mol for –C9H$_3$ and –C1H$_3$, respectively and, for comparison, +0.86 and –0.07 kcal/mol, respectively, for the same terminal groups in *cis* conformer. This clearly shows that rotation of the –C9H$_3$ terminal group in *cis*-2-butene had significantly smaller impact on the interaction energy between covalently bonded C9 and H-atoms. Interestingly, the largest 'penalty' was paid by the C9–H10 bond in *trans* conformer, $\Delta E_{\mathrm{int}}^{\mathrm{C9,H10}}$ = +1.50 kcal/mol, due to lost alignment between H10 and H8 in *trans*-TS and this is mimicked by the C9–H11 bond in *cis* conformer ($\Delta E_{\mathrm{int}}^{\mathrm{C9,H11}}$ = +1.61kcal/mol) because H11 was aligned with H8 in *cis*-TS. This corroborates very well with our observation that rotating a terminal group results in a set of unique structural and many energy terms changes which are not influenced much by conformational state of a molecule. This is further supported by the trends in $\Delta E_{\mathrm{int}}^{\mathrm{X,Y}}$ values found for the C1–C5, C5–C7 and C7–C9 bonds and we found 0.06, 0.34 and –2.05 kcal/mol, respectively, for *trans*-eq (it sums up to –1.65 kcal/mol) and 0.22, 0.31 and –1.68 kcal/mol, respectively, for *cis*-eq (it sums up to –1.14 kcal/mol).

FAMSEC-based analysis of 2-atom fragments

Focusing on the {H8,H10} fragment in *trans*-eq (Figure S20), it is characterized by a common feature with the {H8,H11} in *cis*-eq, namely these atoms are aligned in TSs of these two isomers. Consequently, these two fragments became destabilized by +0.3 and +0.6 kcal/mol when in *trans*-eq and *cis*-eq, respectively, with significant contribution coming from less attractive diatomic interaction in each case. Furthermore, the {H8,H10} fragment destabilized *trans*-eq, with the $E_{\text{attr-mol}}^{\mathfrak{F}}$ value of +1.5 kcal/mol, which mimics the value found for {H8,H11} when *cis*-TS changed to *cis*-eq. These findings nicely illustrate 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.

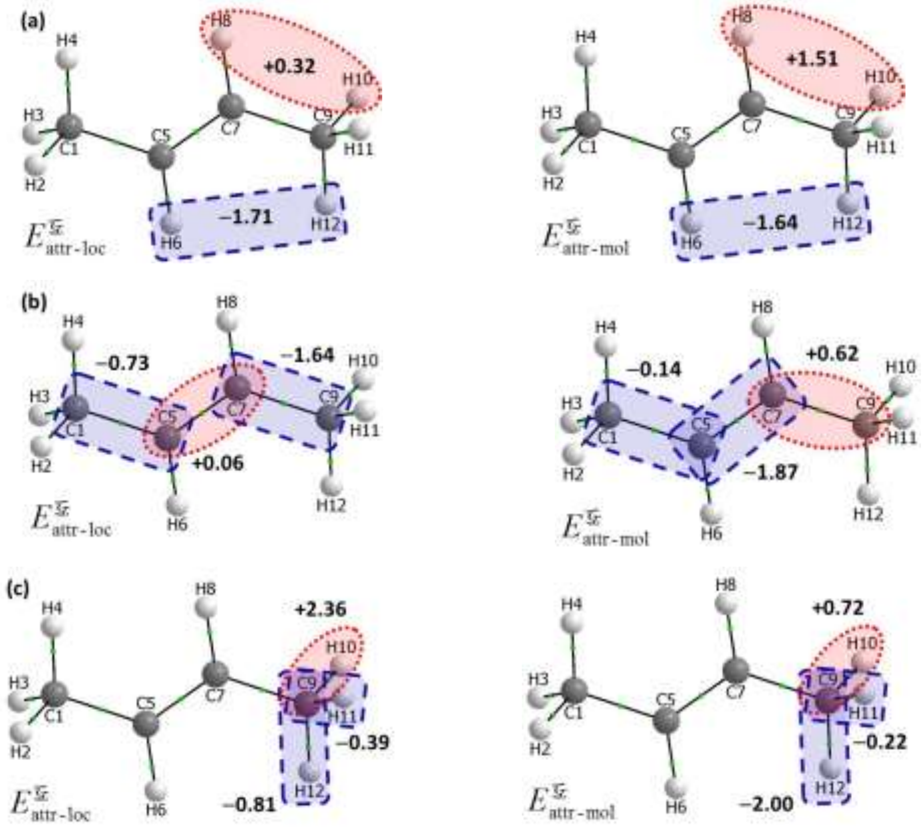


Figure S20. Schematic representation of *loc*-FAMSEC and *mol*-FAMSEC contributions made by diatomic molecular fragments: interacting H-atoms (part a), covalently bonded C-atoms (part b) and covalently bonded C- and H-atoms of the terminal methyl group (part c); values in kcal/mol.

Considering fragments made of covalently bonded C-atoms shown in Figure S20(b), we found {C7,C9}/{C5,C7} being most stabilized/destabilized in *trans*-eq with $E_{\text{attr-loc}}^{\mathcal{G}}$ of –1.6 and +0.1 kcal/mol, respectively; this trend is also observed for *cis*-TS→*cis*-eq with very much similar $E_{\text{attr-loc}}^{\mathcal{G}}$ values of –1.8 and +0.1 kcal/mol for {C7,C9} and {C5,C7}, respectively. The only and significant difference is observed for the {C1,C5} fragment which is stabilized by –0.7 kcal/mol in *trans*-eq but slightly destabilized by +0.1 kcal/mol in *cis*-eq. Focusing on *mol*-FAMSEC, Figure 20(b), we found that the trend for {C5,C7} and {C7,C9} with $E_{\text{attr-mol}}^{\mathcal{G}}$ of –1.9 and +0.6 kcal/mol, respectively, in *trans*-eq is also observed in *cis*-eq, with $E_{\text{attr-mol}}^{\mathcal{G}}$ of –1.3 and +1.2 kcal/mol, respectively. However, whereas the {C1,C5} fragment added –0.1 kcal/mol to stability of *trans*-eq, it has increased the energy of *cis*-eq, relative to *cis*-TS, by +0.9 kcal/mol. Additional data for covalently bonded atoms is shown in Figure S21.

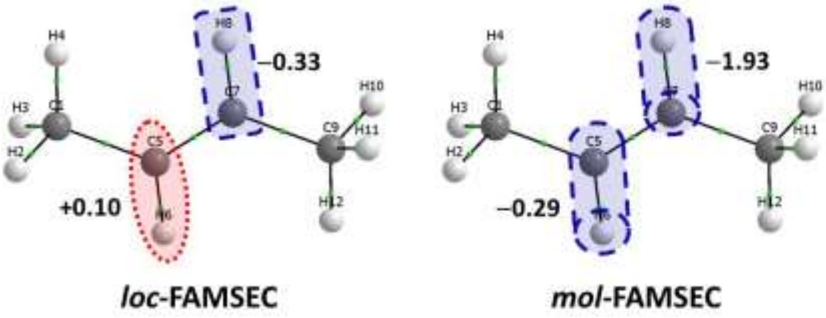


Figure S21. Schematic representation of *loc*-FAMSEC and *mol*-FAMSEC energy contributions made by diatomic molecular fragments made of covalently bonded C- and H-atoms; stabilizing contributions - blue colour and dashed line, destabilizing contributions – red colour and dotted line.. All values in kcal/mol.

FAMSEC-based analysis of 4-atom fragments

For consistency and to perform comparative analyses, we will use the same molecular fragments as in *cis*-eq except {C1,H4,H12,C9} with the BP-linked H4•••H12 interaction, which is replaced by equivalent and relevant {C5,H6,H12,C9} with the BP-free H6•••H12 interaction.

Starting with *loc*-FAMSEC terms, it is seen in Figure S22(a) that the -C9H$_3$ terminal group became destabilized by +0.5 kcal/mol in *trans*-eq relative to *trans*-TS. This picture is consistent with that obtained for *cis*-eq and, in addition, the *loc*-FAMSEC terms in both conformers are of similar value. On the other hand, the -C1H$_3$ terminal group became stabilized and this is most likely due to the fact that the intramolecular BP-free H4•••H8 interaction has no competing BP-free H4•••H10 interaction in *trans*-eq. Interestingly, the {C5,H6,C9,H12} fragment in Figure S22(b) is stabilized by –1.7 kcal/mol, as much as {C1,H4,H12,C9} with the BP-linked H4•••H12 in *cis*-eq.

Regarding the *mol*-FAMSEC terms of the terminal groups, Figure S22(a), contribution to molecular stability is provided by the -C9H$_3$ group in both, *trans*-eq and *cis*-eq, but more significantly in case of *trans*-TS. Considering the -C1H$_3$ group, we found $E^{\mathcal{G}}_{\text{attr-loc}} < 0$ and $E^{\mathcal{G}}_{\text{attr-mol}} < 0$ for *trans*-TS→*trans*-eq whereas $E^{\mathcal{G}}_{\text{attr-loc}} > 0$ and $E^{\mathcal{G}}_{\text{attr-mol}} > 0$ apply to *cis*-TS→*cis*-eq. Looking at the *mol*-FAMSEC terms in Figure S22(b) we note that the middle part of the molecule, the $\mathcal{G}$ = {C5,H6,C7,H8} fragment, made a significant contribution to molecular stability, by –2.7 kcal/mol, whereas significantly smaller contribution of –1.7 kcal/mol was found for *cis*-TS→*cis*-eq.

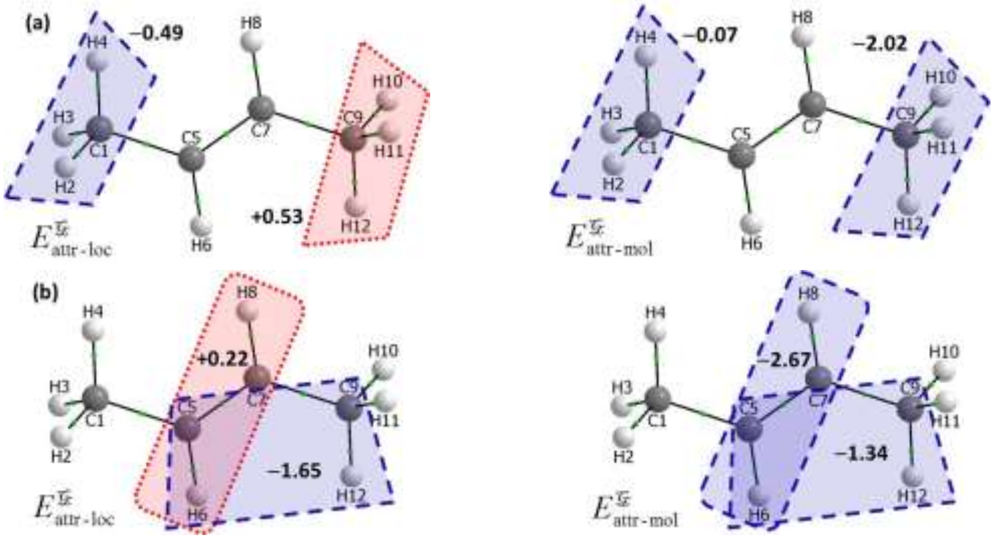


Figure S22. Schematic representation of indicated four-atom fragment attributed *loc*-FAMSEC) and *mol*-FAMSEC energy contributions made when *trans*-TS changed to trans-eq; values are in kcal/mol.

Somewhat unexpectedly, considering {C1,H4,H12,C9} in *cis*-eq with the BP-linked H4•••H12 interaction and relevant {C5,H6,H12,C9} with the BP-free H6•••H12 interaction, the former contributed *mol*-FAMSEC = +0.2 kcal/mol when *cis*-TS changed to *cis*-eq, but the latter stabilized *trans*-eq by –1.3 kcal/mol (Figure S22b). The origin of such big difference can be traced to the interfragment interaction energy term, $\Delta E_{\text{int}}^{\mathcal{GH}}$, +2.0 and +0.3 kcal/mol for *cis*-TS→*cis*-eq and *trans*-TS→*trans*-eq, respectively, because the $E_{\text{attr-loc}}^{\mathcal{G}}$ values are virtually identical, –1.7 kcal/mol for *cis*-eq and *trans*-eq. By decomposing $\Delta E_{\text{int}}^{\mathcal{GH}}$ to contributions made by individual atoms we found that C1 and H4 made comparable and most significant contribution of +0.85±0.1 kcal/mol.

Additional data from the ETS-NOCV-based analysis

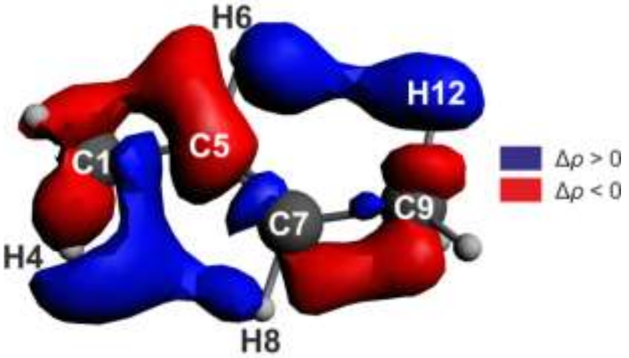
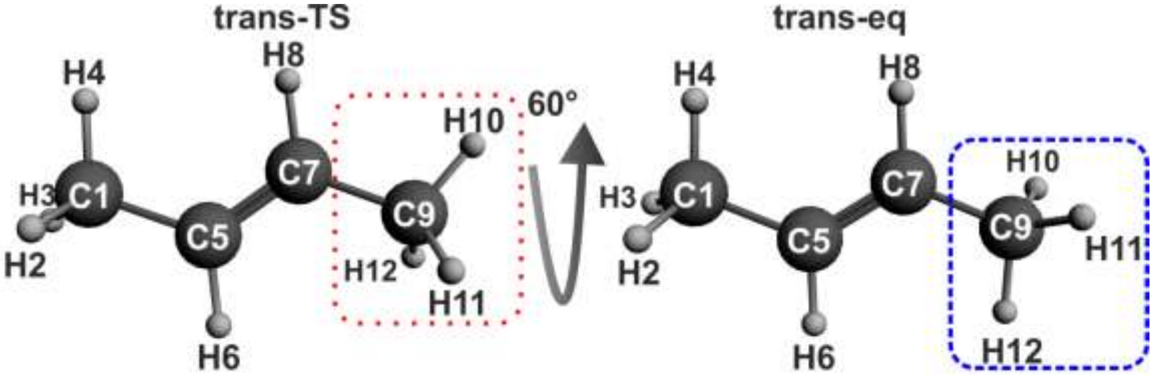
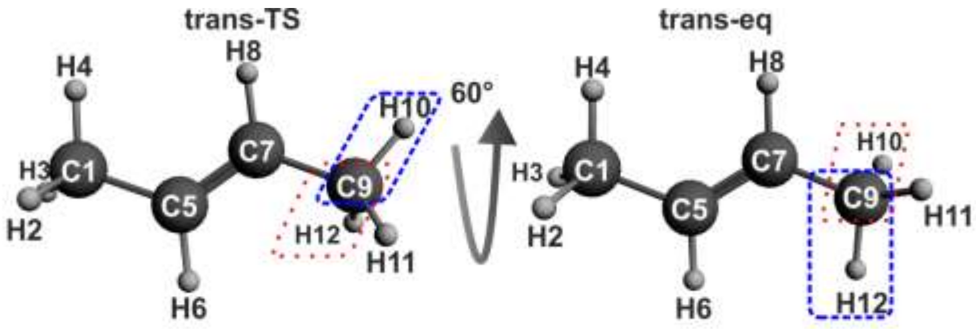


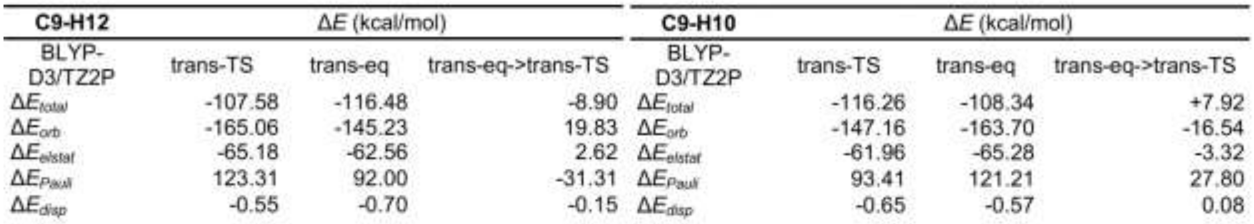
Figure S23. NOCV deformation density channel demonstrating the charge delocalization due to H--H interaction in *trans*-2-butene (the triplet fragments MeHC carrying opposite spin polarizations are applied).



$C9H_3$-C_3H_5	ΔE (kcal/mol)		
BLYP-D3/TZ2P	trans-TS	trans-eq	trans-eq->trans-TS
ΔE_{total}	-117.29	-118.72	-1.43
ΔE_{orb}	-198.02	-202.35	-4.33
ΔE_{elstat}	-142.45	-146.11	-3.66
ΔE_{Pauli}	226.01	232.57	6.56
ΔE_{disp}	-2.83	-2.83	0.00

Figure S24. ETS-NOCV-based energy decomposition of *trans*-TS→*trans*-eq rotation. Following fragmentation was considered: $C9H_3|C_3H_5$. $\Delta E_{total} = \Delta E_{orb} + \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{disp}$.





C9-H12	ΔE (kcal/mol)		
BLYP-D3/TZ2P	trans-TS	trans-eq	trans-eq->trans-TS
ΔE_{total}	-107.58	-116.48	-8.90
ΔE_{orb}	-165.06	-145.23	19.83
ΔE_{elstat}	-65.18	-62.56	2.62
ΔE_{Pauli}	123.31	92.00	-31.31
ΔE_{disp}	-0.55	-0.70	-0.15

C9-H10	ΔE (kcal/mol)		
BLYP-D3/TZ2P	trans-TS	trans-eq	trans-eq->trans-TS
ΔE_{total}	-116.26	-108.34	+7.92
ΔE_{orb}	-147.16	-163.70	-16.54
ΔE_{elstat}	-61.96	-65.28	-3.32
ΔE_{Pauli}	93.41	121.21	27.80
ΔE_{disp}	-0.65	-0.57	0.08

Figure S25. ETS-NOCV-based energy decomposition of *trans*-TS→*trans*-eq rotation. Following fragmentation was considered: H12|C_4H_7. $\Delta E_{total} = \Delta E_{orb} + \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{disp}$.