Conformational preference analysis in C$_2$H$_6$ using Orbital Forces and Non-Covalent Interactions; comparison with related systems

Trinidad Novoa, Julia Contreras-García, Patrick Chaquin

1 Laboratoire de Chimie Théorique (LCT)
Sorbonne Université, CNRS, F-75005 Paris
E-mail: chaquin@lct.jussieu.fr

Abstract

Dynamic Orbital Forces (DOF) and Non-Covalent Interactions (NCIs) allow an analysis of the attractive/repulsive interactions whose variations lead to the staggered preference of ethane and some related compounds. In ethane, it is found that CH$_3$···CH$_3$ attractive interactions are predominant in the staggered preference with respect to adiabatic eclipsed conformation, with an important σ contribution. On the contrary, vertical eclipsed ethane is destabilized almost only by repulsive π interactions. Weak long-range H···H repulsions favor the staggered conformation. From the sum of DOFs, the energy barrier can be decomposed into C-H and C-C bond energies. It is found due to the weakening of the C-C bond (ca. 7 kcal/mol), moderated by a strengthening of C-H ones (ca. 4 kcal/mol) arising from the decrease of hyperconjugation with respect to the staggered conformation.

In the compounds CH$_3$-SiH$_3$, SiH$_3$-SiH$_3$, CH$_3$-CF$_3$ and CF$_3$-CF$_3$, the conformational preference is predominantly or exclusively due to repulsive interactions, with respect as well to adiabatic as to vertical eclipsed structures.

1. Introduction

The preference of ethane for the staggered (S) conformation over the eclipsed (E) one has been qualitatively explained on the basis of molecular orbital (MO) interactions between the two CH$_3$ groups, yielding the couple of degenerate MOs $e_u,e_g$ and $e',e''$ respectively (Fig 1, see also Fig. 2 in section 3).
In a first step, we consider only the 4-electron interactions (a) of two CH$_3$ moieties leading to Pauli repulsion. Due to a smaller overlap, this interaction is globally less repulsive in S conformation. This interaction, as “steric hindrance”, was for a long time considered as the only responsible of the conformational preference of ethane, as presented in most of Organic Chemistry textbooks. In a second step, we consider the interactions (b) of these degenerate couples with empty MOs of C-H antibonding character. It results in a stabilization of both bonding (e$_u$, e') and antibonding (e$_g$, e'') MOs. Due to a greater overlap, this interaction, also known as hyperconjugation, is more stabilizing in the S conformation. The nature of the prominent interaction, Pauli repulsion vs. hyperconjugation, and more generally repulsive vs. attractive interactions, was the subject of many debates. Pophristic, Goodman et al., from NBO analysis, concluded that hyperconjugation was the main factor of the ethane conformational preference. Moreover, these authors highlighted the importance of the structural changes from S to E conformer, concerning CC and also CH bonds, respectively shorter and longer in the S conformer. The study of electrostatic forces from Hellman-Feynman theorem or Ehrenfest forces confirmed the attractive origin of the S conformation. These conclusions were contested by several works on the basis of various energy partitions, claiming the repulsive origin of the destabilization of the E conformer with respect to the S one, in turn rebutted by Weinhold. In addition, contrasted results are reported when considering either adiabatic (geometry optimized) or vertical (with the same bond lengths and angles as the S structure) geometry of the eclipsed form.

We intend here to analyze the interactions leading to the preferential conformation of ethane and some compounds of general formula X$_3$A-BY$_3$ on the basis of two independent methods: dynamic orbital forces (DOF) and non-covalent interactions (NCIs).
Dynamic Orbital Forces (DOF)

From generalized Koopman’s theorem, the energy \( \varepsilon_i \) of a canonical MO can be written as:

\[
\varepsilon_i = E^0 - E_i^+
\]

where \( E^0 \) is the Hartree-Fock (H-F) energy of the neutral molecule and \( E_i^+ \) is the energy of the cation resulting from the removal of one electron from the \( i^{\text{th}} \) MO, in the frozen MO approximation. The derivative with respect to any internuclear distance \( R \), if the geometry has been optimized for the neutral species, is:

\[
\frac{d\varepsilon_i}{dR} = \frac{dE^0}{dR} - \frac{dE_i^+}{dR} = - \frac{dE_i^+}{dR} \tag{1}
\]

This quantity is positive or negative and represents the force exerted on nuclei upon vertical ionization from the \( i^{\text{th}} \) MO. A positive value of \( \frac{d\varepsilon_i}{dR} \) means that a repulsive force is exerted in the cation and thus that the missing electron was bonding. It provides a measure of the intrinsic bonding/antibonding character of each MO along \( R \),\(^8\) and was used to determine the properties of “lone pair” MOs.\(^8,9\)

Let us now consider the sum \( \Sigma \) over valence MOs occupied by \( n \) electrons:

\[
\Sigma_t = \sum_{i}^{\text{valence}} n_i \frac{d\varepsilon_i}{dR} \tag{2}
\]

This quantity has been recognized as an index of bond strength, as far as the molecule is satisfactorily described at the Hartree-Fock (H-F) level.\(^10\) Moreover, dealing with CC bonds in hydrocarbons, it was found to be linearly correlated to bond energy, allowing its evaluation in constrained systems\(^11\) and partition into \( \sigma/\pi \) contributions to bonding.\(^3,12\) Thus the sum \( \Sigma_t \) thus can be exploited in different ways.

i) If \( n_b \) bonding and \( n_a \) antibonding electrons are present, the total contribution to bond strength can be decomposed into attractive \( \Sigma_b \) and repulsive \( \Sigma^* \) components:

\[
\Sigma_t = \Sigma_b + \Sigma^* = \sum_{j}^{\text{bonding}} n_j \frac{d\varepsilon_j}{dR} + \sum_{k}^{\text{antibonding}} n_k \frac{dE_k}{dR} \tag{3}
\]

ii) If \( n_\sigma \) sigma and \( n_\pi \) pi electrons are present, the total contribution to bond strength can be decomposed into sigma \( \Sigma_\sigma \) and pi \( \Sigma_\pi \) components:

\[
\Sigma_t = \Sigma_\sigma + \Sigma_\pi = \sum \frac{d\varepsilon_\sigma}{dR} + \sum \frac{d\varepsilon_\pi}{dR} \tag{4}
\]
iii) For a small variation $\Delta \Sigma_t$ of $\Sigma_t$, one can assume the corresponding variation $\Delta(BE)$ of the intrinsic bonding energy $BE$ is:

$$\Delta(BE) \approx BE \frac{\Delta \Sigma_t}{\Sigma_t}$$

It results in a variation $\Delta E$ of molecular energy:

$$\Delta E \approx -BE \frac{\Delta \Sigma_t}{\Sigma_t} \quad (5)$$

Non-Covalent Interactions (NCIs)

The non-covalent interaction (NCI) index is a density ($\rho$) derived function enabling to reveal non-covalent interactions in real space.\textsuperscript{13}

It is based on the analysis of the reduced density gradient:

$$s(\rho) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla \rho|}{\rho^{4/3}}$$

It is a dimensionless quantity used in DFT to describe the deviation from a homogenous electron distribution. By plotting $s$ isosurfaces at low electron density values, the weak interactions of the system are revealed. In order to differentiate between the different types of interactions, we will use the following colour code:

- Blue for highly attractive weak interactions (such as hydrogen bonds).
- Green for extremely weak interactions (such as van der Waals).
- Red for repulsive interactions (such as steric clashes).

2. Calculation methods

Geometry optimizations and rotation barriers were computed at the Hartree-Fock/aug-cc-pvQZ level. MO energy derivatives were computed by finite differences ranging from 0.005 Å to 0.02 Å according to the case, thanks to a home-made code (available on request). The GAUSSIAN series of programs\textsuperscript{14} was used throughout the work. NCI images were obtained with NCIPLOT.\textsuperscript{15}
3. Conformation of ethane

3.1. Orbital forces in ethane conformers

We report in Fig. 1 the DOF of staggered S and eclipsed adiabatic E conformers in their optimized geometry (H-F/aug-cc-pvQZ, S: CC=1.524135 Å; CH = 1.083538 Å; HCC = 111.209°; E: CC = 1.538668 Å; CH = 1.082331 Å; HCC = 111.614°), together with those of the vertical eclipsed conformer E(V) (CC, CH and HCC parameters of the S conformer). These forces correspond to the derivatives with respect to the CC distance (cf. Equation 1), the other parameters (C-H bond lengths and HCC angles) remaining unchanged. These quantities are thus a measure of the attractive (DOF > 0) or repulsive (DOF < 0) interaction of one CH$_3$ group to another exerted by one electron occupying a given MO.

![Figure 1](image1.png)

<table>
<thead>
<tr>
<th></th>
<th>S</th>
<th>E</th>
<th>E(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a$_1$y/a'$_1$</td>
<td>0.1286</td>
<td>0.1233</td>
<td>0.1283</td>
</tr>
<tr>
<td>a$_2$/a''$_2$</td>
<td>-0.0492</td>
<td>-0.0492</td>
<td>-0.0503</td>
</tr>
<tr>
<td>e$_y$/e'</td>
<td>0.0609</td>
<td>0.0593</td>
<td>0.0619</td>
</tr>
<tr>
<td>e$_z$/e''</td>
<td>0.1183</td>
<td>0.1177</td>
<td>0.1175</td>
</tr>
<tr>
<td>DOF</td>
<td>-0.0558</td>
<td>-0.0585</td>
<td>-0.0598</td>
</tr>
</tbody>
</table>

Figure 2. Valence shell dynamic orbital forces (DOF) of optimized staggered (S) and eclipsed (E), vertical eclipsed (E(V)) ethane with respect to H3C-CH3 distance (a.u.). Only the MOs of the S conformer are represented.

The DOFs of MOs 3-4 and 6-7 (i.e. π orbitals) agree with the qualitative analysis of Introduction (Fig 1). The addition of short CC distance and low hyperconjugation yields for E(V) the maximum bonding for 3-4 and maximum antibonding for 6-7. Nevertheless, in all three S, E and E(V) cases, MOs 3-4 are more bonding than MOs 6-7 are antibonding, which means that the set of MOs 3, 4, 6 and 7 have a neat bonding balance.
Figure 3. DOF differences (10^{-3} a.u.) with respect to the H_3C-CH_3 distance for each valence shell MO between S and E conformations; (a) adiabatic E structure; (b) vertical E structure. (A positive value means that the MO favors the staggered conformation.)

In order to compare the roles of the MOs in the conformation preference, we report for each of them (Figure 3), the force difference DOF(S) – DOF(E) between the staggered and the eclipsed conformations: (a) adiabatic E and (b) vertical EV; a positive value thus means that the corresponding MO favors the S conformation. Figure 3(a) shows that all MOs favor the S conformation with respect to adiabatic E, except MO 2 which has no significant effect, and that MO 1 of \( \sigma \) type plays an important role. By contrast (Figure 3(b)), MOs 3 and 4 favor the vertical eclipsed form (where the overlap is bigger), in which the S preference is dominated by a decrease of MO 6-7 repulsion.

3.2. Sum of orbital forces as an index of bond strength; decompositions into attractive/repulsive and \( \sigma/\pi \) components

We will now consider the variations, during adiabatic and vertical rotations, of the sum \( \Sigma \) (Equation 2) as an index of total CH_3-CH_3 bond strength. This quantity can be decomposed into attractive \( \Sigma_b \) and repulsive \( \Sigma^* \) components (Equation 3). We report (Figure 4) for each of these cases the differences \( \Delta \Sigma = \Sigma(\theta)-\Sigma(S) \) as functions of \( \theta \) = H-C-C-H dihedron (a positive value thus favors the \( \theta \) conformer over the S (\( \theta = \pm 60^\circ \)) one).
Figure 4. Variation of the sums of orbital forces (m a.u.) along CH₃-CH₃ as a function of the H-C-C-H dihedron with respect to the staggered (S) conformer: (a) adiabatic (optimized geometry); (b) vertical rotation; dots: total sum $\Delta \Sigma_t$; triangles up: sum of bonding MO (attracting) forces $\Delta \Sigma_b$; triangles down: sum of antibonding (repulsive) forces $\Delta \Sigma^*$.

From Fig. 4(a) and values reported in Table 1, it appears that the adiabatic energy barrier, reflected by a decrease of $\Sigma_t$, originates in both decreased attracting forces $\Sigma_b$ and increased repulsive ones $\Sigma^*$, in an approximate 2:1 ratio (4.6 % vs 2.6 %). By contrast, in the vertical rotation, the barrier (Figure 4(b) and Table 1) is only due to repulsive interactions (4.5 %), so we can understand that the C-C distance elongates to release the repulsion. The variation of attractive forces is very weak and seems to slightly favor the eclipsed conformer (-0.5 %).

Table 1. Sums $\Sigma$ of DOFs (a.u.) and relative differences of $\Delta \Sigma = \Sigma(S) - \Sigma(E)$ (a positive $\Delta \Sigma$ favors the S conformer): S and E, fully relaxed structures; E(V) vertical eclipsed structure; $\Sigma_t$ total DOF sum; $\Sigma_b$ bonding MO DOF sum; $\Sigma^*$ antibonding MO DOF sum; $\Sigma_\sigma$-type MO (a symmetry) sum; $\Sigma_\pi$-type MOs (e symmetry) sum; $\Delta \Sigma$: energy barrier (kcal/mol, H-F/aug-cc-pvQZ).

<table>
<thead>
<tr>
<th></th>
<th>H₃C—CH₃</th>
<th>6 C—H</th>
<th>$\Delta \Sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Sigma_t$</td>
<td>0.4154</td>
<td>0.3868</td>
<td>0.3995</td>
</tr>
<tr>
<td>$\Sigma_b$</td>
<td>0.7374</td>
<td>0.7192</td>
<td>0.7392</td>
</tr>
<tr>
<td>$\Sigma_\sigma$</td>
<td>-0.3216</td>
<td>-0.3324</td>
<td>-0.3398</td>
</tr>
<tr>
<td>$\Sigma_\pi$</td>
<td>0.3954</td>
<td>0.3836</td>
<td>0.3911</td>
</tr>
<tr>
<td>$\Sigma_\pi$</td>
<td>0.0204</td>
<td>0.0032</td>
<td>0.0084</td>
</tr>
<tr>
<td>$\Delta \Sigma_t$</td>
<td>1.7537</td>
<td>1.7664</td>
<td>1.7579</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$\Delta \Sigma_t$</th>
<th>$\Delta \Sigma_b$</th>
<th>$\Delta \Sigma_\sigma$</th>
<th>$\Delta \Sigma_\pi$</th>
<th>$\Delta \Sigma_\pi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-E</td>
<td>7.2 %</td>
<td>4.6 %</td>
<td>2.6 %</td>
<td>3.0 %</td>
<td>4.3 %</td>
</tr>
<tr>
<td>S-E(V)</td>
<td>4.0 %</td>
<td>-0.5 %</td>
<td>4.5 %</td>
<td>0.4 %</td>
<td>3.0 %</td>
</tr>
</tbody>
</table>

We report also in Table 1 the decomposition of $\Sigma_t$ into $\sigma$ and $\pi$ components (Equation 4).
The sum $\sum_\pi$ of $\pi$-type interactions (MOs of $e$ symmetry) is positive, thus globally attractive in all three $S$, $E$ and $E(V)$ structures, which means, as already noted in section 3.1, that the stabilization by hyperconjugation overcomes the 4-electron repulsion.

In the adiabatic rotation, the $\pi$-type components are only slightly predominant over $\sigma$-type ones (MOs of $a$ symmetry) as indicated by the values $\Delta \Sigma_\sigma/\Sigma_\pi = 4.3\%$ and $\Delta \Sigma_\sigma/\Sigma_\pi = 3.0\%$. This important $\sigma$-type contribution mainly arises from MO 1: this MO increases considerably its attractive power in the $S$ conformation, due to a shorter C-C distance with respect to $E$, and thus an increased overlap (this MO cannot, for symmetry reasons, take part in hyperconjugation). Indeed, its bonding character is almost the same in the $S$ and vertical $E(V)$ structures which have the same CC distance (cf. fig. 2(b)). Though regarding the total sum of orbital forces, the attractive component $\Sigma_b$ is predominant in the $S$ preference, dealing with $\pi$ interactions only, the variation of the 4-electron repulsive term (10.8 m.a.u.) dominates that of the attractive ones (6.4 m.a.u.) in the $S$ preference (MOs 6-7 and 3-4 respectively in Figure 3(a)).

In the vertical rotation, the barrier is almost exclusively due to the increased antibonding character of $\pi$ MOs 6-7, originating from the 4-electron repulsion in Fig.1 (cf. also Fig. 2(b)).

### 3.3. Long range H···H interactions

A further decomposition of orbital forces can be carried out. For this purpose, MO derivatives has been computed:

- with respect to the C-C distance, keeping H···H distances constant: $\frac{d\varepsilon_l}{d(C-C)}$
- with respect to the H$_3$···H$_3$ plane distance, keeping C-C distance constant $\frac{d\varepsilon_l}{d(H_3...H_3)}$

It requires a small variation of HCC angles of a negligible consequence, as it can be verified that, within less than 3%, we get:

$$\frac{d\varepsilon_l}{d(CH_3 - CH_3)} \approx \frac{d\varepsilon_l}{d(C - C)} + \frac{d\varepsilon_l}{d(H_3...H_3)}$$

As shown in Table 2, the sum of orbital forces between CH$_3$ groups results from an attractive contribution along C-C and a repulsive contribution between hydrogen atoms.
Table 2. Sum $\Sigma_t$ of orbital energy derivatives (a.u.) with respect to various R parameters. ($R = CH_3-CH_3, C-C$ and $H_3\cdots H_3$) in the S and E conformers.

<table>
<thead>
<tr>
<th></th>
<th>S</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>CH$_3$-CH$_3$</td>
<td>C-C</td>
</tr>
<tr>
<td>$\Sigma_t$</td>
<td>0.4154</td>
<td>0.4265</td>
</tr>
<tr>
<td>$H_3\cdots H_3$</td>
<td>-0.0111</td>
<td>0.3868</td>
</tr>
<tr>
<td>CH$_3$-CH$_3$</td>
<td>0.4054</td>
<td>-0.0175</td>
</tr>
</tbody>
</table>

In order to have a localized view of the $H_3\cdots H_3$ interaction, we have plotted the NCI surfaces which reflect the deformations. Given the long-range nature of these interactions, they are very subtly reflected in the NCI plot. Hence, cutoffs need to be carefully selected in order to choose the interactions we are interested in, and only those. For ethane, $\rho_{\text{max}}=0.037$ a.u. and $s=0.8$ is a good compromise (see S.I. for a thorough explanation of this choice). This allows reflecting the $H\cdots H$ nonbonded contacts for the vertical and eclipsed states with respect to the staggered one (see Scheme 1).

In both E and E(V) cases, the interaction $H_3\cdots H_3$ between hydrogens appears slightly repulsive and favors the S conformer. The total strengthening $\Sigma_t (S) - \Sigma_t (E)$ of CH$_3$-CH$_3$ bond in the S conformation with respect to E one (0.0386 a.u.) can be decomposed into 0.0211 a.u. from more attractive C···C interaction and only 0.0064 a.u. from less repulsive H···H interactions. This agrees qualitatively with the NCI pattern, indicating a weak long-range repulsion in both E conformer, too weak to be detected in the S one.

3.4 Decomposition of the energy barrier into bond energy variations; effect of hyperconjugation

The energy barrier $\Delta E$ does not arise only from the variation of CH$_3$-CH$_3$ bond strength analyzed in the preceding section. We must keep in mind that indeed hyperconjugation stabilizes the system by
increasing BE(CH$_3$-$CH_3$), but in turn weakens C-H bonds by some electron transfer in C-H antibonding MOs. From Equation 5, the total energy barrier $\Delta E$ can be written as:

$$\Delta E \approx -BE(CH_3-CH_3) \frac{\Delta \Sigma_t(CH_3-CH_3)}{\Sigma_t(CH_3-CH_3)} - 6BE(C-H) \frac{\Delta \Sigma_t(C-H)}{\Sigma_t(C-H)}$$  

(6)

As reported in Table 1, the relative variation $\Delta \Sigma_t/\Sigma_t$ of the sum of orbital forces along CH$_3$-CH$_3$ bond in the S conformation with respect to the E one increases by 7.2 % while the six CH bonds are weakened by -0.72 %. Taking $BE(CH_3-CH_3) \approx 90$ kcal/mol and $BE(CH) \approx 100$ kcal/mol, Equation (6) yields a total $\Delta E$ barrier of 2.2 kcal/mol (+6.5 kcal/mol from CH$_3$-CH$_3$ bond and -4.3 kcal/mol from six C-H bonds). This value, as compared to H-F barrier (3.04 kcal/mol; exp: 2.88 kcal/mol), is rather satisfactory, taking account the approximation of Equation 6, possible errors from the small differences $\Delta \Sigma_t$ and some uncertainty on the intrinsic BE values.

The effects of geometry optimization on energy barrier are detailed in Figure 5, according to Equation 5. The following structures have been considered: (a) S, optimized, taken as origin; (b) E, vertical; (c) E with optimized CC distance; (d) E fully optimized. These results can be explained as follows.

- The step (a)-(b) consists only in the rotation which increases both 4-electron destabilization of C-C and decreases hyperconjugation which, on the contrary, stabilizes the C-H bonds.
- The step (b)-(c) lengthens the CC distance, with a further destabilization of the CC bond, due now mainly to the decrease of the bonding character of the $\sigma$ MO 1 (the decrease of hyperconjugation and 4-electron repulsion are partly cancelling), whereas the decrease in hyperconjugation overlap stabilizes again the C-H bonds.
- The step (c)-(d) is the optimization of C-H bond lengths which are stabilized, with a negligible effect on C-C bonding energy. As already noted by the barrier is the same dealing with vertical (b) or adiabatic (d) E structure ($\Delta E$(total) = 2.2 kcal/mol) due to an almost exact
compensation of CC and CH bond energies variations, in agreement with H-F results ($\Delta E(H-F)$ = 3.17 kcal/mol and 3.04 kcal/mol).

This way, the energy barrier appears as mainly due to the interaction of both CH$_3$ groups which weakens H$_3$C-CH$_3$ bond energy, strongly moderated by a stabilization of C-H bonds. This result agrees, at least qualitatively, with that reported by Goodman et al. using a different method.$^{2a}$

### 4. Comparison with some related X$_3$A-BY$_3$ systems

From the preceding section, it appears that the leading interactions between two CH$_3$ groups, which controls the S preference, can be analyzed using orbital forces. Most notably, it allows the decomposition of the sum $\Sigma_t$ of orbital forces into attracting ($\Sigma_b$) and repulsive ($\Sigma^*$) ones and into $\sigma$ ($\Sigma_{\sigma}$) and $\pi$ ($\Sigma_{\pi}$) type origin. We will compare these four salient parameters of ethane to those of the following related systems: SiH$_3$-CH$_3$, SiH$_3$-SiH$_3$, CH$_3$-CF$_3$ and CF$_3$-CF$_3$. All these systems, like ethane exhibit a more or less marked preference for the S conformation (Table 3). Moreover, the rotation barrier for adiabatic and vertical rotations are very close to each other.

<table>
<thead>
<tr>
<th></th>
<th>CH$_3$-CH$_3$</th>
<th>CH$_3$-SiH$_3$</th>
<th>SiH$_3$-SiH$_3$</th>
<th>CH$_3$-CF$_3$</th>
<th>CF$_3$-CF$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E(A)$</td>
<td>3.07</td>
<td>1.65</td>
<td>1.10</td>
<td>3.44</td>
<td>4.94</td>
</tr>
<tr>
<td>$\Delta E(A)$ (exp)</td>
<td>2.88$^a$</td>
<td>1.86$^b$</td>
<td>1.18$^c$</td>
<td>3.18$^d$</td>
<td>4.40$^e$</td>
</tr>
<tr>
<td>$\Delta E(V)$</td>
<td>3.18</td>
<td>1.66</td>
<td>1.02</td>
<td>3.55</td>
<td>4.50</td>
</tr>
</tbody>
</table>


In Figure 6 and 7 are reported some relative variations $\Delta \Sigma/\Sigma_t$ of sums $\Sigma$ of MO forces between staggered and eclipsed forms, according to $\Delta \Sigma = \Sigma(S) - \Sigma(E)$. A positive value thus means that the corresponding interaction $\Sigma$ favors the staggered conformation. Both cases of adiabatic (A) and vertical (V) eclipsed conformations have been considered for each species.

In Figure 6 are compared the sums $\Sigma_b$ of bonding (attractive) forces and $\Sigma^*$ of antibonding (repulsive) ones. In Figure 7 are compared the sums $\Sigma_{\sigma}$ of $\sigma$ (of a symmetry) and $\Sigma_{\pi}$ of $\pi$ orbital forces (of $e$ symmetry).
Figure 6. Relative variations (%) of the sums of MO forces: $\Sigma_b$ bonding (attracting) MOs; $\Sigma^*$ antibonding (repulsive); a positive value favors the S conformation over the adiabatic (A)/vertical (V) eclipsed one.

Figure 7. Relative variations (%) of the sums of MO forces: $\Sigma_\sigma$: $\sigma$-type (a symmetry) MOs; $\Sigma_\pi$: $\pi$-type (e symmetry) MOs; a positive value favors the S conformation over the adiabatic (A)/vertical (V) eclipsed one.

Dealing with adiabatic rotation, C$_2$H$_6$ is the only case where attractive forces are dominant to favor the S structure; these forces are slightly lower than repulsive ones in CH$_3$-SiH$_3$ and negligible in SiH$_3$-SiH$_3$. This trend can be explained in part by the differences of central bond lengthening in the E
conformation. This bond length is increased by 2.3 % in CH₃-CH₃, 0.6 % in CH₃-SiH₃ and 0.5 % in SiH₃-SiH₃, thus the bonding character of the σ MO (MO 1 in C₂H₆) is almost the same in the E and V structures of the latter two compounds. This evolution is confirmed by Figure 7, which shows comparable σ and π contributions for ethane, and strongly dominant π interactions in silicon compounds.

In the fluorine compounds CF₃-CH₃ and CF₃-CF₃, the S preference arises practically from repulsive forces only, and that CF₃-CF₃ appears as the opposite situation to C₂H₆. The decomposition of the total sum of orbital forces into C···C and F₃···F₃ components is displayed in Table 4.

Table 4. Sum Σₜ of orbital energy derivatives (a.u.) with respect to various R parameters. (R = CF₃-CF₃, C-C, F₃···F₃ and C-F) in the S and E conformers.

<table>
<thead>
<tr>
<th></th>
<th>S</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>CF₃-CF₃</td>
<td>C-C</td>
</tr>
<tr>
<td>Σₜ</td>
<td>0.8081</td>
<td>1.0293</td>
</tr>
</tbody>
</table>

As expected from the presence of fluorine lone pairs, the F₃···F₃ interaction is strongly repulsive, as compared with H₃···H₃ in ethane. Their contribution to total CF₃···CF₃ interaction is of the same order of magnitude as the C···C one. This can be visualized in Scheme 2, where NCI surfaces have been plotted at s = 0.6 to highlight conformational interplays. In this case, the thin repulsive surfaces of ethane are replaced by well-defined interaction surfaces highlight the non-bonded F···F contacts. Contrary to ethane, in this case the strong repulsive interactions can explain alone the preference for the staggered conformation. Note that for higher s cutoffs, the F···F interactions also appear, in this case both inter and intramolecular (see Fig S2 in SI).

A weakening of the C-F bonds in the S conformer with respect to the E one is observed, indicating again a significant electron transfer towards C-F antibonding MOs.

Scheme 2. Evolution of NCI surfaces for the different C₂F₆ states. Parameters ρmax=0.04, s=0.6 were chosen to capture the deviations as seen in the s(ρ) plot (see SI).
Conclusion

Dealing with ethane, the answer to “the question”: “should the S preference be attributed to attractive or repulsive forces?” appears somewhat ambiguous. If we compare adiabatic E to S, the analysis of orbital forces indicates that the variation of total (σ + π) attractive forces is dominant in S preference, with an important σ contribution; nevertheless, the variation of the π forces appears dominated by that of the 4-electron repulsion, and not by that of attracting forces. By contrast, the destabilization of the vertical E conformer with respect to the S one is almost exclusively due to an increase of the 4-electron repulsion. It confirms the importance of the geometrical small differences between adiabatic and vertical E conformers. In both cases, weak long-range H…H repulsions favor the S conformer, as supported by NCI analysis. In terms of bond strengths, the rotation barrier is mainly due to the weakening of the CC bond, but partly compensated the strengthening of CH bonds by a partial loss of hyperconjugation.

In related molecules (SiH₃-CH₃, SiH₃-SiH₃, CH₃-CF₃ and CF₃-CF₃), the S preference is due mainly to the variation of repulsive orbital forces. In hexafluoro ethane, strong repulsive F···F long-range interactions are revealed by NCI and orbital forces.


15


