The “Inverted Bonds” Revisited: Analysis of “In Silico” Models and of [1.1.1]Propellane by Using Orbital Forces

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HAL Id: hal-02486194
https://hal.sorbonne-universite.fr/hal-02486194v1

Submitted on 20 Feb 2020

The ‘inverted Bonds’ revisited. Analysis of ‘in silico’ models and of [1.1.1]Propellane using Orbital Forces

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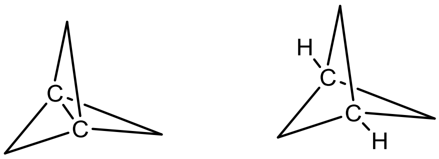
Abstract: This article dwells on the nature of “inverted bonds”, which make reference to the σ interaction between two s-p hybrids by their smaller lobes, and their presence in [1.1.1]propellane **1**. Firstly we study H_3C-C models of C-C bonds with frozen HCC angles reproducing the constraints of various degrees of “inversion”. Secondly, the molecular orbital (MO) properties of [1.1.1]propellane **1** and [1.1.1]bicyclopentane **2** are analyzed with the help of orbital forces as a criterion of bonding/antibonding character and as a basis to evaluate bond energies. Triplet and cationic state of **1** species are also considered to confirm the bonding/antibonding character of MOs in the parent molecule. These approaches show an essentially non-bonding character of the σ central CC interaction in propellane. Within MO theory, this bonding is thus only due to π-type MOs (also called ‘banana’ MOs or ‘bridge’ MOs) and its total energy is evaluated to ca. 50 kcal/mol. In bicyclopentane **2**, despite a strong σ-type repulsion, a weak bonding (15-20 kcal/mol) exists between both central CC, also due to π-type interactions, though no bond is present in the Lewis structure. Overall, the so-called ‘inverted’ bond, as resulting from a σ overlap of the two s-p hybrids by their smaller lobes, appears highly questionable.

Introduction

The nature of the central CC bonding in [1.1.1.] propellane **1** has been the subject of a number of studies, converging towards the possibility of a relatively strong C-C sigma “inverted bond”. This bond would result from the overlap of the two s-p hybrids by their smaller lobes.



1 **2**

Scheme 1

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On the one hand, based on the thermodynamics of the transformation **2** → **1** + 2 H ($\Delta E \approx 140$ kcal/mol), a bond energy of ca. 60 kcal/mol was deduced for the central C-C bond of **1**.[1,2,3] Localized MOs and bond indices also point at a significant interaction between the bridgehead carbons of propellane.[4] From VB calculations, the in situ bonding energy of this same bond was found to be ca. 77 kcal.mol^{-1}, only 19.4 kcal.mol^{-1} less than that of the C-C bond of ethane, due to the presence of "charge-shift" bonding.[5] On the other hand, this inverted bond involves a weak or even negative population overlap, and the total electron density in the bonding region was found similar for **1** and **2** (as shown in scheme 1, a σ bond is expected in **1** but not in **2**).[6] The HOMO of **1**, associated with the σ C-C, bond has been found to be antibonding on the basis of the MO energy variation as a function of the CC distance.[7] Moreover, an essentially non-bonding character of this HOMO was deduced from photoelectron spectra,[8] while electron attachment revealed a relatively low energy σ^* LUMO for a saturated hydrocarbon, which points at a weaker bonding.[9] A bond path with a critical point was found through X-ray study, but with no appreciable charge accumulation at this point.[10] It was thus suggested that the low energy difference between **1** + 2H and **2** could result from a strong four-electron repulsion between both C-H in **2** rather than from a strong CC bonding in **1**,[2] and thus that CC bonding in **1** should be ensured by 2-electron 3-centre interactions (or "banana bonds") arising from MOs located on the "wings" of propellane.

In this work, we will firstly study '*in silico*' models of inverted bonds at various degrees of inversion. Then, these models, as well of propellane **1**, (in ground, cationic and triplet states) and bicyclopentane are analysed by means of Dynamic Orbital Forces (DOF)[11] as a measure of the bonding/antibonding character of Molecular Orbitals (MO). We will end with conclusions on the existence of the "inverted bond" and on the nature of the central bond of propellane **1**.

We will focus in this paper in DOF as a central quantity to determine the nature and the strength of bonds. This quantity is the MO energy derivative with respect to a given geometrical parameter, generally a bond length. In this case, it is equal to the force exerted on the nuclei along this bond by removal of one electron from a given MO, in the frozen MO approximation. Indeed, according to Koopman's theorem, the energy ε_i of the i^{th} MO is:

$$\varepsilon_i = E^0 - E_i^+$$

where E^0 is the Hartree-Fock (HF) energy of neutral molecule, and E_i^+ is the energy of the cation resulting from the removal of one electron from the i^{th} MO. The derivative with respect to an internuclear distance R yields:

$$\frac{d\varepsilon_i}{dR} = \frac{dE^0}{dR} - \frac{dE_i^+}{dR}$$

If the geometry has been taken at its equilibrium value R_e in the neutral species, $dE^0/dR = 0$ and:

$$\left(\frac{d\varepsilon_i}{dR}\right)_{R=R_e} = -\left(\frac{dE_i^+}{dR}\right)_{R=R_e}$$

The DOFs must be distinguished from Bader's "static" forces[12] and have been successfully used to evaluate local MO bonding/antibonding character: a positive DOF value corresponds to a bonding MO[13] and *vice versa*. Moreover, it has been shown that this value is related in a semi-quantitative way to changes in some physical quantities upon ionization or protonation[14] and it is a useful tool in the study of reaction mechanisms.[15]

On the basis of DOFs, we will propose reasonable values of CC bond energies in **1** and in **2**.

Computational details

The C_2H_6 models of inverted bonds and their C-C bonding energies were computed at the CCSD(T)/cc-pVQZ level. All other systems were optimized at the MP2/cc-pVTZ level. The DOFs were computed by a small finite bond length difference (typically 2-8 10^{-3} Å); they are given in atomic units (hartree/bohr), at the HF/cc-pVTZ level. It should be noted that the DOFs may present some marginal error due to the impossibility to increment only one bond length in cyclic structures, keeping constant all the other geometrical internal parameters. In this case, we chose to keep all other bond lengths constant, which requires very small variations in the angles: for a bond variation of 0.004 Å, the angle variation is about 0.2°. In order to discard this source of error, we found that an angular deviation of 1° in the CCC angle of propane has a negligible effect on its DOFs with respect to CC bonds, producing a mean absolute variation of 0.6 10^{-3} a.u.

For open shell species, ROHF MOs were considered. The GAUSSIAN 09 series of programs[16] was used throughout this work.

Results and discussion

1. '*In silico*' models of "inverted" and "semi-inverted" CC bonds

The main problem to conclude on the strength of the inverted bond in propellane **1** is the evident impossibility to break this bond, in order to compute its dissociation energy, without destruction of the whole molecule.

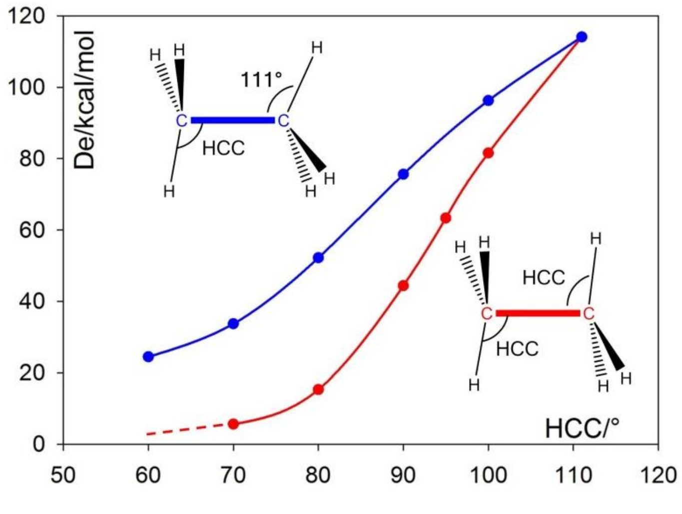


Figure 1. C-C bond dissociation energy *De* as a function of the HCC angles (CCSD(T)/cc-pVQZ), with respect to CH_3 units with the same geometry. Red curve: inverted CC bond (extrapolation to 60° was added with a broken line); blue curve: semi-inverted CC bond.

To bypass this difficulty, inverted bonds were studied using staggered C_2H_6 models in which the six HCC angles have been frozen from 111.2°, their value in ethane, down to 70°; the other parameters, namely CH and CC distances, were optimized. Bond energies *De* were calculated with respect to both isolated CH_3 moieties with frozen geometry so that the obtained energy is only due to the "inverted" interaction. Results are reported in Fig. 1 and Table 1. We observe that *De* decreases rapidly as the HCC angle closes and is nearly vanishing for HCC = 70°. In this case the CC equilibrium distance (2.9 Å) corresponds to a van der Waals complex more than to a classic CC bond. It should be noted that since neither the BSSE nor the zero point correction were taken into account, these values are presumably overestimated. No minimum was found for HCC = 60° (approximate value of the corresponding angle in **1**), thus suggesting a dissociation energy close to zero, as also supported by extrapolating of the curve in Fig. 1. Some eclipsed configurations have also been computed whose results are reported in Table 1.

Table 1. Inverted C_2H_6: C-C bond energies (De); equilibrium distances (Å) of CC (R(CC)) and CH (R(CH); "ec" stands for eclipsed conformation; CCSD(T)/cc-pVQZ level.

HCC	opt	100°	100°ec	95°	90°	90°ec	80°	80°ec	70°
R(CC)	1.527	1.628	1.667	1.709	1.830	1.902	2.231	2.318	2.9
R(CH)	1.091	1.085	1.0819	1.082	1.079	1.075	1.079	1.078	1.089
De$^{(a)}$	114.1	81.6	77.2	63.4	44.5	40.0	15.4	13.2	5.6

[a] with respect to $2CH_3$ of the same geometry;

Semi-inverted C_2H_6 bond energies have been computed similarly, with one CCH angle kept constant (111°), the other one decreasing from 100° to 60°. As expected, the bond energy decreases slower than for the inverted bond and drops down to ca. 26 kcal/mol for HCC = 60°.

Table 2. Semi-Inverted C_2H_6: C-C bond energies (De); equilibrium distances (Å) of CC (R(CC)); (R(CH1), CH bond length on inverted carbon; (R(CH2), CH bond length on non-inverted carbon; CCSD(T)/cc-pVQZ level.

HCC	opt	100°	90°	80°	70°	60°
R(CC)	1.527	1.576	1.648	1.766	1.937	2.119
R(CH1)	1.091	1.085	1.082	1.082	1.090	1.111
R(CH2)	1.091	1.091	1.090	1.090	1.088	1.087
De$^{(a)}$	114.1	97.6	76.9	53.6	35.1	25.9

[a] with respect to $2CH_3$ of the same geometry;

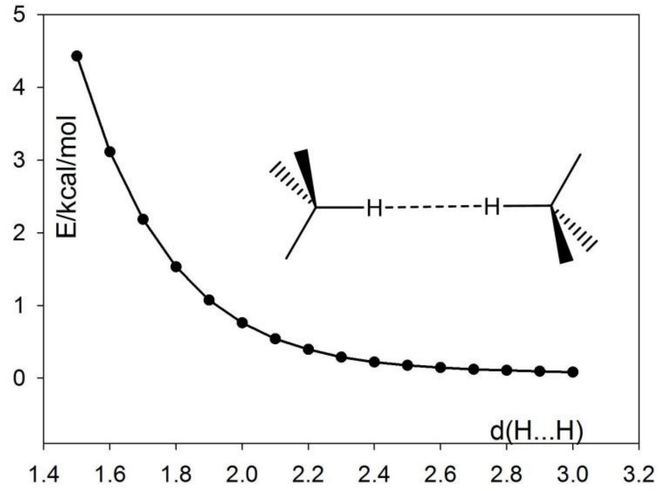


Figure 2. Interaction energy (kcal/mol) in H_3C-H…H-CH_3 as a function of H…H distance (Å).

In order to verify that the optimized C-C distances and thus bond energies are not controlled by H…H repulsions, we report in Table 3 d(H…H) distance of interacting hydrogen atoms in the structures of Tables 1 and 2. The repulsion energy for a couple H...H was evaluated by computing the energy of H_3C-H...H-CH_3 at various H...H distances (Fig. 2). Then the total H…H interaction energy for C_2H_6 was evaluated from these values. In staggered conformations, there are six equivalent H…H pairs, whereas in the eclipsed conformations, there are two non-equivalent sets of three H..H pairs.

Table 3. Hydrogen interactions in C_2H_6 species: d(H…H), distance (Å) of interacting hydrogens; Rep/HH, repulsion energy (kcal/mol) by couple of interacting hydrogens; Tot rep, total repulsion.

					Inverted C_2H_6					
HCC	opt	100°	100ec	95°	90°	90°ec	80°	80°ec	70°	
d(H…H)	2.59	2.27	2.04 [a] 2.72 [b]	2.18	2.12	1.90 [a] 2.66 [b]	2.14	1.94 [a] 2.68 [b]	2.38	
Rep/HH	0.16	0.32	0.65[a] 0.13[b]	0.40	0.51	1.10 [a] 0.10 [b]	0.47	0.94 [a] 0.11 [b]	0.21	
Tot rep	1.0	1.9	3.2	2.4	3.1	3.6	2.8	3.2	1.3	
					Semi-inverted C_2H_6					
HCC	opt	100°			90°		80°		70°	60°
d(H…H)	2.59	2.38			2.28		2.21		2.18	2.18
Rep/HH	0.16	0.23			0.32		0.35		0.4	0.4
Tot rep	1.0	1.4			1.9		2.1		2.4	2.4

[a] eclipsed H; [b] non-eclipsed H.

These results are summarized in Fig. 3. In Fig 3(a) the R(CC) equilibrium distance is plotted vs. d(H..H). In Fig. 3(b), the CC bond energy *De* is plotted vs. the total H…H repulsion energy. In both cases, there is no evident relationship between the two couples of quantities.

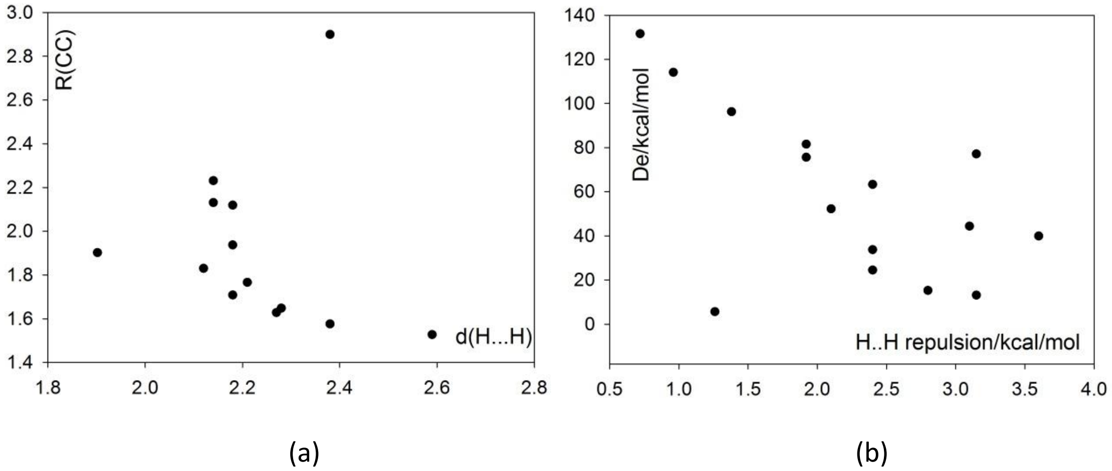


Figure 3. (a) Equilibrium CC distance in C_2H_6 vs. distance d(H…H) (Å) of nearest interacting hydrogens. (b) CC bond energy De vs. total H..H repulsion (from Tables 1-3).

For instance, for a distance d(H…H) ≈ 2.2 (Å), R(CC) may vary from ca. 1.7 Å to 2.2 Å. For a HH repulsion of 3.2 kcal/mol, *De* ranging from 13.2 to 77.2 kcal/mol are found.

A second example is the semi-inverted CH_3-C≡CH systems in which H…H repulsions are absent. The variation of *De* (MP2/cc-pVTZ) as a function of the HCC angle is displayed in Fig. 4. The bond energy drops from 156.4 kcal/mol at equilibrium HCC value to 62.9 kcal/mol for HCC = 60.

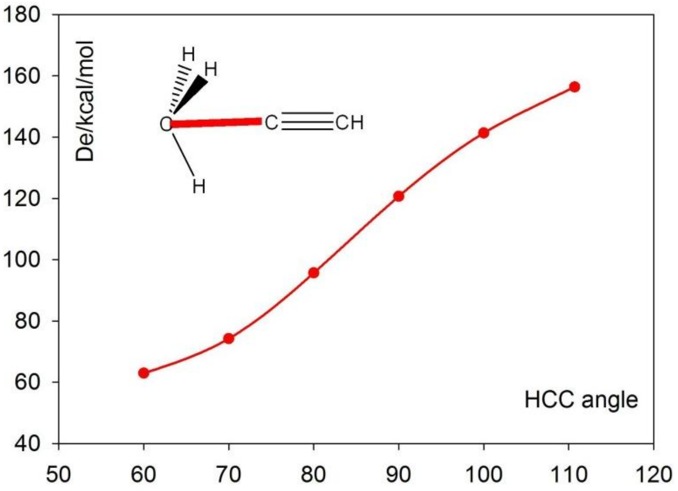


Figure 4. Semi inverted C-C dissociation energy *De* in constrained propyne systems (with respect to fragments with the same geometry).

These examples show that the bond energy decreases dramatically with the inversion of CH_3 group(s). In inverted C_2H_6, this energy becomes nearly zero for inversion angles of 60-70°. In the semi inverted C_2H_6 and CH_3–C≡CH, the bond energy decreases by 80 % and 60 % respectively.

2. Bonding analysis by Dynamic Orbital Forces (DOF) and evaluation of bond energies

*2.1. MO analysis of [1.1.1] propellane **1** and [1.1.1] bicyclopentane **2***

The valence shell MOs of **1** are displayed in Fig. 5. The MOs are labelled in order of decreasing energy from 1 (HOMO) to 13. We report the Dynamic Orbital Force (DOF) for each C-C bond.

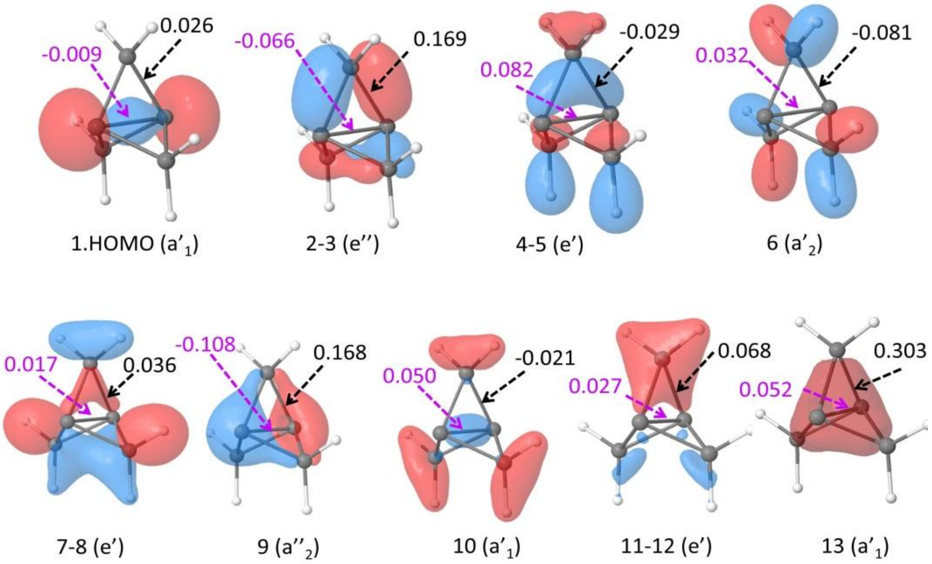
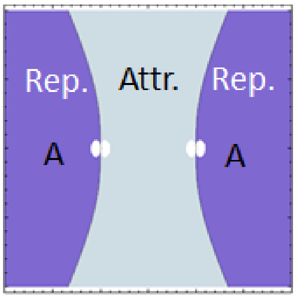


Figure. 5. Valence shell MOs of propellane. DOF (a.u.) of central (purple; left value) and wing (black; right value) CC bond. Only one MO of each degenerate set is reported

The HOMO a'$_1$, associated to the "inverted bond" of propellane, is slightly antibonding (negative DOF) along the central CC bond, as previously pointed out on the same grounds.[7] This result is somewhat counterintuitive because this MO has no nodal plane cutting the bond. It can be qualitatively understood from the fact that most of the electron density is located in the "repulsive" part of the space, as defined by Berlin in the case of a homonuclear diatomic molecule A_2[17]. As displayed in scheme 2, the presence of electron density in the internuclear part of the space (light blue) tends to attract each nucleus towards the other and thus has a bonding effect. On the contrary, electron density in the outer parts to the A-A segment (purple) tends to attract the closer nucleus more strongly than the farther one and has a repulsive, antibonding, effect.

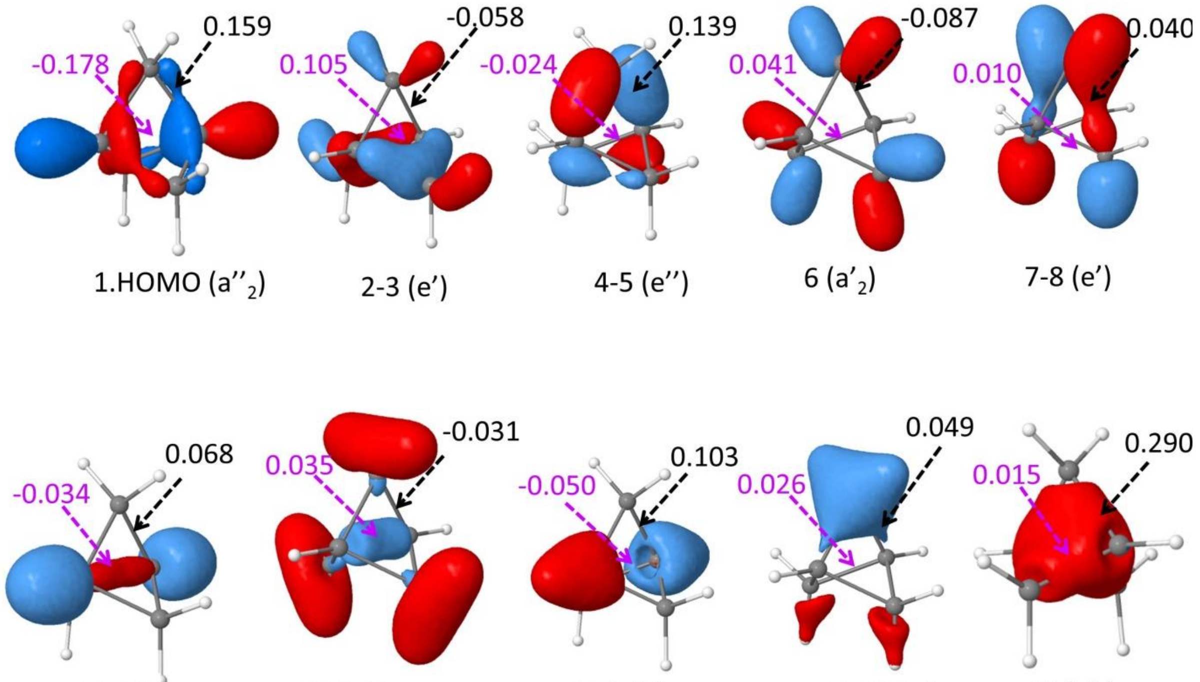


Scheme 2.

Note that similar MOs are found in more familiar systems, such as the highest σ_g^+ MO of N_2 (DOF = 0.047 a.u.), P_2 (DOF = -0.008 a.u.), and As_2 (DOF = 0.003 a.u.), and also the HOMO 5σ of CO (DOF = -0.067 a.u.)[14a]. These MOs are weakly or very weakly bonding or even antibonding. In particular, their

DOFs are consistent with the bond lengthening in N_2^+ and the bond shortening in CO^+, with respect to the neutral species. The σ_g^+ LUMO of C_2, in its dominant configuration, also belongs to the same "inverted" type, with a DOF of -0.003 a.u.[18]

In order to further delve on the nature of these orbitals, we have also analyzed [1.1.1]bicyclopentane **2.** The MOs of **2** mainly differ from the preceding ones by the HOMO a"$_2$, which is strongly antibonding, resulting from the 4-electron interaction of the σ orbitals of both C-H bonds at a very short CC distance (ca. 1.88 Å). Carbon-hydrogen bonding in the two C-H groups is essentially ensured by the HOMO (DOF = 0.064 a.u.) and the MOs 9 (DOF = 0.186 a.u.) and 11 (DOF = 0.109 a.u.).



1.HOMO (a''$_2$) 2-3 (e') 4-5 (e'') 6 (a'$_2$) 7-8 (e')

9 (a'$_1$) 10 (a'$_1$) 11 (a''$_2$) 12-13 (e') 14 (a'$_1$)

Figure 6. Valence shell MOs of bicyclopentane **2**. DOFs (a.u.) of the central (purple; left value) and wing (black; right value) CC bonds. Only one MO of each degenerate set has been reported

2.2. Evaluation of bond energies and σ/π partition

Although the sum Σ of DOFs over occupied MOs is not equal to the total force exerted by electrons on nuclei because the HF energy is not the sum of MO energies[19a], this quantity has been recognized as a comparative index of the strength of similar bonds.[19] Recently, it has been found that the CC bond energy in a series of hydrocarbons is linearly correlated to Σ. Moreover the σ/π partition of the total bonding was obtained by comparing the sums Σ_σ and Σ_π over occupied σ and π MOs, respectively.[18] These results require that the system is essentially mono-configurational. It is indeed the case for propellane as evidenced by the fact that its CASPT2 and MP2 energies differ by less than 0.01 a.u.[5] It also agrees with the fact that the LUMO a"$_2$ of propellane, out-of-phase counterpart of the HOMO, is strongly antibonding (DOF = -0.111 a.u.) and lies at relatively high energy. Moreover, the HOMO → LUMO triplet is 79 kcal/mol above the ground state[2] with a gap of ca. 4 eV between both SOMOs.

The DOFs are reported in Table 2 for the C_2H_6 model of inverted bond, in which we also report Σ_σ, (MOs of a_{1g} and a_{2u} symmetry) and Σ_π (MOs of e_u and e_g symmetry). As expected, Σ_π is weak, which means that π interactions play a minor role in the bonding.

Table 4. Inverted C_2H_6 with various HCH angles (see Fig. 1): DOF (a.u); Σ, sum of DOFs; Σ_σ, sum of DOFs of σ-type MOs (of a_{1g} and a_{2u} symmetry); Σ_π, sum of DOFs of π-type MOs (of e_g and e_u symmetry) over occupied MOs.

111.2°(a)		100°		95°		90°		80°		70°	
MO	DOF	MO	DOF	MO	DOF	MO	DOF	MO	DOF	MO	DOF
e_g HO	-0.056	a_{1g} HO	0.105	a_{1g} HO	0.094	a_{1g}	0.091	a_{1g}	0.043	a_{1g}	0.025
a_{1g}	0.118	e_g	-0.054	e_g	-0.053	e_g	-0.042	e_g	-0.034	e_g	-0.017
e_u	0.061	e_u	0.061	e_u	0.059	e_u	0.037	e_u	0.034	e_u	0.013
a_{2u}	-0.050	a_{2u}	-0.060	a_{2u}	-0.064	a_{2u}	-0.049	a_{2u}	-0.049	a_{2u}	-0.022
a_{1g}	0.128	a_{1g}	0.126	a_{1g}	0.118	a_{1g}	0.082	a_{1g}	0.063	a_{1g}	0.022
Σ_σ	0.392		0.340		0.299		0.248		0.114		0.050
Σ_π	0.020		0.028		0.024		0.020		0.000		-0.016
Σ	0.412		0.368		0.323		0.257		0.114		0.037

(a) optimized value

As displayed in Fig. 7, the calculated CC bond energies D_e in the C_2H_6 inverted series (Table 1) are correlated to Σ (Table 2).

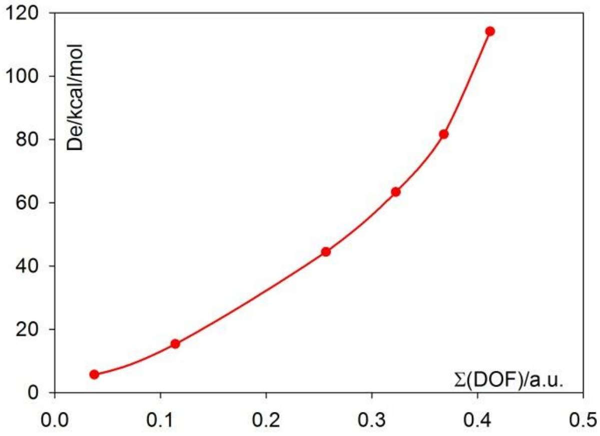


Figure 7. Bond energy of C_2H_6 as a function of Σ(DOF) (a.u.) from Tables 1 and 2.

The results of Fig. 7 can thus be used to propose, by interpolation, a reasonable approximate energy of a CC bond of a given Σ(DOF) in the range Σ = 0 - 0.45 a.u. It is important to note that the Σ values, though computed from a HF single configuration are well correlated with *De* values computed at a high level of correlation (CCSD(T)/cc-pVQZ).

Results for propellane **1**, the corresponding $^2A'_1$ cation and its A''_2 triplet state are given in Table 5. We report the DOFs of frontier MOs, the sum Σ for each bond (CC refers to the central bond and WCC to the other “wing” CC bonds) and the corresponding bond energies. For the central bond, we also report Σ_π corresponding to π-type MOs, and Σ_σ corresponding to σ-type MOs. To decide whether a given MO contributes to σ or π bonding on the central bond, we used the classical criterion of organic chemistry: a MO having a nodal surface containing the bond is π-type. Otherwise, the MO has a non-zero density on the axis containing the nuclei and it is of σ-type. In propellane (Fig. 5), the HOMO 1 and the MOs 9, 10, 13 contribute to σ bonding; the MOs of e’ or e’’ symmetry, possessing one nodal surface containing the central bond, and the MO 6 which possesses three nodal planes containing this bond are of π type, also called “bridge" MOs or “banana” MOs.

Most of these MOs also contribute to the bonding of the wing CC. Some of them, of e’ or e” symmetry (7-8) can be considered as σ MOs on these bonds, but some other MOs (4-5) may appear at the same time of σ type on some bonds and of π type on other ones.

Table 5. Propellane in ground, cationic ($^2A'_1$) and triplet ($^3A''_2$) states. DOF (a.u.) of frontier MOs; sums of DOFs (a.u.) over occupied MOs (Σ_σ: σ-contributing; Σ_π: π-contributing; Σ: total); *De*: bond energies (kcal/mol); R(CX) bond lengths (Å, MP2/cc-pVTZ). CC refers to the central bond, WCC to the wing CH_2-C bonds.

	Propellane (**1**) ($^1A'_1$)			(**1**)$^+$ ($^2A'_1$)		triplet (**1**) ($^3A''_2$)	
MO	DOF(CC)	DOF(WCC)	DOF(CH_2)	MO	DOF(CC)	MO	DOF(CC)
a_2"LUMO	-0.111	-0.022	-0.008	LUMO	-0.098	SOMO	-0.096
a_1' HOMO	-0.009	0.026	-0.011	SOMO	-0.005	SOMO	-0.028
Σ_σ	-0.029				0.042		-0.179
Σ_π	0.304				0.324		0.479
Σ	0.275	1.744	1.931		0.366		0.300
Σ/bond	0.275	0.291	0.322		0.366		0.300
De	48.1	51.4			80.5		53.2
R(CX)	1.596	1.517	1.082		1.540		1.806

The negative value (-0.029 a.u.) of Σ_σ at the central CC bond indicates that the total σ interaction is slightly repulsive: the so-called “inverted bond”, as arising from σ overlap of s-p hybrids by their smaller lobes, should actually have a slightly *destabilizing* contribution energy. It should be noted that the contributions of MOs 9, 10 and 13 (Fig. 5) to this σ bonding almost exactly cancel one another. The central bond is thus totally ensured by π-type (banana) MOs, as already concluded by Allen et al.[3] and its energy can be estimated to be ca. 50 kcal/mol, in agreement with previous evaluations.[1-3] Wing CC present a Σ value per bond (0.291 a.u.) slightly greater than that of the central bond (0.275 a.u.) and are thus expected to show a slightly greater energy (≈ 3 kcal/mol).

A possible objection to the preceding results could be the lack of correlation in the DOFs computed at the H-F level, which can be overcome by using KS MOs. The two B3LYP and the PBE1PBE functional were used for this purpose, with the same cc-pVTZ basis set. As landmarks, they give for the dissociation energy of F_2, ZPE corrected, 36.5 and 34.4 kcal/mol respectively for an experimental value of 37.0 kcal/mol. These results are reported in Table 6, together H-F ones for sake of comparison.

Table 6. DOFs of propellane at the cc-pVTZ/B3LYP, PBE1PBE and H-F levels. N° refers to the MO label in Fig. 5.; Σ_σ and Σ_π are the sums of DOFs over σ and π occupied MOs respectively; Σ, total sum of DOFs over occupied MOs.

MO	N° in Fig. 5	σ/π type	DOF		
			B3LYP	PBE1PBE	HF
a'_1 (HOMO)	1	σ	-0.035	-0.023	-0.009
e''	2,3	π	-0.052	-0.057	-0.066
e'	4,5	π	0.073	0.076	0.082
a_2'	6	π	0.028	0.029	0.032
e'	7,8	π	0.021	0.019	0.017
a_2''	9	σ	-0.093	-0.098	-0.108
a_1'	10	σ	0.040	0.044	0.050
e'	11,12	π	0.028	0.028	0.027
a_1'	13	σ	0.050	0.053	0.052
Σ_σ			-0.076	-0.049	-0.028
Σ_π			0.350	0.309	0.304
Σ			0.274	0.260	0.275

The DOF values obtained by the three methods are close one another. They differ generally by less than 0.01 a.u. The larger differences are found for the HOMO which is found significantly more antibonding for KS MOs (-0.035 a.u. for B3LYP and -0.023 a.u. for PBE1PBE vs. -0.009 for H-F). As a result the total σ bonding Σ_σ is found more negative at KS levels, but the total sums Σ are close one another at the three levels of calculations.

Further insight into the nature of the central C-C bond can be obtained from the analysis of cationic propellane $^2A'_1$. In this species, one electron is removed from the weakly antibonding HOMO of propellane and the bond length is moderately reduced, close to that of ethane C-C bond (1.527 Å in Table 1). The sum Σ_σ becomes slightly positive; moreover, the π-type interactions increase with respect to the neutral species. As a result, an overall bond energy of ca. 80.5 kcal/mol is found.

The repulsive σ interactions in propellane can be enhanced by electron excitation. In the triplet $^3A''_2$ state, one electron occupies the a''_2 SOMO which is rather antibonding. With respect to ground state species, we observe a stronger repulsive σ interaction compensated by an increased bonding π interaction leading to a total bond energy of ca. 55 kcal/mol.

Results for bicyclopentane are given in Table 7. Alike the propellane case, the a'_2 MO (n° 6 in Fig. 6) should be considered as participating to a π-type interaction.

Table 7. Bicyclopentane in ground ($^1A'_1$) states. DOF (a.u.) of highest occupied MOs; sums of DOFs over occupied MOs (Σ_σ: σ-contributing; Σ_π: π-contributing; Σ: total); De: bond energies (kcal/mol); R(CX) bond lengths (Å, MP2/cc-pVTZ). CC refers to the central bond, WCC to the wing CH_2-C bonds.

	Bicyclopentane (**2**) ($^1A'_1$)			
	DOF(CC)	DOF(WCC)	DOF(CH)	DOF(CH_2)
a_2''HOMO	-0.178	0.159	0.064	-0.034
Σ_σ	-0.430		0.502	1.519
Σ_π	0.556			
Σ	0.126	1.680	0.502	1.519
Σ/bond	0.126	0.280	0.251	0.253
De	17.3[a]	49.2[a]		
R(CX)	1.8758	1.5503	1.0874	1.0895

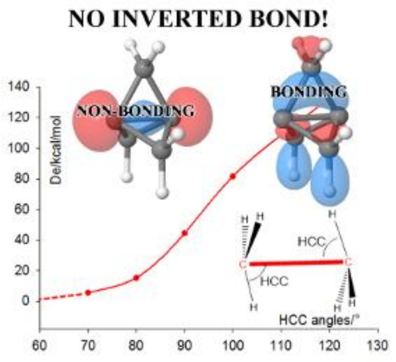
[a] Evaluated from Fig. 7 correlation;

In bicyclopentane **2**, Σ_σ is strongly negative along the central CC couple, mainly due to the strongly antibonding character of the HOMO. This repulsive interaction is compensated by a strong bonding π-type interaction, resulting in weakly positive bond energy of ca. 20 kcal/mol. Though these small differences must be considered with caution, the other "wing" C-C bonds look slightly stronger in **1** than in **2** by about 3 kcal/mol.

Conclusion

The C_2H_6 models of 'inverted' C-C bonds suggest that the bond energy decreases rapidly with the inversion angle and tends to zero, if not negative values, with the same angular constraints as in propellane. This trend is confirmed by models of 'semi-inverted' bonds C_2H_6 and CH_3-C≡CH. Moreover, MO analysis using dynamic orbital forces (DOF) shows that the σ-type interactions in the central CC bond of propellane are slightly repulsive, as well with H-F as KS MOs. This bonding is thus only due to π-type (or 'banana') bonds. From the correlation between the bond energy and the sum of DOFs over occupied MOs, an energy of ca. 50 kcal/mol is proposed for this bond. On the same grounds, a weak bond (15-20 kcal/mol) should exist between the corresponding carbon atoms of bicyclopentane **2** despite a strong σ-type repulsion and the absence of a formal bond.

Keywords: [1.1.1]propellane , Inverted bond, Orbital Force, Bond energy.



The ‘inverted bonds’ revisited. Analysis of ‘*in silico*’ models and of [1.1.1]Propellane using Orbital Forces

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“In silico” models and MO analysis using Dynamic Orbital Forces (DOFs) lead to the conclusion that the so-called “inverted bond” in propellane (σ bond resulting from overlap of the smaller lobes of s-p hybrids) has an energy close to zero. The bonding is only due to π-type (banana) interactions with an energy of about 50 kcal/mol.
Though there is no formal bond and a strong σ repulsion, a weak bonding (ca. 20 kcal/mol) exists between the central CC atoms of bicyclopentane, also due to π interactions.

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