From “inverted” to “superdirect“ bonds: a general concept connecting substituent angles with sigma bond strengths. The case of the CC bonds in hydrocarbons.

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Abstract. The C-C dissociation energy with respect to geometry frozen fragments (BE) has been calculated for C_2H_6 as a function of θ = H-C-C angles. BE decreases rapidly when θ decreases from its equilibrium value to yield the so-called “inverted bonds” for $\theta < 90°$; on the contrary BE increases when θ increases to yield somehow “superdirect” bonds, following a sigmoidal variation. The central bond in Si_2H_6, Ge_2H_6 and N_2H_4 as well as the C-H bond in CH_3-H behaves similarly. The concept of “invertedness”/”directedness” is generalized to any CC sigma bond in hydrocarbons and characterized by the mean angle value $<\theta>$ of substituents. Using dynamic orbital forces (DOF) as indices, the intrinsic σ bond energies are studied as a function of $<\theta>$ for formally single bonds in a panel of 22 molecules. This energy decreases from the strongest “superdirect” bonds in butadiyne, ($<\theta> = 180°$) or tetrahedrylacetylene to the weakest “inverted bond” in cyclobutene, tetrahedrane, bicyclobutane and [1.1.1]propellane ($<\theta> = 60°$), according to a sigmoidal variation. The $<\theta>$ parameter appears as a crude, but straightforward and robust, index of strain in cyclic molecules. Sigma bonds in multiple bonds of a panel of 11 molecules have most of time $<\theta>$ values less than 90° and are significantly weaker than standard single bonds. Thus they can be considered as formally inverted or near inverted.

Introduction

In a recent publication, we revisited the properties of the so-called “inverted bond” in [1.1.1]propellane (Figure 1).[1] Let us recall that inverted bonds result from the overlap of s+p hybrids by their smaller lobe (Figure 1), by contrast to “normal” or “direct” bonds in which

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the overlap occurs between their bigger lobes. The energy of the central CC bond of propellane was evaluated[2] to ca. 60 kcal/mol and this unexpected high value was the subject of many works.[3] Its origin was attributed either to a strong σ bond of "charge shift" nature[3b] or to π-type banana bonds ensured by the CH_2 bridges.[2c]

In ref 1, we used C_2H_6 models to mimic *in silico* the CC bond inversion by decreasing the θ = HCC angle from its optimized value, close to 111°, down to 70°. The CC dissociation energy, computed with respect to geometry frozen CH_3 moieties, was found to decrease rapidly and by extrapolation should tend to zero for HCC = 60° — the value in propellane. The use Dynamic Orbital Forces (DOF) as indices of bond strengths confirmed this result: the intrinsic σ bond energy in propellane should be near zero, and thus the CC bonding is essentially π in nature. In a response by Braïda et al.,[4] this result was contested, arguing that, due to its charge shift nature, the bond strength in propellane could not be evaluated using DOFs.

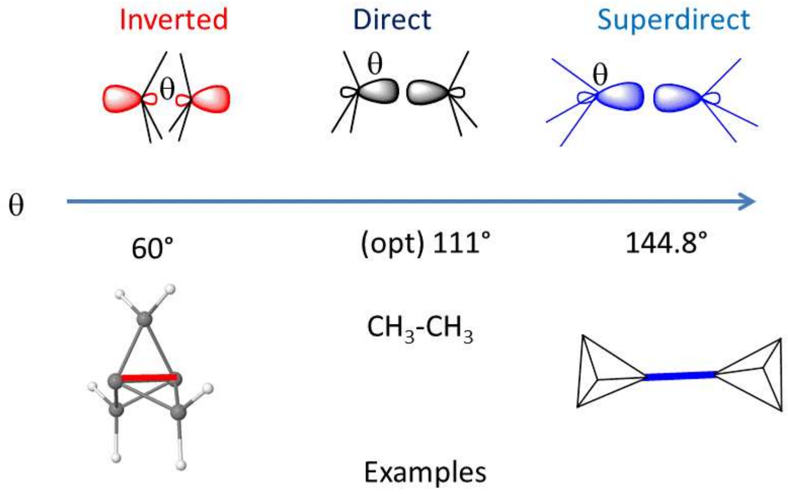


Figure 1. "Inverted", "direct" and "superdirect" bonds according to the θ angle of substituents. [1.1.1]Propellane, ethane and tetrahedryltetrahedrane exemplify these three types of bonds respectively.

By contrast, in some C-C bonds, the substituent angles are significantly greater than their value in ethane, with an increase of the bond energy. Though the unsubstituted molecule is unstable,[5] tetrahedryl-tetraedrane (Figure 1) is the limiting example of such a situation, with substituent angles close to 145° and a central bond remarkably strong (136 kcal/mol) and short (1.426 Å)[6] . We propose the term "superdirect" for such bonds. Thus, as displayed in Figure 1, sigma bonds can be classified into “inverted”, “direct” and “superdirect” according to the value of the θ angle.

In the present work, our aim is to generalize the concept of invertedness vs. directedness to any sigma CC bond in hydrocarbons, in relation with its strength. In a first step C_2H_6 and related models will offer an *in silico* overview of this relation. Then we will characterize the degree of invertedness/directedness/superdirectedness by setting a “mean substituent angle” $<\theta>$ and we will consider the relation of this parameter with σ bond strengths in a panel of 33 molecules. For this purpose, the Dynamic Orbital Forces (DOF) will be used as indices of intrinsic bond energy and as a tool of σ/π partition.

Computational Details

Geometry optimization and bonding energies with respect to geometry frozen fragments have been performed at the CCSD(T)/cc-pVQZ level for C_2H_6 and CH_3-H models, and at the MP2/cc-pVTZ level for Si_2H_6, Ge_2H_6 and N_2H_4. The geometry of molecules **1**-**33** was also optimized at the MP2/cc-pVTZ level. The derivatives of the canonical molecular orbitals were calculated, with the same basis set as geometry optimization, by a finite difference of bond lengths of 0.002 Å to 0.004 Å according to the case, thanks to a home-made script. The Gaussian09 program was used throughout this work.[7]

Results and discussion

1. *In silico* C_2H_6 and related models

1.1. Influence of HCC angles on CC bond energy in C_2H_6

In the C_2H_6 model, all six θ = HCH angles are frozen from 70° to 145°. After optimization of the remaining geometrical parameters, the C-C bond energy (BE) with respect to geometry frozen CH_3 moieties has been computed at the CCSD(T)/cc-pVQZ level. In this model (Table 1 and Figure 2), BE decreases rapidly when θ decreases from the optimized geometry to yield an inverted bond; it increases significantly when θ increases to yield a superdirect bond from the limit of ca. 120°.

Table 1. The C_2H_6 model. Geometrical parameters R(Å) and bonding energy BE (kcal/mol, with respect to two CH_3 at frozen geometry) as function of θ (CCSD(T)/cc-pvQZ). The results for θ ≤ 111.2° are taken from ref. 1.

	C_2H_6							
θ	140°	130°	120°	opt (111.2°)	100°	90°	80°	70°
R(CC)	1.422	1.448	1.483	1.527	1.628	1.830	2.231	2.9
R(CH)	1.135	1.111	1.097	1.091	1.085	1.079	1.079	1.089
BE	152.8	145.0	131.6	114.1	81.6	44.5	15.4	5.6

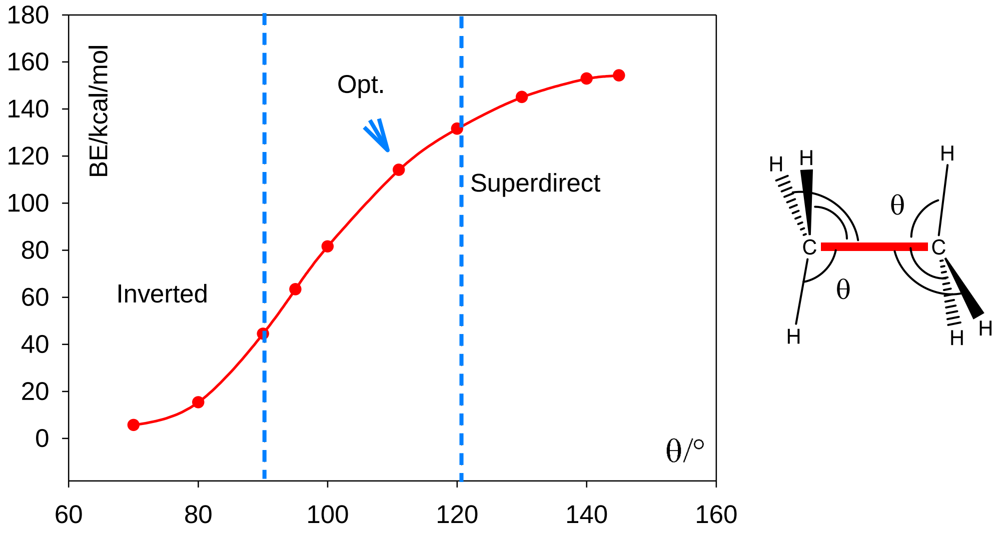
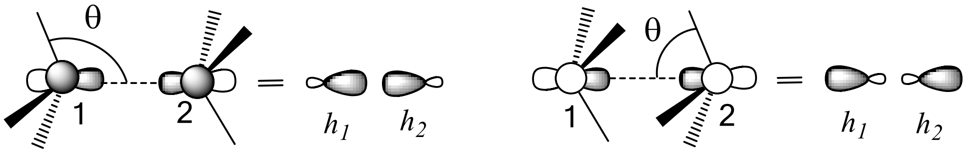


Figure 2. CC bond energy (BE) in C_2H_6 with respect to geometry frozen CH_3 fragments as a function of θ = HCC angles (θ = 111.2° optimized value); CCSD(T)/cc-pvQZ.

1.2. Qualitative interpretation

The overall sigmoidal shape of BE curve as a function of θ can be interpreted qualitatively by an approximate evaluation of the overlap of both s+p hybrids, h_1 and h_2 (Figure 3).



Direct bonding

Inverted bonding

Figure 3. Overlap in direct and inverted bonding.

The hybrids h_1 and h_2 are written as:

$$h_1 = \alpha s_1 + \beta p_1$$
$$h_2 = \alpha s_2 + \beta p_2$$

with $\alpha^2 + \beta^2 = 1$. Setting $\beta > 0$:

$$\alpha < 0 \text{ for } \theta < 90°$$
$$\alpha = 0 \text{ for } \theta = 90°$$
$$\alpha > 0 \text{ for } \theta > 90°$$

The theoretical limits of θ are 0°, with $\alpha = -\beta = -1/\surd 2$ and 180°, with $\alpha = \beta = 1/\surd 2$. The corresponding hybridization states can be referred to as sp^{-1} and sp respectively. Between these limits, the following hybridization states are encountered: sp^{-2} (α = -1/√3), sp^{-3} (α = -1/2), s^0p (α = 0), sp^3 (α = 1/2), sp^2 (α = 1/√3). The following values of α for CH_3 are obtained with the minimal basis STO-3G for CH_3 and various θ (Table 2).

Table 2. Coefficient α of the s AO in the CH_3 SOMO hybrid as a function of θ angle (see Figure 3).

θ	**60**	**70**	**80**	**90**	**100**	**110**	**120**	**130**
α	-0.601	-0.483	-0.294	0.000	0.294	0.483	0.601	0.643

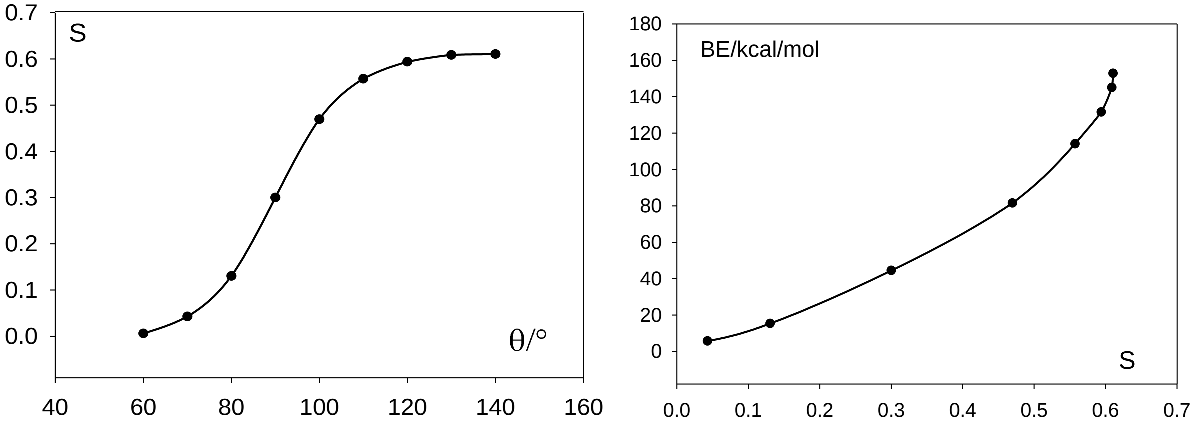
The overlap S of h_1 and h_2 is:

$$S = \langle \alpha s_1 + \beta p_1 | \alpha s_2 + \beta p_2 \rangle = \alpha^2 \langle s_1 | s_2 \rangle + \beta^2 \langle p_1 | p_2 \rangle + 2\alpha\beta \langle s_1 | p_2 \rangle$$

To a first approximation, the three atomic overlaps are close to $S_0 = 0.3$ at CC distances of 1.4-1.6 Å:

$$S \approx S_0(\alpha^2 + \beta^2 + 2\alpha\beta) = S_0(1 + 2\alpha\beta)$$

The overlap S as a function of θ has the same sigmoidal shape as the bonding energy (Figure 3(a)). Moreover, despite the crudeness of the approximations involved, the bonding energy is connected to S, nearly linearly for θ < 120° (Figure 3 (b)). Thus it appears that the bonding energy is closely related to the overlap at the standard bond length distance (≈ 1.5 Å), controlled by the hybridization state of the CH_3 semi-occupied AO according to the θ angle of deformation. Indeed, the final optimized CC distance involves other parameters as evidenced by energy decomposition analysis.[8]



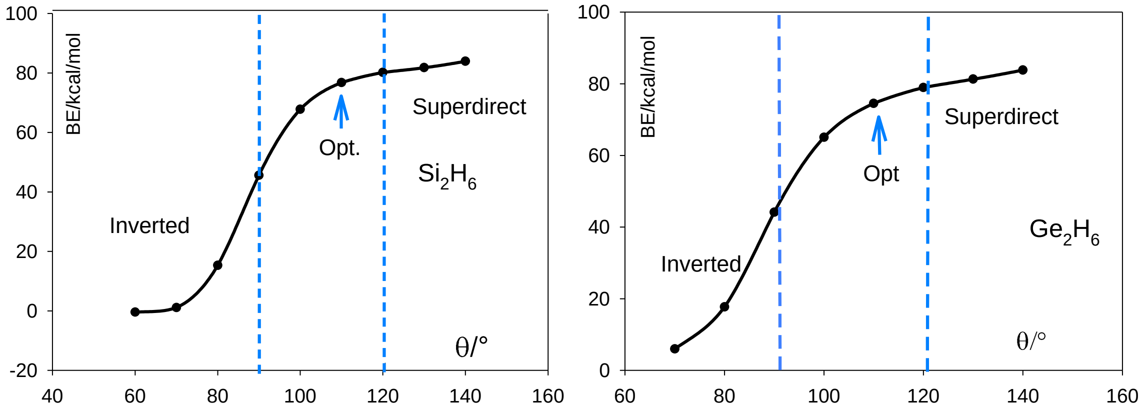
(a) (b)

Figure 3. (a) Variation of overlap S with θ in C_2H_6 model 1, for a CC distance ≈ 1.5 Å. (b) Variation of CC bond energy BE (from Table 1) as a function of S.

1.3. Related models: Si_2H_6, Ge_2H_6, N_2H_4 and CH_4

Though we are mainly interested in CC bonds in this work, we examined some models involving other bonds to compare their behaviour when similar angle constraints are imposed.

Two heavier systems, Si_2H_6 and Ge_2H_6, have been studied at the MP2/cc-pVTZ level following the approach of the C_2H_6 model. Figures 4(a) and 4(b) display the variation of BE as a function of the θ angles H-Si-Si and H-Ge-Ge respectively. The two curves are very similar. They have also the same general shape as for C_2H_6, with a weaker BE increase in the superdirect region (θ > 120°). It appears that the decrease of the ns-np gap in these both species, with respect to C_2H_6, is only of minor consequence as compared to the angle variation.



(a) (b)

Figure 4. Central bond energies of Si_2H_6 (a) and Ge_2H_6 (b) as functions of θ angles (H-Si-Si and H-Ge-Ge respectively).

The BE of the NN bond of NH_2-NH_2 in D_{2d} symmetry was also studied as a function of θ = HNN angles. The dissociation energy was computed with respect to geometry frozen NH_2 fragments in their $^2A_1$ state. It should be noted that N-N bond breaking results in the formation of two NH_2 radicals possessing a lone pair in a 2p AO and a semi occupied s+p hybrid. In its optimized geometry, this state is ca. 34 kcal/mol above the $^2B_1$ ground state.[9] Thus the value of BE in geometry optimized N_2H_4 lies at 68 kcal above the NN dissociation energy into $2NH_2$ in their ground state.

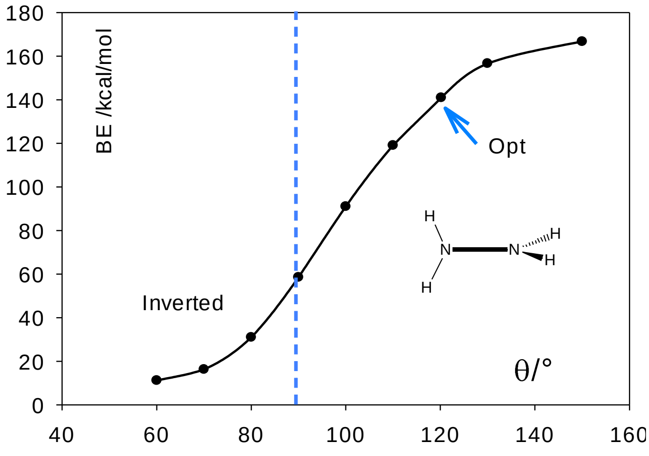


Figure 5. N-N bond energy in N_2H_4 (D_{2d}) as a function of θ = H-N-N angles.

Finally, we studied the energy of one C-H bond in CH_4 as a function of the θ pyramidalization angle of the CH_3 moiety. Results in Table 3 and Figure 6 are similar to the preceding ones. Nevertheless, because we deal here with the deformation of only one CH_3 group, yielding either “semi-inverted” or “semi superdirect” bonds, the relative variation of BE is smaller than in the case of C_2H_6 (cf. Figure 2).

Table 3. H_3C-H. Geometrical parameters R (Å) and bond energy BE of CH (kcal/mol, with respect to H and CH_3 at frozen geometry) as function of θ; opt = 109.5°; CH1 refers to H in CH_3 group; CCSD(T)/cc-pVQZ level of calculation.

				H_3C-H					
θ	140°	130°	120°	opt	100°	90°	80°	70°	60°
R(CH)	1.063	1.068	1.076	1.087	1.105	1.132	1.174	1.229	1.290
R(CH1)	1.134	1.108	1.095	1.087	1.085	1.084	0.876	1.003	1.130
BE	138.4	134.1	127.7	119.4	107.5	90.6	70.8	54.1	44.9

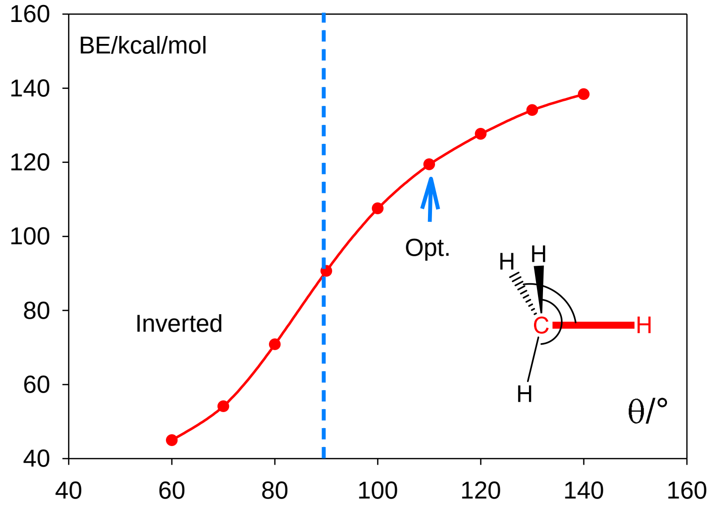


Figure 6. CH bond energy in H_3C-H (red bond) as a function of θ = HCH angles.

All studied models agree with the fact that the bond energy is strongly dependent on the substituent angles: it decreases rapidly with the inverted character of the bond and increases with its superdirect character. These phenomena follow the variation of the hybridization of the s+p AOs overlapping in the bond formation, controlled by these angles. Specifically, BE increases with the s (algebraic) coefficient in the s+p hybrids. This result is well-known for “direct” C-H bonds with aliphatic (sp^3), ethylenic (sp^2) and acetylenic (sp) carbons[10]. It has been also pointed out with direct C-C bonds[11], for example regarding the strong central bond of tetrahedryl-tetraedrane.[6b,12]

2. Inverted, direct, and superdirect bonds: generalization for sigma CC bonds in hydrocarbons

2.1. Mean angle <θ> of substitution

The preceding models preserve a symmetry axis along the bond under scrutiny with equal angles of H substituents on each heavy atom. We will now extend the inverted/direct/superdirect character to any CC σ bond in hydrocarbons, be it formally a single bond or a σ bond in a formally multiple bond. For this purpose, we define a <θ> parameter as simply the mean value of the angles of the six substituents on both carbon atoms; the π bonds are treated as σ ones in these calculations. Two examples are given in Figure 7.

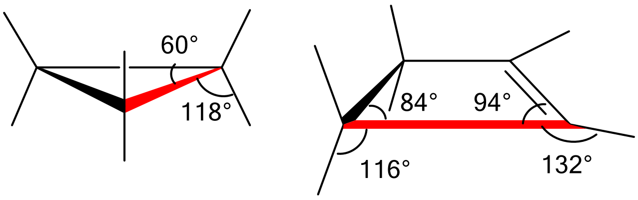


Figure 7. Calculation of the <θ> angle for the red bond in cyclopropane and cyclobutene.

In cyclopropane, the red bond has 4 H at 118° and two C at 60°, yielding <θ>≈ 99°. In cyclobutene, the red bond is considered as having 2 C at 94°, 1 H at 132°, 1 C at 84° and 2H at 116.° yielding <θ> = 106°. This way, the central C-C bond in butadiyne HC≡C—C≡CH has the <θ> theoretical maximum value of 180°. In formally multiple bonds, the <θ> angle is determined in a similar way. For example, in acetylene H-C≡C-H, the σ CC bond in considered as having 4 C at 0° and 2 H at 180°, yielding <θ> = 60°.

2.2. Dynamic orbital forces as index of intrinsic bond energy and tool of σ/π partition

For the study of the relation between σ bond strength and <θ> in real systems, CC bonds of various <θ> were considered in a panel of 33 molecules (Tables 4 and 6). In many of these cases, the BE of C-C bonds can no longer be computed in the same way as in the first section. Thus we will use the dynamic orbital forces (DOF)[13] as indices of bond energies.

The derivative of the i^{th} canonical MO energy ε_i with respect to a bond length (R(CC) in the case of a CC bond) has already been used to characterize the bonding/antibonding character of the MO with respect to this bond.[14] Also it has been shown that a MO of positive DOF has a positive contribution to the dissociation energy.[15] The sum Σ_{tot} of these derivatives over valence occupied MOs by n_i electrons can be decomposed into σ (Σ_σ) and π (Σ_π) components:

$$\Sigma_{tot} = \sum_i^{occ} n_i \frac{d\varepsilon_i}{dR(CC)} = \sum_j^{\sigma occ} n_j \frac{d\varepsilon_j}{dR(CC)} + \sum_k^{\pi occ} n_k \frac{d\varepsilon_k}{dR(CC)} = \Sigma_\sigma + \Sigma_\pi$$

It has been recognized that Σ_{tot} is an index of the "bond strength", as far as the molecule is satisfactorily described at the Hartree-Fock (H-F) level.[16,17] However Σ_{tot} is an intrinsic quantity of the system, whereas the bond energy dissociations with respect to geometry frozen fragments (BE) considered in the preceding sections involve the electronic relaxation of fragments and thus some reorganization energy. This tends to lower BE with respect to the intrinsic bond energy, but this difference should be small if the two following conditions are fulfilled: (i) the bond is symmetrically or nearly symmetrically substituted, resulting in a negligible electron transfer by bond dissociation and (ii) no significant stabilization of the radicals obtained occurs by conjugation or hyperconjugation. In Figure 8, we report Σ_{tot} for the model C_2H_6 and various CC bonds (taken from ref 17). We observe an excellent linear correlation ($R^2 = 0.98$) of BE of CC bonds and Σ_{tot} in the series C_2H_2, C_2H_4, C_6H_6, C_2H_6 and C_3H_6 (black line in Figure 8). Regarding the C_2H_6 model with various θ values (red curve in Figure 8), the curve merges perfectly with the preceding black line for $\Sigma_{tot} > 0.4$. For smaller Σ_{tot} values, the slope decreases and BE tends to zero for $\Sigma_{tot} \approx 0$.

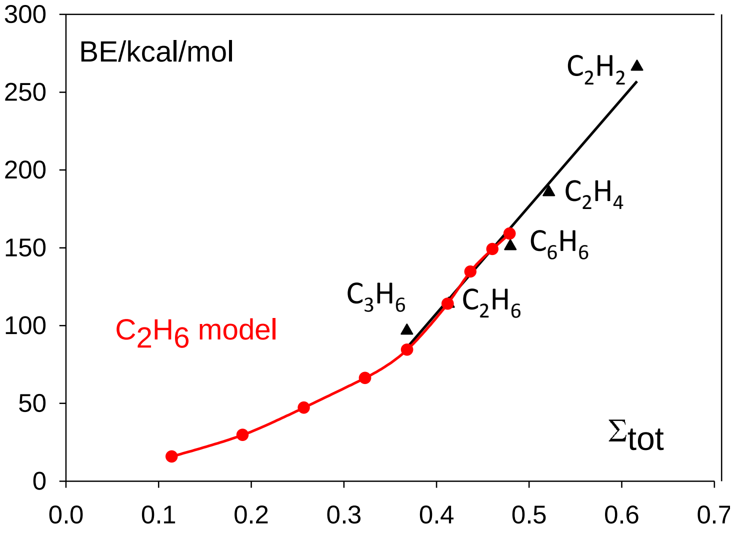


Figure 8. Bond energy (kcal/mol) with respect to geometry frozen fragments (MP2/cc-pVTZ) as a function of Σ_{tot} (a.u.).

This way, Σ_{tot}, though computed from H-F level MOs, is correlated to CC bond strength. This empirical observation is further supported by a large amount of evidence regarding bond energies. Indeed, a very good correlation (R^2 = 0.97) is found with respect to BE values calculated at the DFT ωB97XD/aug-qzvp level for molecules **1**, **3**, **12**, **13**, **24**, **27, 32** of Tables 4 and 6.[18] Moreover, Σ_{tot} can be compared with intrinsic bond energies computed from AIM critical point properties and bond paths (using, of course, correlated electron densities).[10,19] A rather good linear correlation is again obtained (R^2 = 0.94) with the set of molecules **1**, **4**, **8**, **9**, **12**, **13**, **17**, **18**, **24**, **27**, **28**, **32** of Tables 4 and 6. We thus consider Σ_{tot} as a straightforward (even predictive) index allowing the comparison of the CC intrinsic bond energies in hydrocarbons, Σ_σ and Σ_π reflecting their relative σ and π components.

2.3. Sigma CC bond energy and mean angle of substitution <θ>

2.3.1. Formally single bonds

In Table 4, we report the values of Σ_{tot}, Σ_σ and Σ_π in a panel of formally single C-C bonds by order of decreasing values of <θ> from 180° to 60°. The concept of directedness/invertedness concerns σ bonds, and thus we will be interested mainly in the Σ_σ component, though Σ_{tot} and Σ_π could also offer useful information.

Table 4. Values of Σ_{tot} , Σ_σ, Σ_π (a.u.); % of Σ_π in Σ_{tot} and the corresponding values of <θ> (°) for formally single C-C bonds (TET = tetrahedryl; BCP = bicyclopentyl; CUB = cubyl).

Label	**Molecule**	$\boldsymbol{\Sigma_{tot}}$	$\boldsymbol{\Sigma_\sigma}$	$\boldsymbol{\Sigma_\pi}$	**% π**	**<θ>**
1	$HC\equiv C-C\equiv CH$	0.513	0.450	0.064	12.4	180
2	$TET-C\equiv CH$	0.527	0.437	0.090	17.1	163
3	TET—TET	0.468	0.447	0.021	4.5	145
4	$CH_3-C\equiv CH$	0.458	0.415	0.042	9.1	145
5	$TET-CH_3$	0.495	0.442	0.053	10.1	128
6	BCP—BCP	0.489	0.434	0.055	11.3	127
7	CUB—CUB	0.478	0.420	0.058	12.1	125
8	$CH_2=CH-CH=CH_2$	0.478	0.433	0.045	9.4	121
9	$CH_3-CH=CH_2$	0.418	0.399	0.019	4.5	116
10	$Ph-CH_3$	0.415	0.397	0.019	4.6	115
11	$(CH_3)_3C-C(CH_3)_3$	0.439	0.392	0.048	10.8	111
12	CH_3-CH_3	0.413	0.392	0.021	4.9	111
13	cyclohexane	0.445	0.425[a]	0.02[a]	4.5[a]	110
14	cyclopentane	0.420	0.403	0.017[b]	4.3	108
15	cyclobutene (2-3)	0.445	0.400	0.045	10.1	106
16	cyclobutene (3-4)	0.404	0.396	0.008	2.0	105
17	cyclobutane	0.408	0.401	0.007[b]	1.7	105
18	cyclopropane	0.364	0.368	-0.004	-1.1	99
19	cyclopropene	0.281	0.283	-0.002	-2.0	88
20	tetrahedrane	0.353	0.278	0.075	21.2	88
21	bicyclobutane[c]	0.360	0.217	0.143	39.7	82
22	[1.1.1]Propellane[c]	0.275	-0.029	0.304	110.5	60

[a] Estimated on the basis of the same Σ_π =0.02 a.u. as **11**. [b] The π MOs have been visually identified, which can lead to some uncertainty ; [c] central bond (see Fig 10).

Molecules **1**-**8** can be considered as having a superdirect bond, with Σ_σ ranging from 0.415 up to 0.450 a.u. for butadiyne **1,** which has the maximum theoretical value of <θ> (180°). For the direct bonds in molecules **9**-**17,** Σ_σ is generally close to 0.4 a.u. Ethane **12** can be taken as the prototype of "standardl" direct CC bond with Σ_σ = 0.392 a.u. Cyclopropane **18**, though having formally direct CC bonds (<θ> = 99°) has a lower Σ_σ of 0.368 a.u. due to ring strain. Molecules **19**-**21** possess inverted bonds and Σ_σ less than 0.283 a.u., corresponding to strong ring strains, down to a slightly negative value for propellane **22** (-0.029 a.u.) with <θ> = 60°.

We thus observe (Figure 9) a general increase of Σ_σ with $<\theta>$, following the same sigmoidal shape as observed for the models of sections 1 and 3. As a landmark, we report on the same figure the variation of Σ_σ for the C_2H_6 model (red curve), at the same calculation level, showing that the behaviour of real bonds is quite similar to that of the C_2H_6 model.

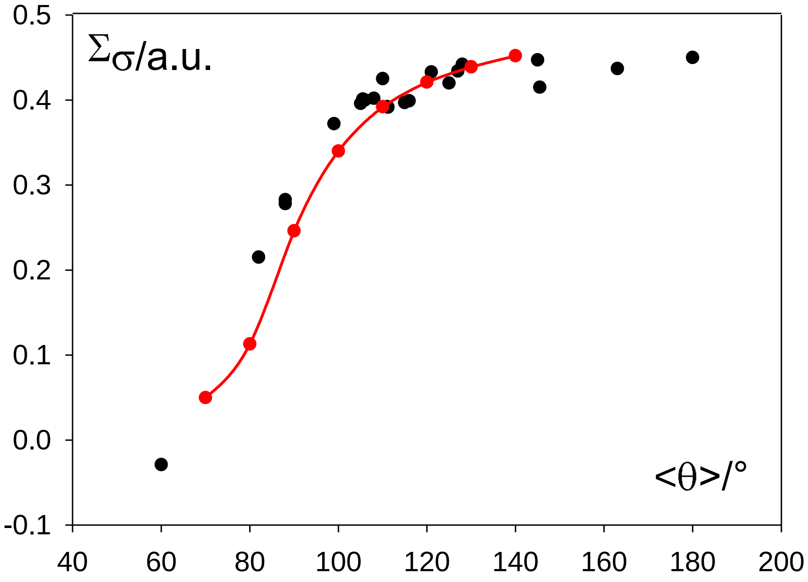
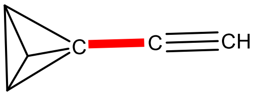
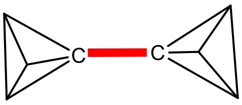
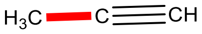
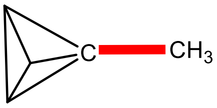


Figure 9. Σ_σ (a.u.) values of molecules 1-22 with respect to the mean substituent angle $<\theta>$ (°). The red curve corresponds to C_2H_6 model.

Bond energies and bond lengths have been calculated for the five superdirect CC bonds in **1**-**5** and are reported in Table 5 (see also data in Table 4). The BE values should be considered with some caution because the criteria (i) and (ii) of section 3.2 are not always fulfilled. Nevertheless, molecules **1** and **2** have the strongest bonds and the greatest Σ_{tot} values. In can be noted that the high BE in butadiyne **1** as compared to that of ethane **12** is due to σ strengthening ($\Delta\Sigma_\sigma$ = 0.058 a.u.) more than to conjugation ($\Delta\Sigma_\pi$ = 0.043 a.u.). Also, it has been proposed that the short bond of **3** originates equally both from its high s character and from hyperconjugation;[20] but in the present work this term appears weak, with only 4.5 % contribution of π MOs to Σ_{tot}. This is further supported by the 12% of π energy that was determined from Energy Decomposition Analysis.[6b]

The value of Σ_{tot} in tetramethylbutane **11** (0.439 a.u.) suggests that its intrinsic bond energy is greater than that of ethane **12** (0.413 a.u.) though its experimental dissociation energy is significantly smaller (78.6 kcal/mol vs. 90.2 kcal/mol).[21] Nevertheless, the BE of both species with respect to geometry frozen fragments (MP2/cc-PVTZ) are nearly equal (113.0 kcal/mol for **11** and 113.9 for **12**). Moreover, the electronic relaxation in $Me_3C^{\cdot}$ radical involves a significant stabilization by hyperconjugation, which leads to an underestimation of the calculated BE of **11** with respect to the actual intrinsic value.

Table 5. Some superdirect CC bonds (in red): Σ_{tot} and Σ_{σ} (a.u.); bond energy (BE) with respect to geometry frozen fragments (kcal/mol) and bond length R(CC) (Å) (MP2/cc-pVTZ).

	Σ_{tot}	Σ_{σ}	% π	R(CC)	BE	<θ>
 **1**	0.513	0.450	12.4	1.368	171.8	180
 **2**	0.527	0.437	17.1	1.394	161.0	163
 **3**	0.463	0.447	4.5	1.419	150.7	145
 **4**	0.458	0.415	10.1	1.458	158.0	145
 **5**	0.495	0.442	10.1	1.476	132.8	128

In the series of cyclanes, we observe a regular decrease of Σ_{tot}, as the ring strain increases: cyclohexane **13** (0.445 a.u.), cyclopentane **14** (0.420 a.u.), cyclobutane **17** (0.408 a.u.) and cyclopropane **18** (0.368 a.u.). Because their rings are non-planar (except cyclopropane **18**), the π MOs have been identified visually for **14** and **17**. For cyclohexane **13** the σ/π partition becomes problematic because most of the MOs have both types of participation; we assumed that Σ_{π} is close to the value observed for ethane. Under these conditions, a decrease of Σ_{σ} is also observed along the series together with <θ>. The weak π participation in **17** and **18** can be due to their quasi-eclipsed conformation, this participation being nearly zero in eclipsed ethane. Furthermore, it is well known that cyclobutane **17** and cyclopropane **18** have very close strain energies, 26.5 kcal/mol and 27.5 kcal/mol respectively[22], though the three-membered cycle could appear as much more strained. Taking into account that these energies involve all the bonds, it has been previously suggested that three weaker CC bonds in cyclopropane are compensated by six stronger CH bonds.[23] Indeed, <θ>(CH) = 109.5° for **17** and 116.3° for **18**: thus the CH bonds in cyclopropane are found to have some superdirect character. Moreover, from Table 3, the C-H BE increase can be evaluated to ca. 6.9 kcal/mol, close to previous determinations (8.6-8.8 kcal/mol).[24]

The series of three-membered ring species **18**, **20**, **21** and **22**, compared to ethane **12** (Figure 10), is of a particular interest. The CC bond (in red, right side of Figure 11) undergoes a progressive inversion with <θ> decreasing from 111.2° (normal bond) to 60° (inverted bond in propellane **22**).

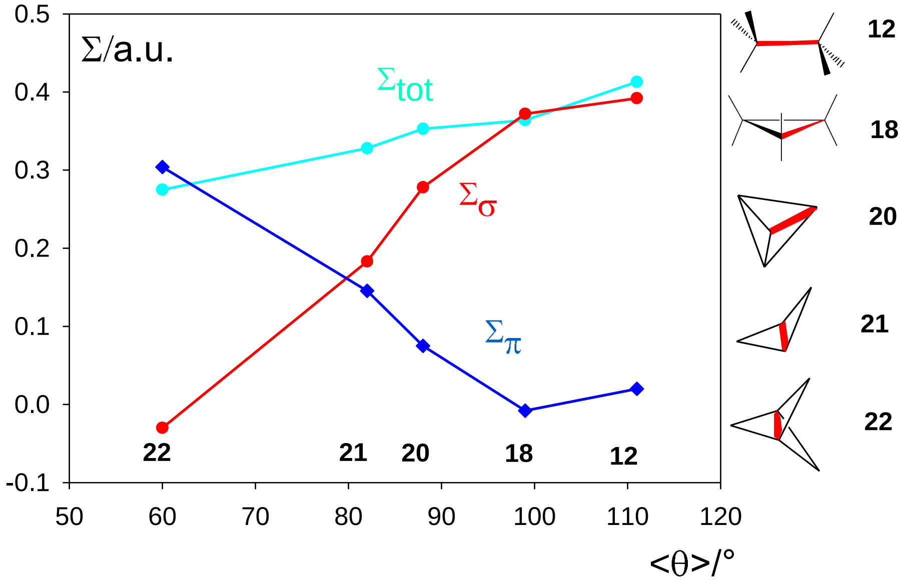


Figure 10. Various Σ values (a.u.) for CC bonds in ethane and a series of three-membered cyclic molecules (red bond).

Σ_σ decreases monotonously from 0.392 a.u. in ethane down to -0.029 a.u. in propellane. But at the same time, this decrease is compensated to a large extend by an increase of Σ_π for **20**, **21** and **22**. As a matter of fact, the presence of two CH bridges in **20**, two and three CH_2 bridges in **21** and **22** respectively, allows the formation of "banana bonds" of π character. It is worthy to insist on the fact that, on the basis of the evolution of the Σ and <θ> values, the central bond of propellane **22** behaves as expected in this series and does not appear as a particular case, in spite of its "charge shift" character within VB theory.

2.3.2. Sigma bonds in formally multiple bonds

From a panel of 11 formally multiple bonds, we report in Table 7 the values of Σ_{tot} , Σ_σ, Σ_π (a.u.) and the mean angle <θ> calculated for the σ component of the bond according to the method presented in section 2.1. For benzene **24**, <θ> = 100° is the mean of the two values of Kékulé structures.

The Σ_{tot} vale ranges from 0.479 a.u. to 0.579 a.u. for double bonds, from 0.577 a.u. to 0.616 a.u. for triple bonds and is 0.480 a.u. for the "half double bond" of benzene. As expected, Σ_{tot} is slightly less in the conjugated **28** and **31** than in the corresponding non conjugated **27** and **32**.

Table 6. Values of Σ_{tot}, Σ_σ, Σ_π (a.u.) for CC bonds in multiple bonds and the corresponding values of <θ> (°) for their σ bond (=C_3H_4 : cyclopropylidene, cf. Table 7).

label	molecule	$\boldsymbol{\Sigma}_{tot}$	$\boldsymbol{\Sigma_\sigma}$	$\boldsymbol{\Sigma_\pi}$	% **π**	< **θ**>
23	$H_2C{=}C{=}CH_2$	0.516	0.315	0.201	39.0	100
24	C_6H_6	0.480	0.342	0.139	29.9	100[a]
25	$H_4C_3{=}C_3H_4$	0.537	0.354	0.183	34.0	97
26	$CH_2{=}C_3H_4$	0.479	0.283	0.196	40.9	90
27	$H_2C{=}CH_2$	0.521	0.267	0.254	48.8	81
28	$CH_2{=}CH\text{-}CH{=}CH_2$	0.488	0.256	0.232	52.6	80
29	cyclobutene	0.519	0.283	0.236	45.5	77
30	cyclopropene	0.579	0.277	0.304	52.5	71.5
31	$HC{\equiv}C\text{-}C{\equiv}CH$	0.577	0.159	0.418	72.4	60
32	$HC{\equiv}CH$	0.616	0.145	0.471	76.5	60
33	cyclopentyne	0.524	0.087	0.437	83	40

[a] Mean value of the two Kékulé structures.

The <θ> values corresponding to the σ part of the double and triple bonds are less than 90° except in **23**, **24** and **25.** Indeed, their Σ_σ values are smaller than that of cyclopropane **18** (0.372 a.u.). The σ participation to Σ_{tot} is generally close to 50% in standard alkenes and no more than ca. 25% in alkynes, which has been already remarked.[17] Their variations as a function of <θ> are shown in Figure 11 with the same scale as in Figure 9 for the sake of comparison. Like in formally single bonds, Σ_σ tends to decrease with <θ>, but significantly more slowly. From these results, the σ bond in multiple bonds can be generally considered as formally inverted.

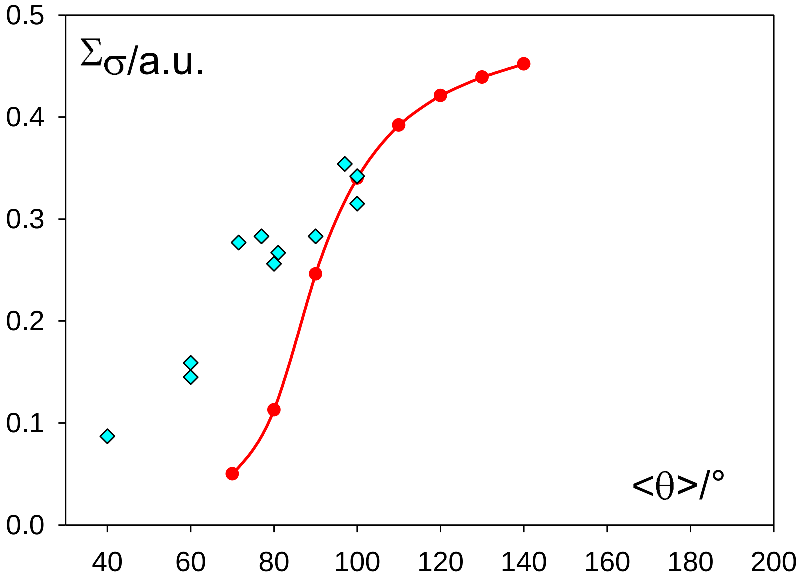
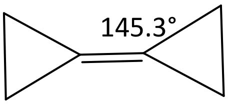
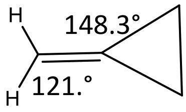
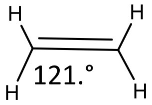


Figure 11. Values of Σ_σ (a.u.) for the σ bond in the formally multiple bond compounds **22**-**33** (cyan diamonds). The red curve corresponds to the C_2H_6 model for comparison.

The series **25**, **26** and **27** is illustrative of the influence of bond angles on σ bonds in double bonds (Table 7).

Table 7. Some properties of the central bond in alkenes **25**, **26** and **27**: Σ (a.u.), R(CC) (Å) and <θ> (°).

		Σ_{tot}	Σ_σ	Σ_π	R(CC)	<θ>
 145.3°	**25**	0.537	0.354	0.183	1.316	97
 H 148.3° H 121.°	**26**	0.479	0.283	0.196	1.323	90
 H H 121.° H H	**27**	0.521	0.267	0.254	1.332	81

The presence of two cyclopropenyl fragments in **25** tends to increase <θ> and Σ_σ, which decreases in **26** and **27**. The same evolution is observed from cyclobutene **29** to cyclopropene **30**.

The σ bonds of alkynes possess formally four C substituents at 0° and thus have a maximum <θ> value of 60°. Because cyclopropyne and cyclobutyne are unstable, cyclopentyne **33** appears to possess a σ bond with the smallest possible <θ> value (40°) and thus the weakest Σ_σ (0.087 a.u.) among all multiple bonds considered. In turn, the small <θ> value for σ in triple bonds entails for <θ>(CH) its maximum theoretical value of 180° in **31** and **32**, in agreement with high CH bond dissociation in acetylene and hydrogen cyanide.

Conclusion

The bonding energy BE of the CC bond in the CH_3 -CH_3 model is strongly dependant of the θ = HCH angle, exhibiting a sigmoidal variation: BE decreases rapidly when θ decreases from equilibrium value to yield “inverted bonds” (θ < 90°) and tends to zero for θ = 60°-70°. On the contrary when θ increases above its equilibrium value, BE increases. We propose the term “superdirect” for the latter type of bonds. Within MO framework, this general behaviour is closely related to the s participation in the s+p hybrid AOs.

These results can be generalized to any CC sigma bond in hydrocarbons by defining a parameter <θ> as the mean value of its substituent angles. Using the sum of dynamic orbital forces (DOF) as index of intrinsic bond energy, the σ strength in formally single CC bonds increases according to a sigmoidal variation as function of <θ> (from a panel of 22 molecules). The <θ> parameter thus appears as a crude, but straightforward and robust, index of the strain exerted on a σ bond: this strain can be “negative” which weakens the bond as its “inverted” character increases; on the contrary, it can be “positive”, resulting in a strengthening of the bond as its “superdirect” character increases. It accounts, among others, for the strain energy of cyclanes. Also in the series cyclopropane, bicyclobutane, tetraedrane and propellane, it is shown that the strength of the σ bond common to 3-membered rings decreases with <θ> with respect to cyclopropane (<θ> = 99°) to vanish in propellane (<θ> = 60°). At the opposite, the strongest σ CC bonds are found in butadiyne (<θ> = 180°) and bonds having tetrahedryl and/or ethynyl substituent(s) (<θ> >120°). The method is also applied to σ bonds in formally multiple bonds, with a panel of 11 molecules. These systems correspond to small <θ> values and σ bonds significantly weaker than in standard single bonds. This way, σ bonds in multiple bonds can be considered as formally inverted in most of cases.

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