Not Carbon s–p Hybridization, but Coordination Number Determines C–H and C–C Bond Length

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Abstract: A fundamental and ubiquitous phenomenon in chemistry is the contraction of both C–H and C–C bonds as the carbon atoms involved vary, in s–p hybridization, along sp2 to sp3 to sp. Our quantum chemical bonding analyses based on Kohn–Sham molecular orbital theory show that the generally accepted rationale behind this trend is incorrect. Inspection of the molecular orbitals and their corresponding orbital overlaps reveals that the above-mentioned shortening in C–H and C–C bonds is not determined by an increasing amount of s-character at the carbon atom in these bonds. Instead, we establish that this structural trend is caused by a diminishing steric (Pauli) repulsion between substituents around the pertinent carbon atom, as the coordination number decreases along sp3 to sp2 to sp.

The geometrical properties of organic (and inorganic) molecules are, in general, explained using hybridization theory, which was introduced by Linus Pauling in 1931.[1,2] A case in point is the fundamental and ubiquitous phenomenon in chemistry that C–H and C–C bonds contract as the carbon atoms involved vary, in s–p hybridization, along sp2 to sp3 to sp. Archetypal examples are the C–H and C–C bonds in ethane, ethene, ethyne and propane, propene, propyne, respectively. Hybridization theory ascribes the shortening of C–H and C–C bond lengths along sp2 to sp3 to sp to the increasing percentage of s-character of the hybrid orbital at the pertinent carbon, as s-orbitals are more contracted to the nucleus than p-orbitals, thus giving rise to an optimal bond overlap at a shorter interatomic distance.[3,4] This model is generally accepted and appears in most (physical) organic chemistry textbooks.[5–8]

Herein, we show that the above standard model is incorrect. Through detailed quantum chemical bonding analyses of a series of representative, archetypal model systems (Figure 1), we have been able to reveal that the above-mentioned shortening in C–H and C–C bonds is not related to an increasing amount of s-character at the carbon atom in these bonds. Instead, we find that a diminishing steric (Pauli) repulsion between substituents around the carbon atom constitutes the physical mechanism behind the universal trend in molecular structure, as the number of substituents around the pertinent carbon atom decreases from 4 to 3 to 2 along sp3 to sp2 to sp hybridization, respectively. Our findings are based on the analysis of the C–H and C–C bond mechanisms in a systematic series of model systems featuring sp3, sp2, and sp-hybridized C–H and C–C bonds in saturated and unsaturated hydrocarbons (Figure 1), using the quantitave molecular orbital (MO) model contained in Kohn–Sham density functional theory (DFT)[9–11] at BP86/TZ2P[12–14] in combination with a matching canonical energy decomposition analysis (EDA) as implemented in the ADF program.[15,16] Our findings are both, novel to the extent that they are paradigm-changing and also suitably consistent with the well-known role of steric repulsion in other contexts of molecular structure, such as, the stereochemical arrangement of substituents around a central atom or the dependence of bond distances on the steric bulk around the bond in question.[17–24]

Not unexpectedly, our DFT computations reproduce the aforementioned trend of a shortening of the C–H and C–C bond lengths as we go along sp3 to sp2 to sp hybridization of the carbon atom involved in such bonds (Table 1). The C–H bond length decreases along ethane (R,C-H, 1.099 Å), methane (R,C-H, 1.091 Å), and ethyne (RC–H, 1.078 Å) while the corresponding C–C single bond lengths decrease along propane (R,C–CH3, 1.553 Å), propene (R,C–CH2, 1.500 Å), and propyne (RC–CH2, 1.466 Å). Note that in all cases, bond shortening correlates with bond strengthening as reflected by the increase in bond dissociation energy (BDE; ΔE = ΔE(BDE) along sp3 to sp2 to sp hybridization. In order to analyze the origin of the trend in bond strengths in more detail, we decompose the bond...
energy $\Delta E$ according to the activation strain model (ASM) of reactivity [Eq. (1)]:

$$\Delta E = \Delta E_{\text{strain}} + \Delta E_{\text{int}}$$

Here, the strain energy $\Delta E_{\text{strain}}$ is the penalty that needs to be paid for deforming the fragments from their equilibrium structure to the geometry they adopt at the equilibrium C–X (X = H, CH$_3$) bond length. On the other hand, the interaction energy $\Delta E_{\text{int}}$ accounts for all mutual interactions that occur between the deformed fragments.

In all cases, the magnitude and trend in C–H and C–C bond dissociation energies appear to be determined by the interaction energies $\Delta E_{\text{int}}$. The strain energy $\Delta E_{\text{strain}}$ has only little influence on the calculated bond energy $\Delta E$ and does not affect the overall trend in relative bond strengths. They originate from the fact that, upon the formation of a new C–H or C–C bond, the other substituents around a carbon atom involved in the new bond bend away in order to reduce the otherwise even more destabilizing steric (Pauli) repulsion. This destabilizing effect is more pronounced when more substituents are around the carbon. Thus, $\Delta E_{\text{strain}}$ is most destabilizing for ethane (R$_3$C–H) and propane (R$_3$C–CH$_3$) in which the intrinsically planar R$_3$C radical undergoes pyramidalization.$^{29}$ The geometrical deformations of the sterically less crowded R$_3$C and RC radical fragments in, for example, ethene (R$_3$C=H) and ethyne (R$_3$C=H) are less severe and, therefore, lead to lower strain energies.

In order to pinpoint the differences between the interaction energies, we have analyzed the various C–H and C–C bonds in great detail by decomposing the $\Delta E_{\text{int}}$ into three physically meaningful terms using the canonical energy decomposition analysis (EDA) scheme [Eq. (2)]:

$$\Delta E_{\text{int}} = \Delta V_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{oi}}$$

In Eq. (2), $\Delta V_{\text{elstat}}$ is the classical electrostatic interaction between the unperturbed charge distributions of the (deformed) reactants. The Pauli repulsion $\Delta E_{\text{Pauli}}$ comprises the destabilizing interaction between occupied orbitals due to the Pauli exclusion principle and is an excellent descriptor of steric repulsion. Finally, the orbital interaction $\Delta E_{\text{oi}}$ includes the formation of the electron-pair bond between two singly occupied molecular orbitals (SOMOs) and orbital relaxation (i.e., charge transfer and polarization).

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**Table 1.** Bond lengths (in Å) and energy decomposition analysis (in kcal mol$^{-1}$) of the sp$^3$, sp$^2$, and sp-hybridized C–H and C–C bonds in their equilibrium geometries.$^{29}$

| System $^{29}$ | Bond length | $\Delta E$ | $\Delta E_{\text{strain}}$ | $\Delta E_{\text{int}}$ | $\Delta V_{\text{elstat}}$ | $\Delta E_{\text{Pauli}}$ | $\Delta E_{\text{oi}}$ |
|----------------|-------------|------------|---------------------|-----------------|---------------------|-----------------|-----------------|
| ethane R$_3$C–H sp$^3$ | 1.099 | -106.8 | 7.2 | -114.0 | 90.2 | -62.8 | -141.4 |
| ethene R$_3$C–H sp$^3$ | 1.091 | -115.8 | 3.1 | -118.9 | 85.4 | -60.1 | -144.1 |
| ethyne R$_3$C–H sp | 1.070 | -140.0 | 0.1 | -140.1 | 40.4 | -41.3 | -139.1 |
| propane R$_3$C–CH$_3$ sp$^3$ | 1.533 | -89.3 | 18.3 | -107.6 | 215.0 | -138.9 | -183.7 |
| propyne R$_3$C–CH$_3$ sp$^3$ | 1.500 | -102.2 | 13.3 | -115.5 | 221.4 | -142.8 | -194.2 |

[a] Computed at BP86/TZ2P level of theory. [b] R$_3$C$^-$ = (H$_3$C)$_3$C$^-$; R$_3$C$^-$ = (H$_3$C)$_2$HC$^-$; RC$^-$ = HCC$^-$ See Figure 1 for the structures of the studied systems.

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**Figure 1.** a) sp$^3$, sp$^2$, and sp-hybridized C–H bonds of ethane, ethene, and ethyne, and b) sp$^3$, sp$^2$, and sp-hybridized C–C bonds of propane, propene, and propyne, where the bond of interest is shown in black (sp$^3$), blue (sp$^2$), and red (sp). c) Schematic molecular orbital diagram of the formation of a generic R$_3$C–X electron-pair bond and interaction with a closed-shell orbital that leads to (steric) Pauli repulsion.
Note that the decomposed interaction energy terms depicted in Table 1 strongly depend on the C–H and C–C bond distance. Therefore, the differences between these energy terms along the hybridization series must be interpreted with special precaution because they emerge not only from the original variation in the intrinsic bonding properties but also from the concomitant geometrical relaxation which affects the original trends. In order to solely focus on the trend in the intrinsic bonding properties of our model systems, we have decomposed the interaction energy: (i) as a function of the C–H and C–C bond distance; while (ii) keeping R,C and H' or CH' fragments fixed in the equilibrium geometry and valence electron configuration of the overall systems, i.e., R,C–H and R,C–CH₂ (n = 1, 2, 3). The former ensures a consistent comparison of the energy terms at any bond distance whereas the latter prevents any other geometrical relaxation within the fragments to mask primary changes in the energy terms. Note that this measure guarantees that none of the primary effects in the interaction energy terms is absorbed into the strain term which remains constant.

Prior to discussing the decomposed interaction energy terms as a function of the bond length, we first examine the orbital overlap integrals corresponding to the C–H and C–C electron-pair bonds (Figures 2a and b; see Figure 1c for molecular orbital diagram). The larger the overlap between the SOMOs of the two fragments, the more stabilizing the corresponding electron-pair bonding orbital interaction. Thus, the point at which the SOMO–SOMO overlap reaches a maximum is often considered as an essential factor in determining the equilibrium bond length. These maxima follow a similar trend as the equilibrium bond lengths themselves, that is, as the fragments approach towards each other, the SOMO–SOMO overlap achieves its maximum earlier, at a longer bond distance, in the case of the sp³-hybridized R,C than for the sp²-hybridized R,C than for the sp-hybridized RC. This observation corresponds well with the spatial extent of the different hybridized SOMOs, which, in line with the current rationale, steadily decreases from the sp³-hybridized R,C to the sp-hybridized RC (Figure 2c), in other words, the SOMO of R,C is closer to the grey vertical line than the SOMO of RC. This can also be seen in the zoom-in of Figure 2d: if one approaches the carbon nucleus from infinity, the orbital function of R,C reaches the value of 0.05 au earlier, i.e., further away from the carbon nucleus, compared to the R,C and RC analogues. In addition, R,C also has a smaller orbital amplitude close to the carbon nucleus compared to R,C and RC (Figure 2d), giving rise to less orbital overlap for the former as seen in Figures 2a and 2b.

Note, however, two striking phenomena: (i) all equilibrium C–H, and C–C, bond distances differ significantly from the distance at which the bond overlaps achieve their maximum, C–H bonds are in fact all longer; and (ii) the contraction of C–H, and also C–C, bonds as the carbon atoms involved vary, in s–p hybridization, along sp³ to sp² to sp, is significantly smaller than the variation in the distance at which the corresponding bond overlaps achieve their maximum (see vertical lines and dots in Figures 2a and b). Thus, despite the fact that the positions of the maximum SOMO–SOMO overlap display the expected trends, other physical mechanisms are crucial for achieving the actual equilibrium bond distances.

Our energy decomposition analysis as a function of the C–X (X = H, CH₃) distance, shows that, in contrast to present-day textbook knowledge, the orbital interactions ΔEₜ are not responsible for the stronger and shorter sp-hybridized C–H and C–C bond (Figures 3a and b). The interaction energy ΔEₜ follows the trend discussed earlier, i.e., bonds involving sp³-hybridized carbon atoms are weaker and have a less stabilizing ΔEₜ than their sp-hybridized analogs. Strikingly, the orbital interactions ΔEₜ however, show an opposite behavior: from sp³ to sp² to sp-hybridized carbon atom in C–X bonds, the ΔEₜ curves become decreasingly stabilizing, although the difference between sp³ and sp² hybridization is only marginal. This trend stems from the shrinking contribution of orbital relaxation which relieves the Pauli repulsion, especially at shorter C–X distances at which closed-shell–closed-shell repulsion becomes very large. Thus, if it were for the orbital interactions alone, C–X bonds would become longer, not shorter, along sp³, sp², and sp hybridization of the carbon atom. The electrostatic attraction ΔVₐₕₑₜ follows a similar trend along the series as ΔEₜ, i.e., the curves become decreasingly stabilizing and shallow along sp³, sp², and sp and, therefore, also favor elongation of the C–X bond distance along this series.

We now identify ΔEₚₑₕₑₜ as the decisive factor in determining the equilibrium bond length because the only difference between the sp³- and sp²-hybridized C–X bonds lies in this repulsive term, which is less destabilizing for the latter. This difference allows the fragments to approach each other more closely, leading to shorter bond distances. Continuing to the bonds involving an sp-hybridized carbon atom, there is a remarkably large drop in Pauli repulsion ΔEₚₑₕₑₜ. This effect partly compensates the weakening of ΔEₜ, and, especially for C–C, also of ΔVₐₕₑₜ. It is therefore the change in ΔEₚₑₕₑₜ that determines the longer bond lengths in sp³-hybridized C–H and C–C bonds compared to their sp²- and sp-hybridized analogs. We recall that this phenomenon is also displayed in the EDA terms corresponding to the equilibrium geometries (Table 1). As shown, a highly destabilizing ΔEₚₑₕₑₜ induces an elongation of the C–X bond, which, in turn, reduces all EDA terms, including the ΔEₚₑₕₑₜ. Nevertheless, the ΔEₚₑₕₑₜ of the longer sp³-hybridized C–X bond is more destabilizing than the less hybridized counterparts, indicating that it is this term that governs the observed lengthening of the C–X bond.

The relation between the Pauli repulsion and the number of sterically hindering substituents becomes even more evident when, in numerical experiments, we explicitly change the size and number of substituents (see Table S1). Increasing substituent size leads to a longer sp³-hybridized C–H bond (Figure 3c; H₃C–H: 1.096 Å to (H(CH₃)₂)C–H: 1.104 Å), whereas a decreasing number of substituents makes this bond shorter (Figure 3d; H₃C–H: 1.096 Å to HC–H: 1.085 Å). Inspection of the corresponding energy plots shows that the modulation of the equilibrium bond length, and consequently bond strength, is again caused by the ΔEₚₑₕₑₜ. The ΔVₐₕₑₜ and ΔEₜ on the contrary, do not vary that much along the series. More precisely, they counteract the observed trend in ΔEₚₑₕₑₜ.
Importantly, our analyses also shed light on the nature, especially the orbital energy, of the \( \sigma^* \)-orbital of the \( sp^3 \)-hybridized \( R_nC-X \) bonds (\( n = 3, 2, 1; X = H, \) alkyl, halogen, etc.), which is of direct relevance for understanding various types of reactions and supramolecular aggregates featuring these bonds.\(^{32-34}\) We find that the \( \sigma^* \)-orbital of \( R_nC-X \) bonds be-

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comes increasingly more stabilized, on going from sp\(^3\) to sp\(^2\) to sp carbon centers, again, due to a reduction in the number of substituents around the pertinent carbon atom. The \(\sigma^*\)-orbital of the sp\(^3\)-hybridized \(\text{R}_n\text{C} \equiv \text{H}\) bond lowers in energy along \(n = 3, 2, 1\), from 1.7 eV for \(\text{R}_3\text{C} \equiv \text{H}\) to 1.4 eV for \(\text{R}_2\text{C} \equiv \text{H}\) to 1.0 eV for \(\text{RC} \equiv \text{H}\), respectively, because the \(\text{R}_n\text{C}\) SOMO becomes gradually more stabilized. This behavior can be ascribed to two phenomena: (i) the \(\text{R}_n\text{C}\) SOMO is \(\text{R}_n\text{C} \equiv \text{C}_\text{\text{2}p}\) antibonding, which reduces as \(n\) decreases from \(n = 3\) to \(2\) to \(1\), due to less orbital overlap; (ii) the \(\text{R}_n\text{C}\) SOMO is also \(\text{R}_n\text{C} \equiv \text{C}_\text{\text{2}s}\) bonding and its bonding capability, i.e., orbital overlap, becomes stronger as \(n\) can align better with \(\text{C}_\text{\text{2}s}\) along this series (see Supporting Information Discussion 1 and Figure S1 for a detailed molecular orbital analysis).

To conclude, we have shown that, in contrast to the present-day paradigm, the contraction of C–H and C–C bond lengths on going from sp\(^3\) to sp\(^2\) to sp carbon centers, originates from a diminished Pauli repulsion, the magnitude of which is directly related to the steric proximity between the substituents around the pertinent carbon atom. The orbital interaction, which was up to this point seen as the driving force, shows behavior that counteracts the observed trend in bond strength and, consequently, is not responsible for the decreasing bond length.

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**Conflict of interest**

The authors declare no conflict of interest.

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