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# Shorter Still: Compressing C−C Single Bonds

**Gerardo Martínez-Guajardo,[†] Kelling J. Donald,*[,‡] Bernard K. Wittmaack,[‡] Miguel Angel Vazquez,[†] and Gabriel Merino*[,†]**

*Departamento de Química, División de Ciencias Naturales y Exactas, Universidad de Guanajuato, Col. Noria Alta s/n C.P. 36050, Guanajuato, Gto., México, and Department of Chemistry, Gottwald Center for the Sciences, University of Richmond, Richmond, Virginia 23173*

*gmerino@quijote.ugto.mx; kdonald@richmond.edu*

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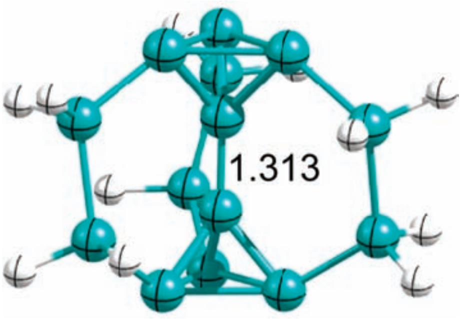
## ABSTRACT



**How short can a C−C single bond get? The bonding in a set of molecules that are related structurally to previously synthesized or theoretically examined systems with short C−C bonds is investigated. According to calculations, a single C−C bond could be compressed to 1.313 Å! To the best of our knowledge, this is the shortest single C−C bond reported to date. This shortening is a consequence of a change in the C−C−C bond angle, *θ*, to minimize strain in the cages and an effort to offset the tension in the surrounding bridges.**

How short can a C−C single bond get?[1] Several properties of molecular fragments such as polarizabilities, interatomic separations, and force constants remain very roughly constant from molecule to molecule. In chemistry, understanding such transferable properties and the limits of their transferability is important.

Significant chemical insight is bound up, for example, in the knowledge that a typical C−C single bond is ~1.54 Å, a C−C double bond is ~1.34 Å, and a C−C triple bond, at ~1.23 Å, is shorter still. But there are significant exceptions, and we should explore, understand, and exploit them. As Hoffmann and Höpf pointed out, “the making of molecules that are untypical or abnormal tests our understanding of that fundamental yet fuzzy entity, the chemical bond”.[2] Unusual characteristics in bonding, such as interatomic separations that are way shorter (or longer) than expected, are interesting partly because they suggest new possibilities for structural chemistry. So, the exploration of the edge of bonding possibilities strengthens our intuition and appreciation of what is possible in structural chemistry.

A wide collection of compounds with short single bonds between saturated C atoms have been synthesized. A remarkable example is the hexakis(trimethylsilyl)tetrahedryltetrahedrane reported by Tanaka and Sekiguchi: X-ray crystallographic analysis revealed that the linking C−C single bond is 1.436 Å.[3] This is the shortest known noncyclic C−C single bond in a saturated hydrocarbon system. Using the block-localized wave function (BLW) method, Mo[4] demonstrated that both hybrid-

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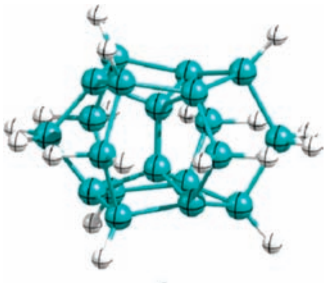
[†] Universidad de Guanajuato.
[‡] University of Richmond.
(1) Hopf, H. *Chem. Unserer Zeit* **1976**, *10*, 114.
(2) Hoffmann, R.; Hopf, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 4474.
(3) Tanaka, M.; Sekiguchi, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 5821.

10.1021/ol101671m

ization and hyperconjugation contribute to the shortening of the central C−C bond in tetrahedryltetrahedrane.

More recently, Huntley et al. investigated several structural strategies for squeezing C−C single bonds—using cages, intramolecular repulsion, or strain, rather than electronic effects.[5] A tour through several structures uncovered a C−C single bond of 1.32 Å, for **1**.[6]



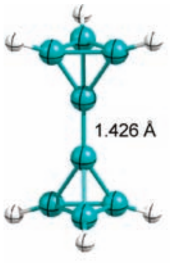
**1**

As Huntley et al. showed, it is expensive to compress molecules. Squeezing ethane to reduce the C−C bond by 0.15 Å costs about 37.7 kJ·mol$^{-1}$.[5] For several molecules in which exceptionally short C−C or other bonds have been observed, the cost for the bond contraction is paid for by a destabilization and elongation of some of the other bonds in the structure. In endohedral systems, for example, bonds in the cages elongate, while bonds in the molecule within the cage are compressed.[5,7] Thus, the (theoretical and experimental) quest to understand the tolerance of C−C single bonds for structural compression is a real challenge in molecular design. The viable candidate structures must have fragments that absorb (by stretching) the cost to shorten one or two bonds. If the system is to be a minimum on the potential energy surface, however, it is important to maximize the strain at the target C−C bonds while preserving some flexibility in other parts of the structure.

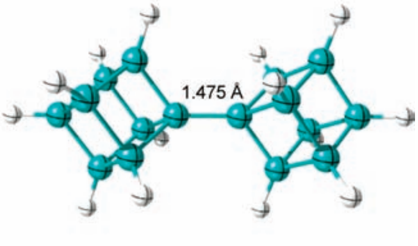
In this contribution, we investigate the bonding in a set of molecules that are related structurally to previously synthesized or theoretically examined systems with a short C−C bond (group A in the Supporting Information, SI). We focus on unexplored cases in which the primary motivation for the C−C bond contraction is structural strain, rather than electronic effects. For comparison, we include some familiar molecules, such as 1,3-butadiyne, with a range of C−C bond lengths for which electronic effects are more important (group B).

All our geometry optimizations have been carried out with the Gaussian 03 suite of programs[8] using the B3LYP[9] functional in conjunction with the 6-311G(d,p) basis sets. The nature of each stationary point has been determined by calculating and diagonalizing the Hessian matrix. To analyze the bonding mechanisms, a natural bond orbital analysis (NBO)[10] was carried out.

Tetrahedryltetrahedrane **2** and cubylcubane **3**[11] were chosen as our basic building blocks. The central C−C bond lengths in these systems are 1.426 and 1.475 Å, respectively. The systems we examine differ primarily in the nature of the bridges connecting the two vertex-bonded polyhedra.

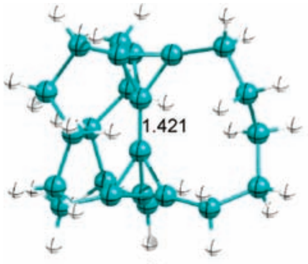


**2**

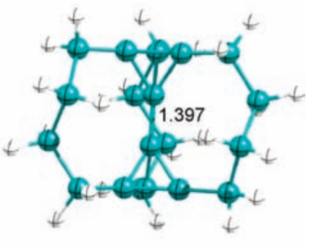


**3**

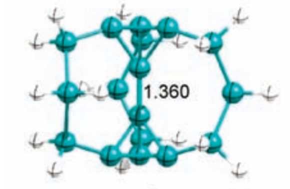
Let us consider the tetrahedryltetrahedrane derivatives. According to our calculations, the central C−C bond is compressed from 1.426 Å in **2** to 1.313 Å in **7**! The C−C bond contraction that is accomplished in **7** outstrips, to the best of our knowledge, all the previously published records for the single C−C bond.



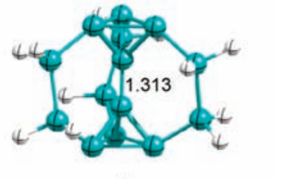
**4**



**5**



**6**



**7**

A reoptimization of structures **1** and **7** at the B3LYP and MP2(full) levels for several basis sets (see SI) confirms that the bond in **7** is significantly shorter.

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(5) Huntley, D. R.; Markopoulos, G.; Donovan, P. M.; Scott, L. T.; Hoffmann, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 7549.

(6) Our results show that the central C−C bond length in **1** is 1.350 Å, which is slighly larger than that reported by Huntley et al. at the same level (1.32 Å).

(7) Cerpa, E.; Krapp, A.; Flores-Moreno, R.; Donald, K. J.; Merino, G. *Chem.—Eur. J.* **2009**, *15*, 1985.

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How to explain this squeezing? A number of systems with short bonds have been identified in the past few years, but a model of C−C bond contraction that allows us to predict that a given bonding environment will stabilize short bonds is still illusive.

As a step toward such an understanding, we investigated the relationship between bond distance and the charge distribution in the short C−C bonds formed by the C atoms at highly strained vertices (Figure 1).

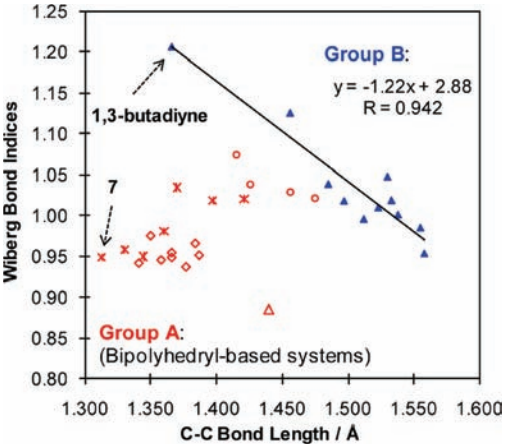

**Figure 1.** Wiberg Bond indices (WBI) for the short C−C bonds in the groups A (red) and B (blue) systems. In group A, ° denotes a simple vertex bonded bipolyhedra like **2** and **3**. The others are backstrapped (for details, see Figure S.1 and Table S.1 in the SI).

Interestingly, the WBIs in the highly strained group A systems decrease slightly as the bond gets shorter in Figure 1. Does this suggest that in the backstrapped vertex bonded polyhedra the short C−C bonds are stabilized by moving charge density out of the internuclear region into the rest of the molecule? The situation is not clear. Going from **4** to **7**, for example, the index changes by only a tiny $\Delta_{\text{WBI}} = -0.07$ (Table S.1, SI). As one reviewer suggested, the reduction in the WBIs in group A may be explained by changes in the extent of the C(s-p) − C(s-p) valence hybrid orbital overlap coupled with the repulsion of the core (*s*) shells causing a net reduction in the electron density in the bonding region.

How does the nature of the C−C $\sigma$ bond change in these compressed systems? How "single" are these extremely short bonds? In structures **4**−**7** and in the short bonds in group A in general, the overlap between the s-p hybridized orbitals along the bond axis is the primary bonding interaction. A qualitative molecular orbital (MO) analysis confirms this net (s-p) $\sigma$-character of the C−C bonds; Figure S.2a in the SI illustrates, e.g., a $\sigma$-type C−C orbital interaction in **4**. Several C−C ($p_x$-$p_x$ and $p_y$-$p_y$) $\pi$-like interactions (Figure S.2b, SI) are observed as well among the MOs in structures **4**−**7**, but these interactions are counterbalanced by C−C $\pi$-antibonding MOs such as that shown in Figure S.2c (SI).

To understand the squeezing of the C−C bond in **4**−**7**, we assessed the overlap populations (see Table S.4, SI). An orbital by orbital break down of the overlap population has been difficult to achieve using the ab initio computational software available to us. An analysis at the extended Hückel (EH) MO level[12] suggests, however, extremely weak net ($p_x$-$p_x$ and $p_y$-$p_y$) $\pi$ influences on the short C−C bonds in **4**−**7** (compared, for example, to ethane) in addition to the dominant (s-p) $\sigma$ character of the bond. Moreover, we find that the total (bond or reduced) overlap population (ROP) for the short C−C bond increases, but only slightly ($\Delta_{\text{ROP}} = +0.16\ e$), as the bond contracts going from **4** to **7** (Table S.3, SI). This EH result runs contrary to the WBI data ($\Delta_{\text{WBI}} = -0.07$) mentioned previously. However, a basic (qualitative) consensus between the two results is that the charge density in the bonding region of the C−C bond changes rather insignificantly going from 1.421 Å in **4** to 1.313 Å in **7**.

In moderately strained systems or those controlled by electronic effects such as 1,3-butadiyne (blue in Figure 1), the opposite and more common relationship between bond order and bond length is observed where the *bond order increases as the bond distance decreases*. The difference in the behavior of the molecules in groups A and B is obvious, for example, from a comparison of **7** and 1,3-butadiyne. **7** has one of the lowest bond orders (0.95) and the shortest bond (1.313 Å). 1,3-Butadiyne on the other hand has the shortest bond in group B (1.366 Å) while boasting the highest bond order.

Given this dramatic disparity in the bond order vs the bond lengths in groups A and B (Figure 1), the reactivity and spectroscopic properties of the short C−C single bonds in the two groups will likely be quite different, even if the bond lengths are identical (cf. structure **12** in Table S.1, and 1,3-butadiyne).

An increase in the s orbital composition is typically associated with a shortening of C−X bonds. This has been explained in terms of the increase in orbital electronegativities as the *n*s composition increases.

The results in Figure 2 are instructive. Here we find, as well, a systematic difference in the behavior of the group A and B molecules. For the group B systems, bond contraction is accompanied by an increase in the % s compositions at the C atoms in the C−C bond (following the trend line in Figure 2). Put another way, the electronically stabilized short C−C bonds relax and elongate as the C sites involved in the bond are saturated (i.e., rehybridized, going progressively from sp to $sp^3$).

For the group A systems, this correlation breaks down dramatically in the high-strain regime. The group A systems that are not backstrapped, such as **2**, **3**, **10**, and **13** (see the SI), and those with long loose bridges such as **4** follow the same behavior described by the best fit line for group B. As the bridge becomes shorter and stiffer, however (going from **4** to **7** above,

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(10) (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

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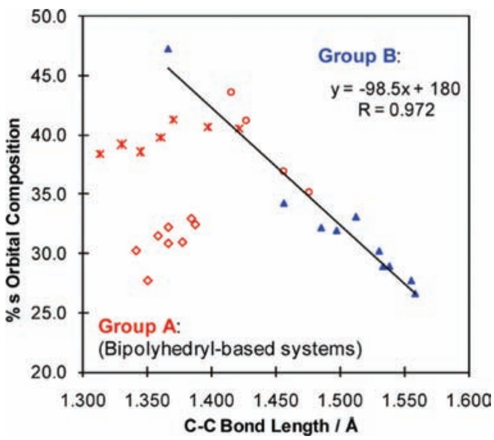

**Figure 2.** C % s orbital composition vs the C−C bond length for symmetric systems in groups A and B.

for example), the aspiration toward the behavior represented by the best fit line is rapidly quenched. Indeed, the opposite behavior is observed; the bond contraction is accompanied by slight decreases in the s orbital composition (see group A in Figure 2). Interestingly, Figure 2 accomplishes an even finer partition of the group A systems. The group A systems are cleanly divided into (i) nonbridged systems, which generally behave like group B systems, (ii) systems based on **2**, with higher % s contributions, and (iii) open and closed systems based on **3** with lower % s compositions (cf. Figure S.1 and Table S.1 in SI).

Why do the backstrapped group A systems deviate from the lines in Figures 1 and 2? Evidently, the molecules compensate for the strain of the bridge in two ways: by a contraction in the central C−C bond and simultaneously by a decrease in the C−C−C bond angle (see Figure 3). As Figure 3 confirms, this decrease in the bond angle is partnered by a decrease in the % s contribution of the hybrid orbital involved in the bonding.

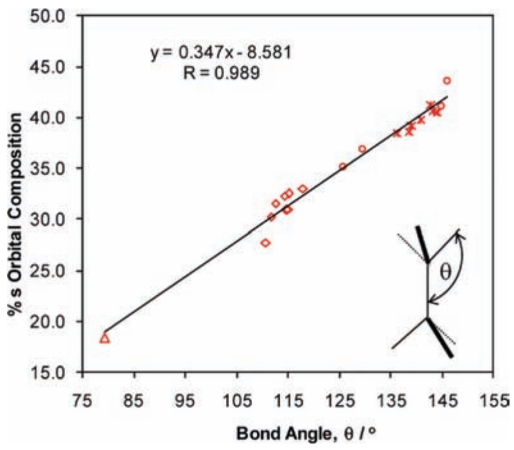

**Figure 3.** Orbital composition as function of bond angle for the molecules in group A.

Remarkably, the linear relationship

$$\% \text{ s composition} = 0.35 \times \text{bond angle}/° - 8.58$$

between orbital composition and bond angle for group A systems shown in Figure 3 extends down to as far as 79.4° in an adamantane-like $C_{11}H_{12}$ structure. The latter structure (**11**) is the only one we consider in group A in which the two C atoms are in different bonding environments.

To be sure, simple empirical relationships have previously been identified linking the bond angles between different substituents in carbon compounds. We can mention an important analysis by Root et al.,[13] for example. Here, we show that a simple direct correlation between orbital composition and bond angle is obtained even for highly strained systems that show exceptional behavior in other regards as in Figures 1 and 2.

Given the convincing correlation between orbital composition and bond angle in Figure 3, it is apparent that for any bipolyhedryl structure—bridged or not—we can predict the orbital composition from $\theta$. It is clear from Figures 2 and 3, however, that there is no universal relationship between orbital composition or $\theta$ and bond length. The bond length depends on the exact structure of the molecule and not just the orbital composition or bond angle at the C−C bond. This is obvious, for instance, from the clear separation in Figures 2 and 3 between the bitetrahedryl series and the bicubyl series.

In assessing the evidence outline above, we are quite convinced that the best chance at C−C bonds in hydrocarbons as short as 1.31 Å, or even shorter still, is to be found in systems where the C−C bond is formed by vertex bonded bipolyhedryls that are strongly strapped together by short bridges. However, *these bridges must be short enough to strain the polyhedryls but long enough so that the cages do not disassemble* to give, for example, propellane-like structures. Ultimately, the shortest bonds we find—**7**, **8**, and **9**—are consequences of a change in $\theta$ to minimize strain in the cages and an effort to offset the tension in the surrounding bridges.

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**Note Added after ASAP Publication.** The formula after Figure 3 contained an error in the version published ASAP August 18, 2010; the correct version reposted August 24, 2010.

**Supporting Information Available:** Optimized geometries of the systems studied, representative molecular orbitals and additional MO, and EH data. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] Root, D. A.; Landis, C. R.; Cleveland, T. *J. Am. Chem. Soc.* **1993**, *115*, 4201.