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Squeezing C–C Bonds**

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Making C–C bonds long is a going enterprise; dozens of bonds that are 0.10–0.15 Å longer than a normal 1.54 Å C–C bond are known. It is possible to weaken a bond through electronic effects, but strain is the major factor. What about short C–C bonds? Single bonds between two- and three-coordinate carbon atoms (e.g., the central C–C bonds in 1,3-butadiyne and 1,3-butadiene) are certainly short—a phenomenon usually interpreted in terms of hybridization. However, short single bonds between two four-coordinate carbon atoms are rare. Two examples that have caught the attention of the community are the π-acceptor-substituent-influenced bond in a bridged bicyclobutane **1**, with a C–C bond length of 1.41 Å,[1] and the external bonds between two bicyclobutane bridgeheads in **2** and **3** with lengths of near 1.44 Å.[2] An interesting theoretical discussion of these and the related bonds in the bitetrahedryl and bicubyl molecules, **4** and **5**,[3a] has appeared.[3b–g] Recently, Tanaka and Sekiguchi published the synthesis and structure of the hexakis(trimethylsilyl) derivative of **4**, which contains a very short exocyclic C–C bond (1.436 Å).[4]

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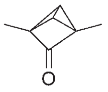

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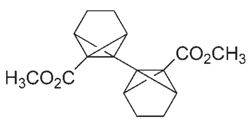

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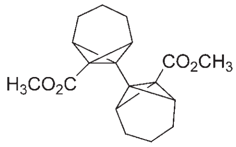

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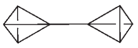

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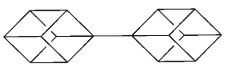

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One might think that the normal shape of a molecular potential argues against a short C–C single bond: Aren't all such potentials anharmonic, with elongation less costly energetically than contraction? For "small" deviations (ca. 0.05 Å) it really doesn't matter that much. Single-point calculations on D_{3d} ethane (Figure 1) are indicative: it takes 2.8 kJ mol^{-1} to stretch the C–C bond by 0.05 Å from its equilibrium value and only 3.5 kJ mol^{-1} to squeeze it by the same amount; on the other hand, stretching and squeezing by 0.15 Å requires 21.9 and 37.7 kJ mol^{-1}, respectively.[5]

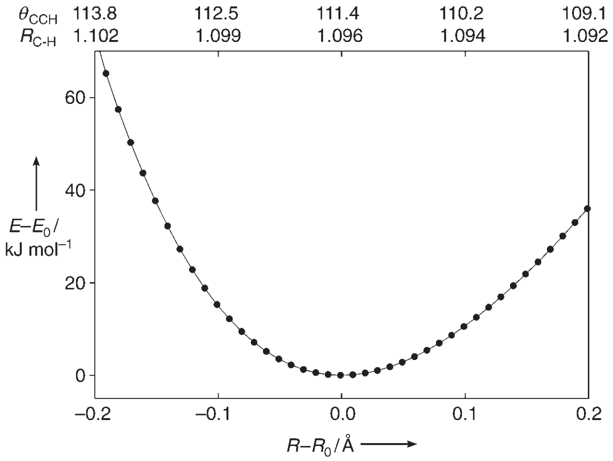


Figure 1. Computed potential-energy curve for ethane showing the energetic cost of bond stretching ($R-R_0>0.0$) and compression ($R-R_0<0.0$). At each fixed distance, the C–H bond length (R) and C-C-H angle (θ), as shown at the top of the graph, were optimized within a D_{3d} constraint.

So why do we see so few shortened C–C bonds? We think it is because strain dissipates in a multitude of ways. It is not easy to concentrate stress into a specific bond or in a single phase of the stretching motion. Herein, we report our attempts to design such squeezed C–C single bonds, making use of the reliability of contemporary computational methods to monitor how well we do. In doing so, we are responding to a question raised 29 years ago by Henning Hopf.[6] He asked "*Wie kurz kann eine Einfachbindung werden? Wie stark lässt sie sich stauchen?*" (How short can a single bond be? How strongly can it be compressed?)

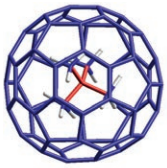
We constrained ourselves (arbitrarily) to C–C bonds in which the carbon atoms involved are tetracoordinate. Also, for the initial moves in the game,[7] we did not allow substitution at either of the tetracoordinate carbon atoms by atoms other than hydrogen or carbon. Also, to rely on well-understood electronic effects (as are operative in **1**) was deemed "unsporting."

Computational Methods

Structures were optimized with the B3LYP hybrid functional and the 6-31G(d) basis set as implemented in the Gaussian 03 program.[8] This functional has been shown to be reliable for the determination of normal and anomalous C–C bond lengths using both 6-31G(d) and 6-31G(d,p) basis sets above.[3g,9] In a few cases (indicated in footnotes), a smaller basis set (6-31G) was used. Frequency calculations were performed to confirm that every structure represents a true energy minimum. Many of the structures were also optimized using the BLYP functional and triple-zeta Slater orbital basis set (TZ2P) with the Amsterdam Density Functional Program,[10] and effectively identical results were obtained. Our structures are color-coded as follows: C atoms blue; N atoms green; O atoms yellow; H atoms white; and Si atoms cyan (one exception will be specified later); the shortened bonds are highlighted in red.

Caging

The simplest strategy for applying pressure to one C–C single bond (or a group of such) is to encapsulate it in a reasonably inert cage, a game that is easier to play theoretically than experimentally. In the examples pictured here, **6** puts a molecule of neopentane inside C_{60}, **7** puts ethane in silsesquioxane $(SiH)_8O_{12}$, and **8** puts a molecule of ethane into a "diamond skin." (This last structure requires further explanation: Begin with an extended cubic diamond structure. Discard from it a C_2 unit as well as the six attached carbon atoms. Place C_2H_6 inside that space, then sculpt the outside to form a thin diamondoid layer around the molecule of ethane, and "heal" the inside cavity by replacing the 18 carbon atoms that face the ethane by nitrogen atoms. The outside of the diamond skin is passivated with hydrogen atoms.[11]) This kind of brute-force pressure leads to optimized C–C bond lengths of 1.36 Å in **6**,[12] 1.40 Å in **7**, and 1.46 Å in **8**.[13,14]



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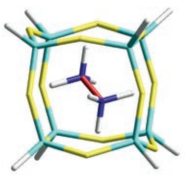

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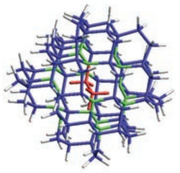

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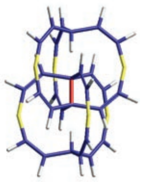
Capsule and encapsulated entities can also be combined in a single molecule. Cyclophane **9** presses a methyl group towards the aromatic ring, in a similar manner to the "iron maidens" recently reviewed by Pascal.[15] The steric congestion at the center of this molecule leads to a shortened bond length of 1.43 Å.[16] Song, Ho, and Pascal recently synthesized related in-cyclophanes with short C–Me bonds of 1.475 and 1.495 Å.[17] Tightening the cage around such an in-methyl group, as in **10**, leads to a corresponding C−C bond length of just 1.41 Å.

9

10



11

The Spiderane

A unique topology (a spiderane) is demonstrated by **11**,[12] in which the above principle is applied twice. This "back-strapped" structure with two intertwined cages has a central C−C bond length of 1.44 Å. The hydrogen atoms pointing towards the short C−C bond are essential; replacing the CH groups with nitrogen atoms leads to a more typical bond length of 1.51 Å.

Shortening a Bond without Pushing on It

Though the spiderane **11** is sui generis, van der Waals repulsion has been crucial in our strategy so far. Many other variations are possible in which shortened bonds are achieved solely by covalent means. For example, **12** forces a carbon atom into the adamantane framework, removing the bridgehead hydrogen atoms along the way. A set of four equally shortened C−C bonds (1.44 Å) arises as a result of the small covalent cage. Next, we replaced the six bridging methylene groups with NH groups, resulting in a more compressed structure that has a central bond length of 1.39 Å.[18]

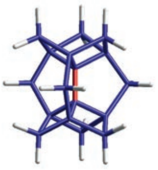
12

13

Rotation around one of the eclipsed C−C bonds in **12** and reconnection of the "bridges" in a staggered manner leads to the closely related structure **13** (bridging group $X = CH_2$). Here, we observed that one bond becomes even shorter (1.38 Å), while the three basal C−C bonds relax to a normal C−C bond length (1.54 Å). Still, the squeeze comes at a cost: the surrounding bond angles are very distorted, and the bonds to the methylene carbon atoms (1.70 and 1.84 Å) are very elongated. The use of longer bridges ($X = C_2H_2$, C_2H_4, C_3H_4, C_3H_6) reduces the distortions but also leads to a gradual lengthening of the short bond to 1.48 Å for the trimethylene species ($X = C_3H_6$).

Stiffened and Strapped, Eclipsed and Staggered

A different look at **12** opens the door to another variation: the lower part of the molecule is comprised of three fused cyclobutane rings. This connectivity provides a highly strained but rigid framework at one end of an eclipsed ethane unit. If that fused-ring system were repeated at the other end, we would have molecules that are reminiscent of bicubyl or bis(bicyclo[1.1.1]pentyl), which are known to have short central bonds.[3] Those bonds should get even shorter if we impose further geometric constraints. Implementing this idea, with three bridging methylene groups, leads to a central bond of length of 1.37 Å in **14**.



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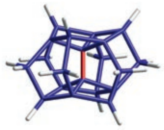
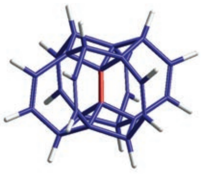


15a

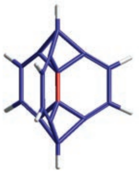


15b

Application of this concept to the "staggered" system **13** allows six bridging methylene units and leads to the shortest carbon–carbon single bond observed in the course of this study: 1.32 Å in **15a**. Although this molecule is highly congested and very, very strained, a single-bond distance in the regime of double-bond lengths is quite remarkable. The other C−C bonds in the molecule all fall in the range of 1.60–1.64 Å. Replacement of the methylene bridges in **15a** with ethyleno groups (C_2H_2) results in slight elongation of the central C−C bond to 1.35 Å (**15b**).

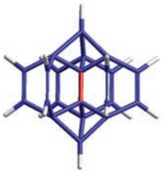
Tied-Up Bicycloalkanes

Clearly, stiffening both ends of an ethane unit and tying them together is a promising approach to obtain short bonds. Other examples include interior propellanes formed by strapping bicyclo[*n.n.n*]alkane units together. Many variations in the bridges are possible; herein, we show only the use of *exo* double bonds (1.37 Å in **16a**) and ethano bridges (1.39 Å in **16b**). The triply methylene-bridged analogue of **16a** has a central C−C bond of 1.35 Å, but some external bonds are quite long (1.74 Å).[19] Merging the strategies of **15** (hexuple straps) and **16b** (linking bicylic units) leads to **17**, which has a central C−C bond length of 1.34 Å, again with some long C−C bonds in the bicyclic systems (1.74 Å).



16a

16b



17

Less-strained frameworks, which might be more easily synthesized, were also tested and still show significantly shortened bonds. System **18a** has a shortened bond of 1.46 Å.

Introduction of heteroatoms leads to a stronger squeeze, as shown for **18b** (1.41 Å).

18a

18b

Not Just s Character

In the course of this stroll into the largely neglected land of short bonds, we have developed a menagerie of molecules that are predicted to have very short bonds between coupled four-coordinate carbon atoms. Is it simple hybridization that drives this bond shortening, as others have rather convincingly argued for bicubyl **5**, the bicyclobutane dimers **2** and **3**, bitetrahedryl **4**, and Tanaka's derivative?[3,4] We don't think so. In Figure 2, we have used natural bond orbital (NBO) analysis[20] to determine the hybridization in our short bonds. The C–C bond lengths are plotted as a function of the percentage s orbital character in the bond for selected[21] molecules discussed herein as well as for some of the dimers previously studied. It is clear from Figure 2 that our molecules have C–C single bonds that are shorter by approximately 0.1 Å or more than what would be expected from hybridization alone. The additional strain caused by the threefold symmetric geometry constraints is responsible for this effect. Our short bonds simply cannot achieve "typical" lengths without wreaking havoc elsewhere in the molecule.

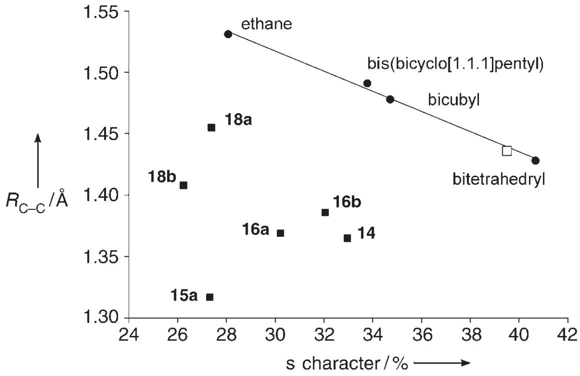


Figure 2. Percentage s orbital character (from an NBO analysis) and optimized C–C bond lengths for some selected molecules. The open square corresponds to Tanaka and Sekiguchi's hexakis(trimethylsilyl)bitetrahedryl. The squeezed bonds in the molecules proposed by us are shorter by approximately 0.1 Å or more than the lengths expected on the basis of hybridization arguments.

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[3] a) Bicubyls have been synthesized—the observed intercubyl distances in two examples are 1.458 and 1.474 Å; see: R. Gilardi, M. Maggini, P. E. Eaton, *J. Am. Chem: Soc.* **1988**, *110*, 7232–7234; b) P. von R. Schleyer, M. Bremer, *Angew. Chem.* ***1989***, *101*, 1264–1266; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1226–1228; c) Y. Xie, H. F. Schaefer, III, *Chem. Phys. Lett.* **1989**, *161*, 516–518; d) Y. Xie, H. F. Schaefer, III, *Chem. Phys. Lett.* **1990**, *168*, 249–252; e) Y. Xie, H. F. Schaefer, III, P. Aped, K. Chen, N. L. Allinger, *Int. J. Quantum Chem.* **1992**, *42*, 953–963; f) M.-J. Huang, N. Bodor, *Chem. Phys. Lett.* **1992**, *190*, 25–28; g) V. Gallasso, I. Carmichael, *J. Phys. Chem. A* **2000**, *104*, 6271–6276.

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[5] In D_{3d} or D_{3h} ethane, there are three structural parameters that may be chosen as the C–C and C–H bond lengths, and a C-C-H (or H-C-H) angle. In Figure 1, the energy is plotted as a function of the C–C bond length, with the other structural parameters optimized. Schleyer and Bremer[3b] performed a similar optimization, in which the C–C bond length was plotted versus the C-C-H angle in the optimized geometries.

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[7] Indeed, this work began as a competition between the research groups.

[8] Gaussian 03 (Revision B.04): M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian Inc., Pittsburgh PA, **2003**.

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[10] ADF2004.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.

[11] A cutaway image of this unusual structure is included in the Supporting Information.

[12] Calculations performed at the B3LYP/6-31G level.

[13] In this structure, the red highlighting shows the entire central ethane unit that contains the short bond. The calculation was performed using the ONIOM method, with the ethane treated at the B3LYP/6-31G* level and the diamond cage treated with AM1.

[14] For some cautionary considerations on calculations of encapsulation, see: H. Dodziuk, *Chem. Phys. Lett.* **2004**, *410*, 39–41.

[15] R. A. Pascal, Jr., *Eur. J. Org. Chem.* **2004**, 3763–3771.

[16] From here on, red indicates only the strained C–C bond.

[17] Q. Song, D. M. Ho, R. A. Pascal, Jr, *J. Am. Chem. Soc.* **2005**, *127*, 11246–11247.

[18] Replacement of the bridges with oxygen atoms gives a structure that is unstable with respect to dissociation into CO and CO_2. However, replacement of only the three bridging methylene groups associated with one inverted carbon center with nitrogen

(or oxygen) results in stable structures with two inequivalent bond lengths, one very short bond of 1.39 (1.38) Å and a set of three less-shortened bonds of 1.43 (1.45) Å.

[19] Recent calculation suggest that C–C bonds of 1.74 Å are right on the edge of stability; see: A. A. Zavitsas, *J. Phys. Chem. A* **2003**, *107*, 897–898 for a general discussion and T. Vreven, K. Morokuma, *J. Phys. Chem. A* **2002**, *106*, 6167–6170 for detailed calculations on hexaphenylethane.

[20] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926.

[21] Only those molecules in which the short-bonded carbon atoms are symmetrically equivalent were used. For some of our molecules, the NBO C–C bonding molecular orbitals have somewhat low occupancies, for instance, 1.916 in **15a**.