Why Is the Linking C–C Bond in Tetrahedranyltetrahedrane so Short?
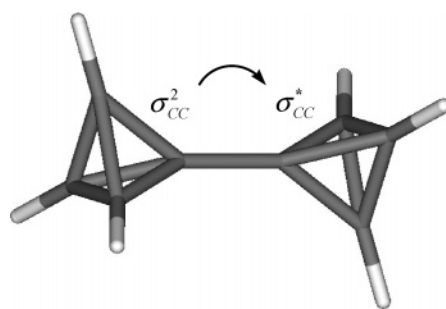
Yirong Mo*

Department of Chemistry, Western Michigan University, Kalamazoo, Michigan 49008

ymo@wmich.edu

ABSTRACT

The block-localized wave function (BLW) method has been employed to probe the origin of the very short linking C–C bond (1.436 Å) in tetrahedranyltetrahedrane. Computations show that the vicinal hyperconjugative interactions between the two tetrahedranyl groups is stronger than the conjugation in butadiene, and if there were no hyperconjugation effect, the bond distance would be 1.491 Å. Thus, both the hybridization mode and hyperconjugative interactions contribute to the shortening of the central C–C bond in tetrahedranyltetrahedrane.

Very recently, Tanaka and Sekiguchi synthesized trimethylsilyl-substituted tetrahedranyltetrahedrane, and their subsequent X-ray crystallographic analysis revealed that the linking C–C single bond is remarkably shortened to 1.436 Å.[1] This is essentially the shortest known noncyclic C–C single bond in a saturated hydrocarbon system, compared with, for instance, 1.531 Å in ethane. This finding is in accord with previous theoretical prediction.[2] Following the conventional theory,[3] Tanaka and Sekiguchi ascribed this very short bond length to the high s character in the exocyclic bond of tetrahedrane, which is supported by the NBO calculations ($sp^{1.53}$).[4] However, it should be noted that the low s character ($sp^{3.98}$) in the skeletal C–C bonds apparently is not consistent with their similarly short distances (1.483 Å in trimethylsilyl-substituted tetrahedranyltetrahedrane[1]) and the very high cage
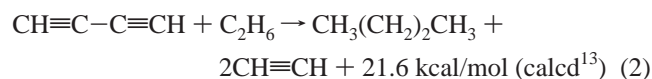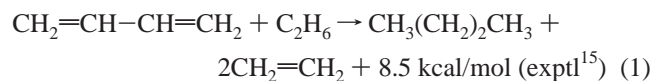
strain in tetrahedranyl groups, although the short skeletal C–C bonds have been well understood in terms of super σ-aromaticity within tetrahedrane.[5] Thus, it seems that the hybridization mode is not the sole factor determining bond distances.

Furthermore, as we repeatedly pointed out before,[6,7] the closeness among the C–H bonds in ethane (1.096 Å), ethene (1.085 Å), and ethyne (1.061 Å)[8] strongly indicates that the carbon hybridization mode actually imposes a moderate effect on the bond distances. NBO analyses at the HF/6-311+G(d,p) level found that the s character in the above three types of C–H bonds are $sp^{3.26}$, $sp^{2.39}$, and $sp^{1.11}$, respectively. As a consequence, aside from the hybridization mode, there must be other important factors contributing to or even dictating the significant fluctuation of the C–C bond lengths (e.g., the C–C single bond in tetraphenyldihydro-

(1) Tanaka, M.; Sekiguchi, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 5821.
(2) Xie, Y.; Schaefer, H. F., III. *Chem. Phys. Lett.* **1989**, *161*, 516.
(3) (a) Dewar, M. J. S.; Schmeising, H. N. *Tetrahedron* **1959**, *5*, 166. (b) Alden, R. A.; Kraut, J.; Traylor, T. G. *J. Am. Chem. Soc.* **1968**, *90*, 74. (c) Osawa, S.; Sakai, M.; Osawa, E. *J. Phys. Chem. A* **1997**, *101*, 1378.
(4) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. Theoretical Chemistry Institute, University of Wisconsin: Madison, WI, 2001.

(5) (a) Balci, M.; McKee, M. L.; Schleyer, P. v. R. *J. Phys. Chem. A* **2000**, *104*, 1246. (b) Moran, D.; Manoharan, M.; Heine, T.; Schleyer, P. v. R. *Org. Lett.* **2003**, *5*, 23.
(6) Mo, Y.; Lin, Z.; Wu, W.; Zhang, Q. *J. Phys. Chem.* **1996**, *100*, 11569.
(7) Mo, Y.; Schleyer, P. v. R. *Euro. J. Chem.* **2005**, in press.
(8) Delley, B. *J. Chem. Phys.* **1991**, *94*, 7245.

cyclobutaarenes is as long as 1.720 Å[9]). In general, through-bond interaction, steric repulsion and ring or cage strain elongate bonds,[9] whereas attractive orbital interaction or electron delocalization (conjugation and hyperconjugation) shortens bonds;[10] e.g., the short central C−C bond in butadiene has been historically attributed to the diene conjugation over the bond. Lately, we developed the block-localized wave function (BLW) method, which is a variation of the ab initio valence bond (VB) method.[11] Here, the term "block-localizaion" refers to the localization of electrons to a specific area (block) of the system; e.g., in the Kekulé structure of benzene, every two π electrons are localized to a pair of carbon atoms which forms a block. In contrast to the molecular orbital (MO) theory, individual resonance structures (either covalent or ionic structures) can be uniquely characterized with Heitler−London−Slater−Pauling (HLSP) functions within the VB theory. Based on the BLW method, we optimized the geometries of the most stable covalent structures of butadiene and butadiyne, and found that the optimal lengths of the central single Csp^2-Csp^2 and $Csp-Csp$ bonds would be 1.517 and 1.458 Å at the HF/6-311+G-(d,p) level if there were no conjugation over them, compared with 1.468 and 1.385 Å with conjugation considered. Therefore, we propose that both electron delocalization and hybridization mode make comparable contributions to the bond shortenings in butadiene and butadiyne. Our BLW method can be validated by the estimation of the conjugative stabilizations in both butadiene and butadiyne which centered a recent controversy.[12,13] Our BLW computations show that the resonance energy in butadiyne (−20.1 kcal/mol) is two times larger than in butadiene (−9.9 kcal/mol). These BLW data are in accord with the fact that there are two sets of diene conjugations in butadiyne but only one in butadiene, as well as Kollmar's early calculations[14] and the following isodesmic reaction heats

$$CH_2{=}CH{-}CH{=}CH_2 + C_2H_6 \rightarrow CH_3(CH_2)_2CH_3 +$$
$$2CH_2{=}CH_2 + 8.5 \text{ kcal/mol (exptl}^{15}) \quad (1)$$

$$CH{\equiv}C{-}C{\equiv}CH + C_2H_6 \rightarrow CH_3(CH_2)_2CH_3 +$$
$$2CH{\equiv}CH + 21.6 \text{ kcal/mol (calcd}^{13}) \quad (2)$$

Tetrahedrane is of high cage strain and high reactivity,[16] suggesting that the C−C bond orbitals are at high energy levels and, thus, the energy gap between the occupied σ_{CC} bond orbitals and adjacent virtual antibonding $\sigma_{CC}{*}$ orbitals is low compared with strain-free systems such as ethane. On one hand, the occupied-virtual orbital interactions within a tetrahedranyl moiety result in the three-dimensional σ-aromaticity which has been well recognized.[17] On the other hand, the orbital interactions between the two linking tetrahedranyl groups refer to the hyperconjugation effect which is expected to play a significant role in the shortening of the linking CC bond, much like the conjugation effect in butadiene and butadiyne. The mechanism of this type of hyperconjugation effect is also very much similar to the case of ethane where the nature of the rotation barrier has been debated.[18] Our most recent study by deactivating the vicinal hyperconjugative interactions among the methyl group orbitals in ethane which are self-consistently optimized shows that the steric effect dominates the barrier whereas the hyperconjugation plays a secondary role.[19] In this work, however, we intend to use the same strategy, which was first outlined by Mulliken in 1939,[20] to verify the significant hyperconjugative interaction in tetrahedranyltetrahedrane **1** (Figure 1).
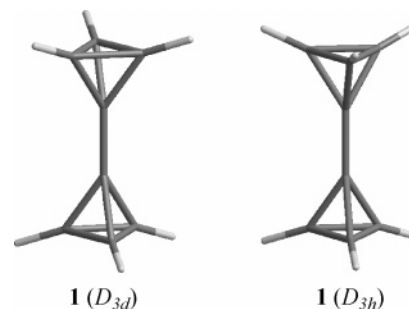
Figure 1. Staggered and eclipsed conformers of tetrahedranyltetrahedrane.

Hyperconjugation originates from the electron transfer from an occupied bond orbital to a vicinal unoccupied antibond orbital, which consequently stabilizes the system. Thus, a plausible approach to study the hyperconjugative interaction is to deactivate this stabilizing effect by confining the movement of electrons with localized group orbitals rather than delocalized molecular orbitals. In other words, a diabatic state in which there is no hyperconjugation effect should be constructed and computed. This is identical to the VB concepts of resonance structure and resonance energy, as the resonance energy is "obtained by subtracting the actual energy of the molecule in question from that of the most stable contributing structure."[21]

(9) Bettinger, H. F.; Schleyer, P. v. R.; Schaefer, H. F., III. *Chem. Commun.* **1998**, 769.
(10) Daudey, J. P.; Trinquier, G.; Barthelat, J. C.; Malrieu, J. P. *Tetrahedron* **1980**, *36*, 3399.
(11) (a) Mo, Y.; Peyerimhoff, S. D. *J. Chem. Phys.* **1998**, *109*, 1687. (b) Mo, Y.; Gao, J.; Peyerimhoff, S. D. *J. Chem. Phys.* **2000**, *112*, 5530.
(12) (a) Rogers, D. W.; Matsunaga, N.; Zavitsas, A. A.; McLafferty, F. J.; Liebman, J. *Org. Lett.* **2003**, *5*, 2373. (b) Cappel, D.; Tullmann, S.; Krapp, A.; Frenking, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 3617.
(13) Jarowski, P. D.; Wodrich, M. D.; Wannere, C. S.; Schleyer, P. v. R.; Houk, K. N. *J. Am. Chem. Soc.* **2004**, *126*, 15036.
(14) Kollmar, H. *J. Am. Chem. Soc.* **1979**, *101*, 4832.
(15) Kistiakowsky, G. B.; Ruhoff, J. R.; Smith, H. A.; Vaughan, W. E. *J. Am. Chem. Soc.* **1936**, *58*, 146.
(16) Maier, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 309.

(17) (a) Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 4781. (b) King, R. B. *Chem. Rev.* **2001**, *101*, 1119.
(18) (a) Brunck, T. K.; Weinhold, F. *J. Am. Chem. Soc.* **1979**, *101*, 1700. (b) Pophristic, V.; Goodman, L. *Nature* **2001**, *411*, 565. (c) Bickelhaupt, F. M.; Baerends, E. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 4183. (d) Mo, Y.; Wu, W.; Song, L.; Lin, M.; Zhang, Q.; Gao, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 1986.
(19) Mo, Y.; Gao, J. To be published.
(20) Mulliken, R. S. *J. Chem. Phys.* **1939**, *7*, 339.
(21) Wheland, G. W. *The Theory of Resonance*; John Wiley & Sons: New York, 1944.

We consider the interaction between two tetrahedranyl groups of C_{3v} symmetry which is the subgroup of both D_{3d} (for the staggered structure of **1**) and D_{3h} (for the eclipsed structure of **1**) point groups. Occupied molecular orbitals in a tetrahedranyl group are categorized into two types of irreducible bases, fully symmetric a_1 and degenerate e. As the linking CC σ bond is of a_1 symmetry, the vicinal $\sigma_{CC}-\sigma_{CC}*$ hyperconjugative interactions concern e-symmetric orbitals only. As a consequnce, we construct the wave function Φ_L of the diabatic state or Lewis (or localized) structure, where the hyperconjugation effect is deactivated, with e-symmetric functional group-localized orbitals

$$\Phi_L = \hat{A}[(1 - 11a_1)^{22}(1 - 8e_1)^{16}(1 - 8e_2)^{16}] \quad (3)$$

where group-localized orbitals $\{e_1\}$ or $\{e_2\}$ are constrained to be expanded with the basis functions of either of the two tetrahedranyl moieties only. Equation 3 corresponds to a hypothetical state where each tetrahedranyl moiety has 16 e electrons and these electrons do not penetrate into the other moiety. The derivation and self-consistent optimization of Φ_L is based on the BLW method which has been extensively applied to the study of aromaticity recently.[7] In contrast, the traditional MO theory leads to the wave function Ψ for the adiabatic state where all electrons are delocalized

$$\Psi = \hat{A}[(1 - 11a_1)^{22}(1 - 16e)^{32}] \quad (4)$$

The difference between Φ_L and Ψ lies in the e-symmetric orbitals. In Ψ, all e orbitals are delocalized to the whole molecule, i.e., expanded with the basis functions of both the tetrahedranyl moieties. But in Φ_L, e orbitals are confined to only one tetrahedranyl group and are thus nonorthogonal among those belonging to different moieties. This strategy essentially follows what Mulliken initially suggested for the study of hyperconjugation in ethane.[20] All orbitals in Ψ and Φ_L (here at the Hartree–Fock level) are self-consistently optimized, and the hyperconjugative interaction is measured as the energy difference between Φ_L and Ψ

$$E_{hc} = E(\Psi) - E(\Phi_L) \quad (5)$$

We optimized the geometries of both the staggered and eclipsed conformers of **1** at the HF, DFT and MP2 levels with 6-311+G(d,p) (see Table 1), and found that electron correlation slightly shortens the linking bond and lengthens the skeletal bonds, but the C(exo)−C(exo)−C(ske) angle remains unchanged at 144.7° with respect to both the calculation levels and conformers. Interestingly, the rotation barrier, which is around 3 kcal/mol, is similar to that in ethane. At the HF/6-311+G(d,p) geometries, our BLW computations result in the vertical hyperconjugation energy −15.2 kcal/mol in the staggered conformer and −14.1 kcal/mol in the eclipsed conformer. Note that this hyperconjugative capability is even much stronger than the conjugation in butadiene (−9.9 kcal/mol) and also two times larger than the hyperconjugation in ethane (−7.3 and −6.6 kcal/mol for

Table 1. Structural Parameters (Å) and Rotation Barrier (kcal/mol) with the 6-311+G(d,p) Basis Set at Various Levels

level	staggered conf $R(C-C)^a$	eclipsed conf $R(C-C)^a$	rotation barrier ΔE_b
HF	1.436/1.465	1.446/1.467	3.02
DFT-B3LYP	1.426/1.483	1.435/1.485	2.80
MP2	1.423/1.488	1.434/1.490	3.27

^{a} Values refer to the exocyclic/skeletal carbon−carbon bond lengths.

the staggered and eclipsed conformers, respectively).[19] Thus, we anticipate that this remarkable stabilizing force should exert appreciable influence on the central linking C−C bond, but its energetic contribution (1.1 kcal/mol) to the rotation barrier (3.0 kcal/mol) seems minor and the barrier is supposed to be dominated by the steric repulsion. It should be emphasized here that we never question the significance of the hyperconjugative interactions even in ethane and its congeners, rather, the magnitude of the contribution from these interactions to the rotation barriers.[18d,19]

Since the current BLW method is established at the HF level, we adopt the HF/6-311+G(d,p) geometry and optimize the central linking C−C bond length with the BLW method (Figure 2) for the staggered conformer of **1**. The BLW/6-
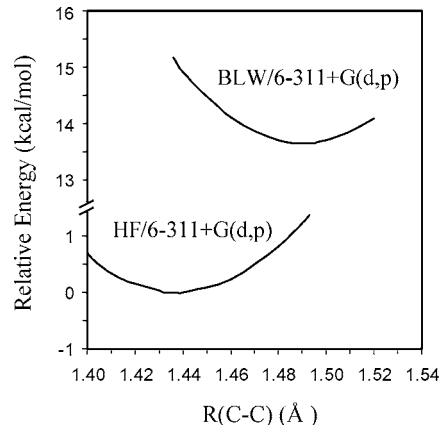
Figure 2. Energy changes with respect to the linking carbon−carbon bond distance when the vicinal hyperconjugative interactions in **1** are considered (HF) or not (BLW).

311+G(d,p) optimal bond distance 1.491 Å corresponds to the hypothetical situation with the hyperconjugative interaction between the two tetrahedranyl groups quenched. This value (1.491 Å) also lies exactly between the single Csp^2-Csp^2 (1.517 Å) and $Csp-Csp$ (1.458 Å) bond lengths, in excellent agreement with the hybrid orbital analysis ($Csp^{1.53}-Csp^{1.53}$) by the NBO method. Thus, we conclude that the stabilizing hyperconjugation effect shortens the central C−C bond in tetrahedranyltetrahedrane by 0.055 Å. To evaluate the influence of the hybridization mode on the bond length,

however, we need take ethane as a reference, whose C−C bond length is 1.531 Å (experimental value[8]) or 1.527 Å (at the HF/6-311+G(d,p) level). But as we mentioned in the above, there is also considerable hyperconjugation effect between the two methyl groups in ethane. With the similar procedure, the C−C bond length in ethane devoid of hyperconjugation was optimized with the BLW method and the optimal value is 1.567 Å. Therefore, the hyperconjugation effect shortens the C−C bond of ethane by 0.040 Å. As the hybridization mode for carbon atoms in the C−C bond of ethane is $sp^{2.35}$ based on the NBO analysis,[4] the comparison between tetrahedranyltetrahedrane and ethane suggests that the increasing of the s character for the exocyclic carbon hybrid orbitals ($sp^{1.53}$) shortens the C−C bond by 0.076 Å.

In summary, we verify that the shortest known noncyclic C−C single bond found recently in trimethylsilyl-substituted tetrahedranyltetrahedrane[1] has two comparable origins, namely the high s character in the exocyclic bond of tetrahedrane (58%), as well as the vicinal hyperconjugative interactions between the two tetrahedranyl groups (42%). Notably, the hyperconjugation over the central C−C bond in tetrahedranyltetrahedrane is even much more significant than the conjugation in butadiene. Electron-donating substituted groups attached to tetrahedranyl groups which can further lift the energy levels of the C−C bond electrons can enhance the hyperconjugative interactions and thus further shorten the linking C−C bond length and in the meanwhile stabilize the system.

OL052921Q