Symmetric C···H···C Hydrogen Bonds Predicted by Quantum Chemical Calculations

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Ⓢ Supporting Information

ABSTRACT: The symmetry of hydrogen bonds is a fundamental question regarding hydrogen bonding interactions. Although asymmetric C−H···C hydrogen bonds are known in the literature, no symmetric C···H···C hydrogen bonds have been reported. Herein, we propose the theoretical possibility of symmetric C···H···C hydrogen bonds on the basis of quantum chemical calculations. Several bridged carbanions with intramolecular symmetric C···H···C hydrogen bonds were designed computationally. The key to this design is to shorten the C···C distance to ca. 2.5 Å, which is predicted to be necessary for a single-well C···H···C hydrogen bond.

d(C···C) = 2.93 Å
asymmetric

d(C···C) = 2.53 Å
symmetric
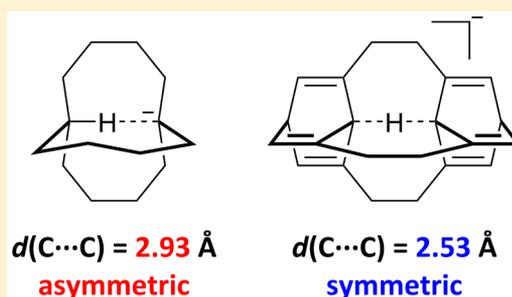
INTRODUCTION

The importance of hydrogen bonds[1] in natural science has been demonstrated by an enormous number of experimental and theoretical studies.[2] A frequently discussed topic related to the nature of hydrogen bonding is the symmetry of hydrogen bonds.[3] If the electron donors are identical, the hydrogen bond is either symmetric (X···H···X) or asymmetric (X−H···X). These two kinds of hydrogen bonds can be described by single- and double-well potentials, respectively (Figure 1a). Some representative examples of symmetric hydrogen bonds are given in Figure 1b (X = N,[4] O,[5] and F[6]).

Besides nitrogen, oxygen, and fluorine, carbon is also known to be more electronegative than hydrogen.[7] Thus, not only a C−H bond can act as the hydrogen bond donor but also a carbon atom may serve as the hydrogen bond acceptor.[2b,c] Even C−H···C,[2b,8] C−H···π[2b,c] and π···H$^+$···π[9] hydrogen bonds are known in the literature. To the best of our knowledge, all the reported C−H···C hydrogen bonds are asymmetric and no symmetric C···H···C hydrogen bonds have been reported, which is in sharp contrast to the other elements (N, O, and F) in the same period (row) of the periodic table. Therefore, it is important to answer the question of whether symmetric C···H···C hydrogen bonds exist or not, which may shed more light on the nature of hydrogen bonding.

Here, we propose the theoretical possibility of symmetric C···H···C hydrogen bonds. Several bridged carbanions with intramolecular symmetric C···H···C hydrogen bonds were predicted by quantum chemical calculations. To the best of our knowledge, these carbanions are the first examples of symmetric C···H···C hydrogen bonds.

COMPUTATIONAL METHODS

All quantum chemical calculations were performed with Gaussian 09.[10] For ab initio calculations, all electrons were included in the correlation calculations. For density functional theory (DFT) calculations, pruned integration grids with 99 radial shells and 590 angular points per shell were used. Potential energy surface scans were carried out at either the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level[11] or the ωB97XD/6-311+G(d,p) level.[12] Geometry optimizations of the stationary points were carried out at the ωB97XD/6-311+G(d,p) level. We chose this level of theory based on our previous ab initio benchmark study on carbon-to-carbon proton transfers.[13] Unscaled harmonic frequency calculations at the same level were performed to validate each structure as either a minimum or a transition state and to evaluate its zero-point energy and thermal corrections at 298 K and 1 atm. Quasiharmonic corrections were

(a)

(b)
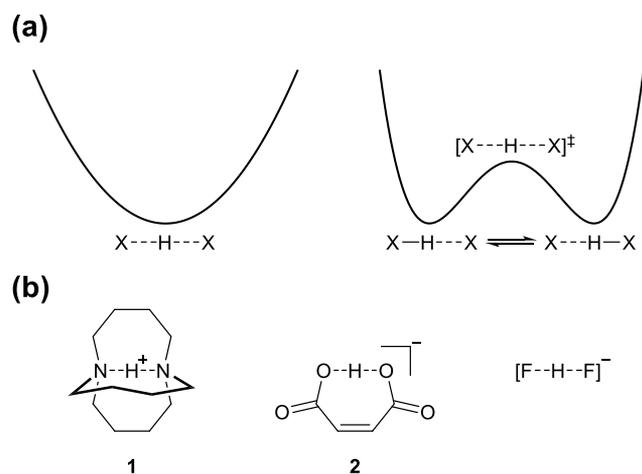
Figure 1. (a) Single- and double-well potentials for hydrogen bonding. (b) Representative examples of symmetric hydrogen bonds.

applied during the entropy calculations by setting all of the positive frequencies that are less than 100 cm^{-1} to 100 cm^{-1}.[14] Three-dimensional (3D) structures were prepared with CYLview.[15] Topological analyses were performed with Multiwfn 3.6.[16]

■ RESULTS AND DISCUSSION

Previous studies on X—H···X and X···H···X hydrogen bonds have demonstrated that at a shorter X···X distance the potential energy surface changes from double-well to single-well.[17] Therefore, we envisioned that if the C···C distance of an asymmetric C—H···C hydrogen bond decreased to a certain extent, it would become a symmetric C···H···C hydrogen bond. To justify this hypothesis, we performed potential energy surface scans on the hydrogen-bonded complex of methane and methyl anion by using the C···H distances (R1 and R2) as variables at the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level (Figure 2). When the C···C distance is fixed to 2.90 Å, the
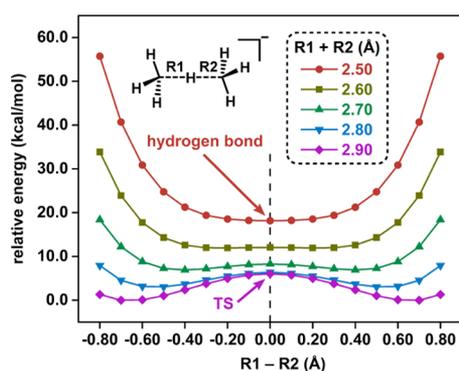
Figure 2. Potential energy surface scans on [H$_3$C···H···CH$_3$]$^-$. C_{3v} symmetry was applied. Computed at the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level. The relative energy of the global minima (R1 + R2 = 2.90 Å; R1 − R2 = ±0.70 Å) was set to 0.0 kcal/mol. TS = transition state.

potential energy surface is double-well and the symmetric structure is a transition state.[13,18] With the decrease in the C···C distance, the activation barrier decreases. Finally, at a fixed C···C distance of 2.50 Å, the symmetric structure becomes a minimum on the potential energy surface and can be regarded as a symmetric hydrogen-bonded complex.

By far, we have proposed the theoretical possibility of a symmetric C···H···C hydrogen bond. But one question still remains: how to overcome the Pauli repulsion of the two carbon atoms at a distance as short as ca. 2.5 Å. To solve this problem, we then turned our attention to the rational design of molecules with symmetric C···H···C hydrogen bonds. Inspired by the previous work on inside-protonated 1,6-diazabicyclo[4.4.4]tetradecane (1) with a short N···N distance of 2.53 Å,[4] we replaced the nitrogen atoms by carbon atoms and obtained an isoelectronic *in*-bicyclo[4.4.4]-1-tetradecyl anion (3) with D_3 symmetry (Scheme 1).[19] After geometry optimization at the ωB97XD/6-311+G(d,p) level, the C···C distance of this bridged carbanion 3 increased from 2.53 to 2.76 Å. To our disappointment, frequency analysis indicated that 3 is not an energy minimum but a transition state for the intramolecular 1,6-proton transfer within the C_3-symmetric carbanion 4. The Gibbs energy of activation for such a tautomerization is only 1.5 kcal/mol at 298 K, suggesting that the C—H···C hydrogen bond in 4 can be regarded as low-barrier hydrogen bond.[3a]

Scheme 1. Isoelectronic Inside-Protonated 1,6-Diazabicyclo[4.4.4]tetradecane (1) and *in*-Bicyclo[4.4.4]-1-tetradecyl Anions (3 and 4)^a
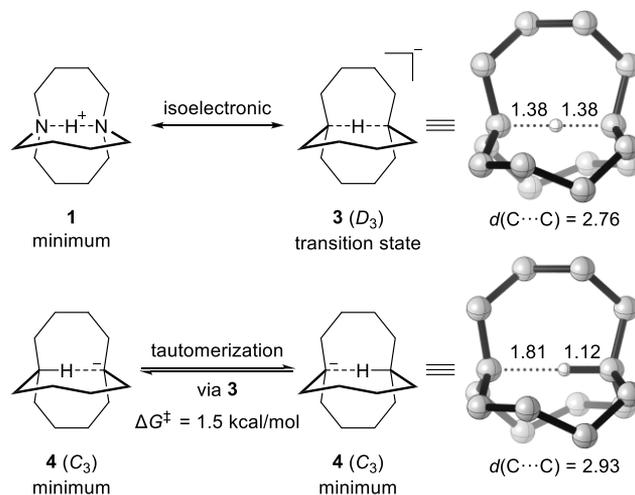
^{a}Computed at the ωB97XD/6-311+G(d,p) level. Bond distances are reported in Å. Hydrogens are not fully shown for clarity.

Then, bridgehead carbanions generated from cage precursors were introduced to increase the rigidity of the molecular skeleton so that the C···C distance might be further shortened (Scheme 2).[20] Three cage precursors, i.e.,

Scheme 2. Introduction of Bridgehead Carbanions Generated from Cage Precursors
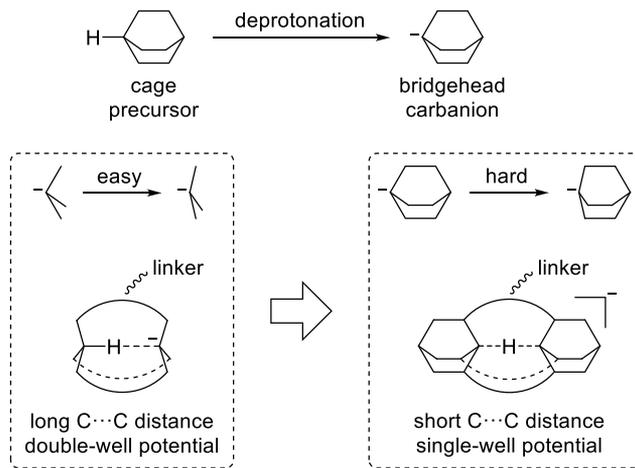
bicyclo[2.2.2]octane, quinuclidine, and barrelene, were considered. To our delight, the resulting D_3-symmetric 5−7 were all found to be energy minima (Figure 3). The DFT-predicted C···C distances are 2.56, 2.54, and 2.53 Å, respectively. Replacement of the saturated −CH$_2$CH$_2$− linker by an unsaturated (and shorter) −CH═CH− linker leads to carbanion 8 with an even shorter C···C distance of 2.49 Å. In this case, the intramolecular hydrogen bond also has a single-well potential (Figure 4), which resembles the potential energy surface of [H$_3$C···H···CH$_3$]$^-$ with a fixed C···C distance of 2.50 Å (Figure 2). To the best of our knowledge, these computationally designed bridged carbanions are the first examples of symmetric C···H···C hydrogen bonds. Notably, these carbanions can be regarded as "frozen" proton transfer transition states.[21]
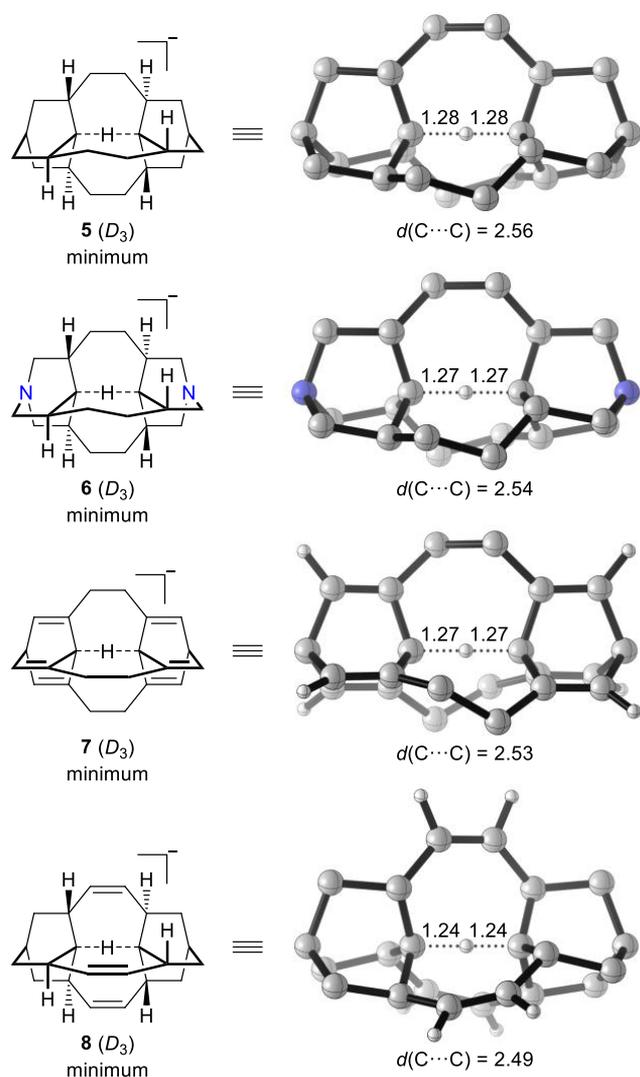
Figure 3. Bridged carbanions **5−8** with symmetric C···H···C hydrogen bonds. Computed at the ωB97XD/6-311+G(d,p) level. Bond distances are reported in Å. Hydrogens are not fully shown for clarity.
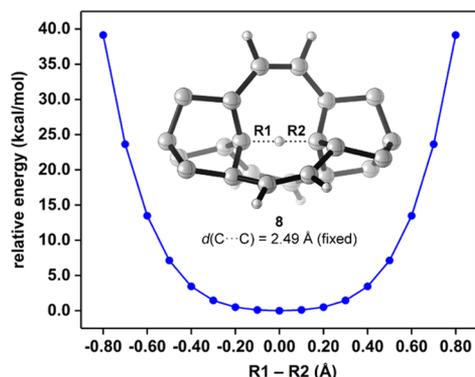
Figure 4. Potential energy surface scan on carbanion **8**. C_3 symmetry was applied. Computed at the ωB97XD/6-311+G(d,p) level. The relative energy of the minimum (R1 = R2) was set to 0.0 kcal/mol. Hydrogens are not fully shown for clarity.

Topological analyses provided additional evidence for the presence of hydrogen bonds in carbanions **4−8** (Table 1). First, the Quantum Theory of Atoms in Molecules

Table 1. Topological Analyses[a]

species	X−H···Y/X···H···Y	ρ (a.u.)	$\nabla^2\rho$ (a.u.)	CVB index
		properties at the Y···H BCP		
4	C−H···C	0.056	+0.062	−0.255
5	C···H···C	0.179	−0.268	−0.748
6	C···H···C	0.183	−0.277	−0.745
7	C···H···C	0.185	−0.285	−0.741
8	C···H···C	0.192	−0.305	−0.746
F−H···CO	F−H···C	0.021	+0.066	+0.013
F−H···N_2	F−H···N	0.017	+0.069	+0.046
F−H···OC	F−H···O	0.013	+0.060	+0.064
[F···H···F]$^-$	F···H···F	0.175	−0.320	−0.533

[a]Computed at the ωB97XD/6-311+G(d,p) level. BCP = bond critical point. ρ = electron density. $\nabla^2\rho$ = Laplacian of electron density. CVB = core−valence bifurcation.

(QTAIM)[22] was applied to characterize the C−H···C and C···H···C hydrogen bonds. The characteristic C···H bond critical points (BCPs) can be located in all cases. QTAIM parameters, such as the electron density (ρ) and its Laplacian ($\nabla^2\rho$) at the BCP, as well as the core−valence bifurcation (CVB) index[23] have been widely used to study the nature of intra- and intermolecular hydrogen bonds.[24] For weak hydrogen bonds with electrostatic character (e.g., those in complexes of HF with CO and N_2), ρ at BCP is small while $\nabla^2\rho$ at BCP and CVB index are positive; however, for strong hydrogen bonds with partial covalent character (e.g., [F···H···F]$^-$), ρ at BCP is large while $\nabla^2\rho$ at BCP and CVB index are negative (Table 1).[24] Based on these criteria, we suggested that the symmetric C···H···C hydrogen bonds in carbanions **5−8** are partially covalent in nature.

Finally, we investigated the proton affinities of carbanions **5−8** (Table 2).[25] The DFT-predicted sequence of proton

Table 2. Proton Affinities Computed at the ωB97XD/6-311+G(d,p) Level
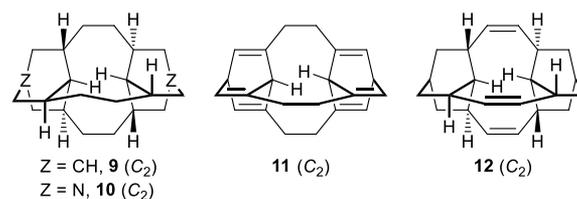
species	conjugated acid	proton affinity (kcal/mol)
5	**9**	375.3
6	**10**	372.4
7	**11**	369.2
8	**12**	373.5
CH_3^-	CH_4	418.0
NH_2^-	NH_3	405.8
OH^-	H_2O	390.7
F^-	HF	368.8

affinities is $F^- \approx$ **7** < **6** < **8** < **5** < OH^- < NH_2^- < CH_3^-, suggesting that the conjugated acids of carbanions **5−8**, i.e., their neutral hydrocarbon precursors **9−12**, are even more acidic than water in the gas phase. Notably, hydrocarbon **11** and HF are predicted to have similar thermodynamic acidities. We also computed the Gibbs energy profile for the generation of carbanion **7** via deprotonation of **11** with CH_3^-, NH_2^-, and

OH⁻ (Figure 5). The DFT-predicted Gibbs energies of activation are below 20 kcal/mol in all cases at 298 K,
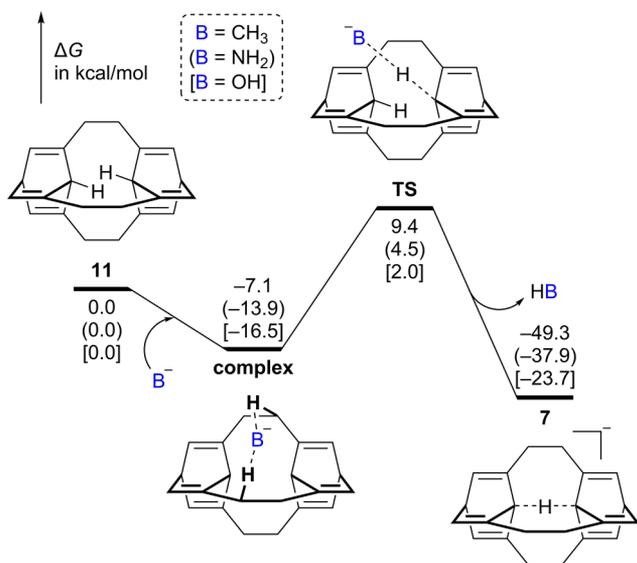
Figure 5. Gibbs energy profile for the generation of carbanion **7** from hydrocarbon **11** at 298 K. Computed at the ωB97XD/6-311+G(d,p) level.

indicating that these proton transfer processes may take place under mild conditions. Although these preliminary computational results are for illustrative purposes only, we hope that these positive results may convince synthetic chemists to design more viable precursors and bases to test our design.

CONCLUSIONS

We have proposed the theoretical possibility of symmetric C··· H···C hydrogen bonds on the basis of quantum chemical calculations. We predicted that a single-well C···H···C hydrogen bond will be present if the C···C distance is shortened to ca. 2.5 Å. Such a hypothesis has been supported by the exemplification of four computationally designed bridged carbanions with intramolecular symmetric C···H···C hydrogen bonds. The conjugated acids of these carbanions were predicted to be more acidic than water in the gas phase.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.9b02407.

> Potential energy surface scans; natural population analysis; computed energies and Cartesian coordinates of the stationary points (PDF)

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Notes

The authors declare no competing financial interest.

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