Discovery of Flexible C-C Bond: Reversible Expansion and Contraction of an Extremely Elongated C-C Single Bond

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Carbon–carbon (C–C) covalent bonds represent the most fundamental concept in organic chemistry. Elucidation of their nature is of great importance for further understanding of chemical phenomena; for instance, to understand what happens at the limits of a bond. Since deviation from the standard causes a large loss of bonding energy, generally C–C bond does not exhibit expansion or contraction. With regard to the C–C single bond, which has a standard length of 1.54 Å, three approaches have been taken to increase the bond length in neutral organic compounds to beyond 1.7 Å: (i) diamondoid dimers,¹ (ii)



fused or clamped hexaphenylethanes,^{2,3} and (iii) diaminocarboranes.⁴ Among them, we focused on the approach (ii) while adopting the intramolecular core-shell strategy which affects the stability of the compound with a weak and elongated bond. Based on the core-shell strategy, we previously designed dispiro[dibenzocycloheptatriene (DBCHT)] derivatives **1a-1c** and reported that **1a-1c** have an extremely elongated C–C single bond whose length is greater than 1.7 Å. Especially, **1c** recorded 1.806(2) Å at 400 K, which is the greatest value among neutral hydrocarbons. The presence of the bond was demonstrated based on the observation of bonding electron by X-ray analysis and of C–C stretching vibration by Raman spectroscopy.⁵

Such a weak and elongated bond should exhibit a unique bond "*flexibility*", which is a reversible expansion and contraction induced by external stimuli such as light or heat. Herein, we are focusing on DBCHT-dimer substructure in **1** since DBCHT-dimer⁶ has been known to show [2+2] photocycloaddition reaction to the caged molecule. If [2+2] photocycloaddition reaction occurs between DBCHT units in **1**, changes not only in physical properties but also in the bond length of the central C–C bond should be observed (Figure 1). Thus, we photoirradiated a solution of **1** at ambient temperature and found that [2+2] photocyclization proceeded quantitatively in **1** to produce caged molecules **2**. Then, we conducted the X-ray analyses at 400 K to determine the C–C bond lengths. As a result of the formation of cyclobutane ring, the neighboring central C–C single bond was certainly contracted. Especially,

2c shows the largest change in the bond length [1.7146(19) Å] from **1c**, which is up to 5% contraction of the bond. In addition, heating of **2** in a solid state, long-bonded compounds **1** were quantitatively regenerated by thermal cycloreversion.

These results revealed the bond "*flexibility*", a new facet of elongated C–C single bonds.⁷ In addition to expansion and contraction of the central bond, interconversion between **1** and **2** causes a large shift in HOMO level.



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