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Author(s)	Ishigaki, Yusuke; Shimajiri, Takuya; Takeda, Takashi; Katoono, Ryo; Suzuki, Takanori
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Longest C—C Single Bond among Neutral Hydrocarbons with a Bond Length beyond 1.8 Å

Yusuke Ishigaki,^{1,*} Takuya Shimajiri,¹ Takashi Takeda,² Ryo Katoono,¹ and Takanori Suzuki^{1,3,**}

¹Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan

²Present address: Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

³Lead Contact

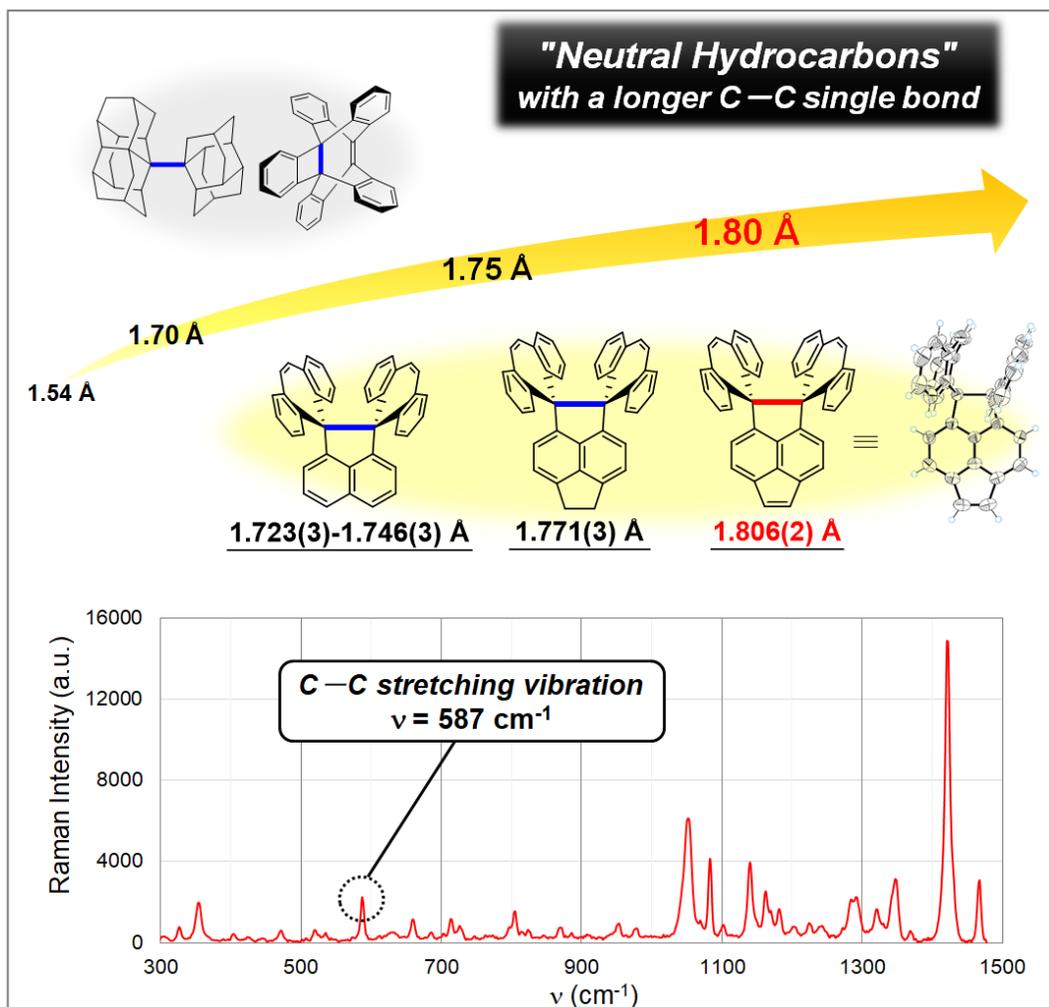
*Correspondence: yishigaki@sci.hokudai.ac.jp

**Correspondence: tak@sci.hokudai.ac.jp

SUMMARY

Based on the intramolecular "core-shell strategy", dihydropyracylene with two spiro(dibenzocycloheptatriene) units was designed, for which theoretical calculations predicted a very weak C-C bond with a bond length around 1.8 Å. This bond is expanded by the forced adoption of an eclipsed conformation and by angle strain through a "scissor effect". The highly strained hydrocarbon was isolated as a thermally stable compound with no signs of diradical contribution because the weak C-C bond (core) is protected by the shape-persistent fused-ring structure (shell). A Raman shift corresponding to the C-C stretching vibration (587 cm^{-1}) is much different from that for ethane (993 cm^{-1}). The bond length determined by X-ray [$1.806(2)\text{ Å}$] is greater than the shortest non-bonded intramolecular C-C contact [$1.80(2)\text{ Å}$]. The assumed limit for C-C bond (1.803 Å) by supposing linear correlation between bond length and bond-dissociation energy for covalent bonding was proven to be invalid.

Keywords: long bond, strained hydrocarbon, extreme structure, hexaphenylethane, polycyclic hydrocarbons, core-shell, scissor effect, DFT calculation, X-ray analysis, Raman spectroscopy



The Bigger Picture

The novel polycyclic hydrocarbons with two spiro(dibenzocycloheptatriene) units are synthesized as stable entities. Their C_{sp³}-C_{sp³} bond lengths determined by X-ray analyses are greater than the previously reported world records for hydrocarbons. Raman spectrum indicates the presence of an ultralong C-C bond, and the much smaller Raman shift corresponds to the very weak C-C stretching vibration.

INTRODUCTION

The C-C covalent bond is the most basic concept of organic compounds, in which bond length, bond angle, and torsion angle among carbon atoms are nearly constant based on their hybrid orbitals. On the other hand, unusual geometrical parameters have been reported for highly strained molecules, such as sterically-congested and/or curved polycyclic aromatic hydrocarbons¹⁻⁸ as well as cyclic π -conjugated molecules including cycloparaphenylenes,⁹⁻¹⁷ which are endowed with special properties that the ordinary hydrocarbons do not have. In these novel aromatic compounds, the pyramidalization of C_{sp^2} carbons as well as deviated bond/torsion angles from the standard values are responsible to form the distorted structures. Less common is the deviation of bond lengths from the standards, because even a small change causes large loss of bond dissociation energy (BDE).

The C_{sp^3} - C_{sp^3} bond length is generally 1.54 Å, as in the case of ethane **1**. While this standard bond length is observed in almost all compounds,¹⁸ several attempts have been made to elongate the C-C bond to gain new insight into the covalent bond and understand its properties upon expansion (Figure 1).¹⁹⁻³¹ For example, a longer C_1 - C_2 bond was predicted for hexaphenylethane (HPE) **2** due to large steric repulsion among its six phenyl groups.³² However, the parent HPE **2** is not stable because of facile fission of the C_1 - C_2 bond to generate two triphenylmethyl radicals, which finally produces the α,p -dimer, the more stable isomer of HPE.¹⁹ By preventing α,p -dimer formation, Mislow *et al.* obtained HPE derivative **3** with bulky *tert*-butyl groups, which is in equilibrium with the bond-dissociated triarylmethyl radical in solution. The length of the C_1 - C_2 bond (d_1) was determined to be 1.67(3) Å by an X-ray crystal structural analysis.²⁰ Although some polycyclic hydrocarbons have been reported to have much longer C-C bonds,^{33,34} those values were later proven to be artifacts due to the coexistence of a bond-dissociated valence isomer.^{35,36} Herges *et al.*²¹ and Toda *et al.*²² synthesized **4** and **5**, which can be regarded as stabilized HPE derivatives that do not undergo valence isomerization. They are stable compounds since C_1 - C_2 bond fission is suppressed due to sharing of two benzene rings of the HPE framework despite much greater d_1 values [1.713(2) Å and 1.734(5) Å, respectively] than in HPE **3**. Not only the HPE-type hydrocarbon **4** but also caged-alkane dimers can possess an expanded bond, as demonstrated by Schreiner *et al.*²⁶ A d_1 value of 1.704(4) Å has been reported for the cross-dimer of triamantane with diamantane **6**. For these caged-alkane dimers, bond dissociation was hampered by attractive dispersion interactions,^{26,27} and the dimers are stable even at high temperature. The theoretical calculations for these alkane dimers suggested that there is a certain limit for d_1 (1.803 Å),³⁷ since BDE becomes zero when the two carbon nuclei are separated beyond this distance. Thus, on the surface, it seems impossible to synthesize a stable hydrocarbon with a bond of d_1 beyond 1.803 Å.

We envisaged that, based on the "expandability" of the extremely expanded C-C bonds found in other types of HPEs **7** and **8**,²⁵ much longer C-C bonds could be realized by proper molecular design. The above theoretical limit for the C-C bond length was estimated by supposing a linear correlation between bond length and BDE. However, it has been known for years that through-bond-coupling can weaken the bond without changing the bond length.^{38,39} Furthermore, to describe the BDE of an expanded C-C bond, the Lennard-Jones-type potential may be more appropriate than a simple linear correlation. Thus, the change in BDE with an increase in the length of pre-strained weak C-C bonds (> 1.7 Å) should be smaller than the energy required to lengthen a normal C-C bond (1.54 Å) to the same degree. In fact, we very recently found that the expanded bond in some tetraarylpyracenes **9** (X = OMe, Y = F; X = OMe, Y = H) exhibited quite different d_1 values in their pseudo polymorphs because the bond length can be altered upon the application of a very slight energy change that is compensated by the crystal packing force, rather than by the electronic factors of the substituents.⁴⁰ Therefore, it is highly likely that we can find a C-C bond that is longer than the theoretically predicted value^{37,41} or the shortest non-bonded C \cdots C contact [1.80(2) Å]⁴² when HPE derivatives with greater steric repulsion could be synthesized as stable entities. Here we propose a new tactic of the intramolecular "core-shell strategy": the weak C_{sp^3} - C_{sp^3} bond (core) is protected by the shape-persistent and chemically inert C_{sp^2} fused rings (shell). In the newly designed dispiro(dibenzocycloheptatriene)-type HPEs, all degradation processes of the weak C_{sp^3} - C_{sp^3} bond are hampered to enable their isolation, and thus we actually found the longest C-C bond among neutral hydrocarbons as detailed below.

RESULTS AND DISCUSSION

Molecular Design and Theoretical Examination

To create novel hydrocarbons with an unprecedented C-C bond length beyond 1.80 Å, we set key points for the molecular design so that the compounds could maintain their chemical stability despite the presence of a very weak C-C bond. With regard to the chemical stability, we have to exclude all degradation processes such as "isomerization", "bond-dissociative ionization", "bond-dissociative addition", and "diradical formation". Degradation reactions must not occur when the degradation products have higher energy than the compound with an expanded bond. By adopting the intramolecular "core-shell strategy", such circumstances could be realized in some HPE derivatives by placing the weak C-C bond within a shape-persistent framework of C_{sp}² fused rings.

The intramolecular "core-shell strategy" applied on the HPE derivatives also favors with regard to bond expansion, since the "shell" structure is directly connected with the "core". By increasing the steric repulsion of the "shell", the C-C bond of the "core" is more expanded. In addition, we have shown that a "scissor effect"^{43,44} is a reliable structural modification for further expanding the "expandable" weak bond in fused HPE derivatives: the greater bond length for the C₁-C₂ bond in **8** or **9** than in **7** can be rationalized by considering the angle strain caused by the ethano bridge at the opposite *peri*-position. Thus, we could apply the "scissor effect" by attaching the fused ring at the terminal part of the "shell".

Restriction of the HPE skeleton to a highly eclipsed conformation to gain greater "eclipseness" is another key to realizing a greater d_I value, as demonstrated in **7-9**: a more eclipsed molecule in the crystal exhibits a greater bond length than a derivative with a less eclipsed geometry. Bridging of the two phenyl rings of HPE into a spiro ring is effective for favoring the eclipsed conformation. In fact, dispiro(acridan)-substituted pyracene (**DSAP**) in crystal form adopts a nearly eclipsed geometry. The precisely determined d_I value has been considered the longest C_{sp}³-C_{sp}³ bond [1.791(3) Å at 413 K] among neutral organic compounds. However, a single crystal of **DSAP** contains another crystallographically independent molecule with a skewed conformation and a smaller d_I value of 1.719(3) Å.²⁵ A density functional theory (DFT) calculation⁴⁵ shows that the skewed conformer is more stable in the case of **DSAP** (Figure 2N), and thus spiro-cyclization alone is not enough to assure restriction to the eclipsed conformation.

After a detailed theoretical examination at the B3LYP/6-31G* level of a series of compounds, we found that spiro(dibenzocycloheptatriene) is a special "shell" framework that can favor the eclipsed form of HPEs (Figure S9). With all above, we designed acenaphthene **10a**, pyracene **10b**, and dihydropyracylene **10c** as novel hydrocarbons. According to DFT calculations at the M06-2X/6-31G* level, they all adopt a completely eclipsed conformation (Figures 2B, 2E, and 2H) with high d_I values (Figure 2N) of 1.730, 1.767, and 1.771 Å, respectively. The highest value for **10c** among them as well as the higher value for **10b** than for **10a** are due to the "scissor effect" since the shorter bridge at the opposite *peri*-position induces greater angle strain on the naphthalene nucleus.

In contrast to the preference for the skewed conformer in **DSAP**, the eclipsed conformer is more stable for **10a-10c** (Figures 2M, S9M and S10). A series of calculations in which the torsion angle of **10c** was fixed predicted a preference for the eclipsed conformation as well as a greater d_I value for a more eclipsed conformation. There were only slight changes in the d_I value and the geometry of **10a-10c** when DFT calculations were performed at the M06-2X/cc-pVTZ level (Table S1).

These calculations showed that the less symmetrical bent geometry for the two spiro rings of the "shell" structure, which is the outstanding structural feature of the spiro(dibenzocycloheptatriene) derivatives **10a-10c**. One spiro ring adopts the well-known folded geometry. The concave face of the tub-shaped seven-membered ring faces another spiro unit, which is less folded. In this way, the two spiro units are overlapped in proximity to gain stabilization through π - π interaction [shortest C...C contact between the vinylic carbons of dibenzocycloheptatriene units: 3.23 Å for **10a**, 3.24 Å for **10b**, and 3.24 Å for **10c**]. Because of the such folded and compact shape of the "shell", any torsional displacement increases the steric repulsion between them and causes some loss of π - π stabilization. This is why the newly designed hydrocarbons **10a-10c** prefer a completely eclipsed geometry.

Such an overlapped geometry of the "shell" is also the key to maintaining chemical stability. Upon homolytic dissociation of the C₁-C₂ bond, dibenzocycloheptatriene units have to adopt a planar geometry that cannot form a face-to-face stacking arrangement with π - π interaction between the vinylic carbons. Thus, upon conversion of single-bonded **10a-10c** to the corresponding diradicals, not only the BDE but also the stabilization energy through π - π interaction would be lost, making "diradical formation" less favorable. In fact, UM06-2X calculations suggest that the bond-dissociated triplet diradical (Figure S11) corresponding to **10c** has a higher energy by 20.43 kcal mol⁻¹. Moreover, the biradical of singlet state has no energy minimum for **10c**, since the DFT calculations started from a single-bonded species and a bond-dissociated species (C \cdots C distance > 3.0 Å) as the initial structures converged to a single-bonded closed-shell species.

Furthermore, for bridged triphenylmethyl radicals, the formation of peroxide or hydrogen abstraction is a representative degradation process ("bond-dissociative addition").^{44,46} However, the "shell" structure of spiro(dibenzocycloheptatriene) derivatives **10a-10c** do not have enough space to accommodate two oxygen bridge or two C-H groups at the *peri*-position. According to DFT calculations, the spiro skeleton induces greater steric repulsion in the corresponding α,o -type isomer ($\Delta E = 22.16$ kcal mol⁻¹, Figure S12) for **10c**, and thus the "isomerization" of **10c** would not occur due to the shape persistency of the "shell". Unlike **DSAP**, which readily undergoes air oxidation to the corresponding bond-dissociated dication,²⁴ the "shell" structures without any heteroatoms in **10a-10c** is chemically inert and exhibits only limited electron-donating ability, and thus "bond-dissociative oxidation" is less probable.

Synthesis and Raman Characterization

Based on the above molecular design process assisted by DFT calculations, synthetic studies on hydrocarbons **10a-10c** have started. As shown in Scheme 1, diols **12a-12c** were obtained in 43-73% yields by lithiation of the corresponding dihalo derivatives **11a-11c** followed by the addition of dibenzosuberone. Diols **12a-12c** were then exposed to acidic conditions in the presence of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), and the resulting precursor dications were reduced with Zn powder to give the desired compounds **10a-10c** in 50-91% yields as colorless crystals for **10a** and **10b** and as an orange crystal for **10c**. The formation of target compounds **10a-10c** was confirmed by ¹H NMR and ¹³C NMR spectra and high resolution mass spectra. They are all thermally stable compounds that can be kept under air at ambient temperature, thus the validity of our intramolecular "core-shell strategy" was confirmed in terms of chemical stability.

We first investigated the stretching vibration of the expanded C₁-C₂ bond by Raman spectroscopy with single crystals at 298 K, which gives direct information regarding the force constant of the bond. Dihydropyrycene **10c** was predicted to have the longest C₁-C₂ bond among **10a-10c** by DFT calculations; its spectrum is shown in Figure 3A. The calculated spectra shown in Figures 3B (B3LYP/6-31G*) and 3C (M06-2X/6-31G*) very nicely reproduces the experimental result, especially when the B3LYP calculated spectrum is scaled with a factor of 0.9613⁴⁷ to consider anharmonicity (Figure S14F). The simulated absorption of symmetric C₁-C₂ stretching vibration in **10c** appeared at 658 cm⁻¹ in Figure 3C (M06-2X/6-31G*), which corresponds to the normal mode with the greatest amplitude along the trajectory of the stretching vibration. The M06-2X calculated Raman shift for **10c** is also smaller than those for the parent HPE **2** (883 cm⁻¹, 1.696 Å) and ethane **1** (1035 cm⁻¹, 1.526 Å) (Figures S15C and S15F). The observed Raman shift for **10c** is 587 cm⁻¹, which represents a large shift compared to that (993 cm⁻¹) in ethane **1**,⁴⁸ because the extremely elongated C-C bond has a much smaller force constant than the ordinary C-C bond (Figure S13); the estimated force constants (108.3 N m⁻¹ for **10c** and 441.0 N m⁻¹ for ethane **1**) were obtained as second derivatives of the energy to the bond length by DFT calculations (M06-2X/6-31G*).²¹ Figures 3A-3C also show other absorptions assigned as normal modes including another stretching vibration and/or deformation vibration.

As in the case of **10c**, observed Raman shifts for **10a** and **10b** (650 cm⁻¹ and 582 cm⁻¹, respectively) are in good agreement with the frequencies for the stretching vibration of the C₁-C₂ bond determined by M06-2X/6-31G* calculations (724 cm⁻¹ for **10a** and 655 cm⁻¹ for **10b**, respectively) (Figures S16 and S17). The Raman experiments demonstrated that dispiro(dibenzocycloheptatriene) derivatives **10a-10c** have a very weak C₁-C₂ bond, as predicted by DFT calculations. Next, we determined the *d_l* values in the crystal of these stable hydrocarbons by X-ray diffraction.

Experimentally Determined Bond Length by X-ray Analyses

X-ray analyses were first performed at 200 K to elucidate the precise bond lengths. For **10a**, three crystallographically independent molecules are apparent, all of which adopt a quite similar eclipsed conformation with less symmetrical bent geometries for the two dibenzocycloheptatriene groups (Figures 4A-I). The structure looks very similar to that of the optimized structure based on DFT calculations. The less symmetrical bent geometry was also observed in crystals of **10b** and **10c** (Figures 4J-O) [shortest C \cdots C contact between the vinylic carbons of dibenzocycloheptatriene units: 3.25(1), 3.16(1), and 3.23(1) Å for **10a**, 3.19(1) Å for **10b**, and 3.21(1) Å for **10c**] (Table S2).

The d_I values at 200 K are 1.720(2), 1.723(2), and 1.742(2) Å for **10a**, 1.773(3) Å for **10b**, and 1.7980(18) Å for **10c**. The last value is greater than that of **DSAP** [1.791(3) Å at 413K]. Moreover, the difference electron density maps (D maps) obviously indicate the presence of bonding electrons between C₁ and C₂ in **10c** (Figure 5A).

While the trends of the bond lengths and their structures by X-ray analyses are in good agreement with those by DFT calculations, the d_I values in the X-ray structures of **10a-10c** are greater than those in the optimized structures. The observed expansion may be related to the "expandability" of the weak bond.

To investigate the stability of these hydrocarbons in crystal form at elevated temperature, variable-temperature (VT) X-ray analyses were carried out at different temperatures (from 200 K to 400 K, every 40 K) by using the same single crystals of **10a-10c** (Figures S18-S27, Tables S3 and S4, and Data S1). The measurements were also conducted on **10c** below 200 K (160 K, 120 K, and 100 K, Table S4 and Data S1). No degradation was suggested in any of the measurements. Even when the X-ray analyses of **10a-10c** were conducted at 400 K, the estimated standard deviations of the C₁-C₂ bond length were less than 0.003 Å, indicating that the measurement was highly accurate even at high temperature (Figure 4S). Moreover, the D map indicates the presence of bonding electrons between C₁ and C₂ in **10c** even at 400 K (Figure 5B) due to the high accuracy of the X-ray measurements. The thermal ellipsoids of the carbon atoms are still small at 400 K, particularly in **10c** (Figures 4P-R), yet the C₁-C₂ bonds marginally expand upon heating. Thus, the greatest d_I value of 1.806(2) Å in **10c** was determined at 400K, which is a new record for an accurately determined C-C bond length. Therefore, the assumed limit for the C-C bond length (1.803 Å)³⁷ by supposing the linear correlation between the bond length and BDE was proven to be invalid in other types of hydrocarbons.

Stability of Hydrocarbons with a Very Weak Bond in Solution

To gain insight into the stability of weak bonds of d_I greater than 1.80 Å, ¹H NMR spectroscopy was conducted on **10a-10c** in solution. The ¹H NMR spectrum of **10c** in CDCl₃ at 296 K (Figure 6B) is similar to those of **10a** and **10b**. The spectrum did not change when the solution was left to stand at ambient temperature for 100 days under air (Figure 6A). No signs of line-broadening were observed for signals in the ¹H NMR spectrum of **10c** even at 400 K (Figure S28), which are assigned to a single species in the singlet state. The spectrum consists of peaks that can be assigned to a single species with C_{2v} symmetry despite the unsymmetrically bent structure in a solid state. No broadening or peak separation occurred even at 190 K (Figure S29), indicating a rapid degenerated conformational change in solution.

The same conclusion was reached when we investigated the ¹³C NMR spectra of **10a-10c**. The spectra showed the signals assigned to the carbon atoms involved in the ultralong bond, which appeared in the quaternary C_{sp³} region (81.82 ppm for **10a**, 86.30 ppm for **10b**, and 87.46 ppm for **10c**). A slight downfield shift was observed with an increase in the C-C bond length, which keeps the carbon nuclei away from bonding electrons. If the central bond was cleaved, we would have seen an obvious upfield shift, which was caused by a shielding effect due to bond-dissociated radicals. These results of ¹H and ¹³C NMR spectroscopy demonstrate that the hydrocarbon **10c** with the ultralong C₁-C₂ bond is extremely stable kinetically and thermodynamically even in solution.

Conclusions

Based on the proposed intramolecular "core-shell strategy", we have designed a series of dispiro(dibenzocycloheptatriene)-type HPE derivatives **10a-10c**. The weak bond in the newly prepared hydrocarbons is expanded by forced adoption of an eclipsed conformation. For the dihydropyrycene **10c**, further expansion was achieved through a "scissor effect". The very small Raman shift corresponding to the C-C stretching vibration as well as the greatest d_I value accurately determined by X-ray analysis revealed that **10c** has a very weak C-C bond. Nonetheless, **10c** and other dispiro(dibenzocycloheptatriene)s are thermodynamically and kinetically stable entities with no signs of diradical contribution even in solution.

Because the observed value is greater than the shortest non-bonded contact in [1.1.1]propellane derivative,⁴² the covalently bonded state and non-bonded state would be seamlessly connected in terms of the interatomic distance. Based on the present results, it is highly likely that we could find an even longer C-C bond ("hyper covalent bond" with a bond length of 1.8-2.0 Å) under the proper molecular design following the intramolecular "core-shell strategy".

EXPERIMENTAL PROCEDURES

Full experimental procedures are provided in the Supplemental Information.

ACCESSION NUMBERS

Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under accession numbers CCDC: 1567390-1567407, 1586191-1586195. These data can be obtained free of charge from the CCDC at http://www.ccdc.cam.ac.uk/data_request/cif.

SUPPLEMENTAL INFORMATION

Supplemental Information includes Supplemental Experimental Procedures, 29 figures and 4 tables can be found with this article online at #####.

Data S1. CIF files of **10a-10c**

AUTHOR CONTRIBUTIONS

Conceptualization, T.Su.; Methodology, Y.I. and T.Su.; Investigation, Y.I., T.Sh., T.T., and T.Su.; Writing – Original Draft, Y.I. and T.Su.; Writing – Review & Editing, Y.I., T.Sh., T.T., R.K., and T.Su.; Supervision, Y.I. and T.Su.; Project Administration, Y.I. and T.Su.; Funding Acquisition, Y.I., R.K., and T.Su.

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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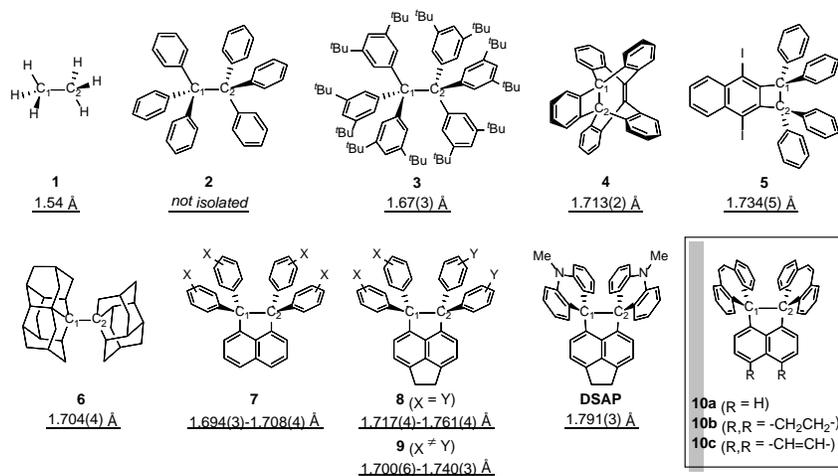


Figure 1. The Compounds in This Paper

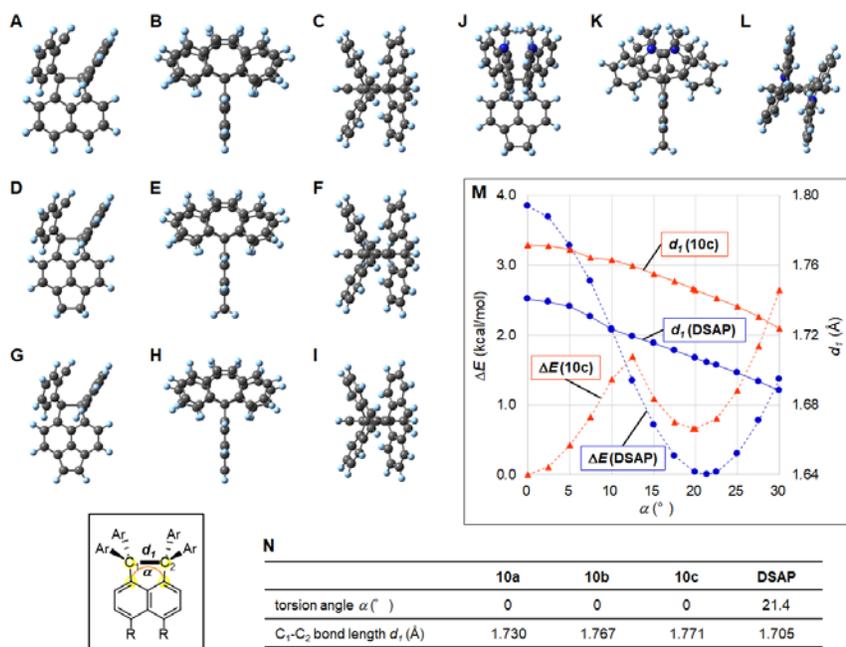


Figure 2. Theoretical Studies (M06-2X/6-31G*) of Newly Designed Derivatives 10a-10c and DSAP

(A-C) Front (A), side (B), and top (C) views of optimized structure for 10a.

(D-F) Front (D), side (E), and top (F) views of optimized structure for 10b.

(G-I) Front (G), side (H), and top (I) views of optimized structure for 10c.

(J-L) Front (D), side (E), and top (F) views of optimized structure for DSAP.

(M) Energy potentials (dotted lines) and d_1 values (solid lines) for 10c (red) and DSAP (blue) calculated by varying the torsion angle α in steps of 2.5° and by considering metastable ($\Delta E = 0.66$ kcal mol⁻¹ for 10c) or the most stable conformations.

(N) Torsion angles α and d_1 values of fully optimized structures for 10a-10c and DSAP.

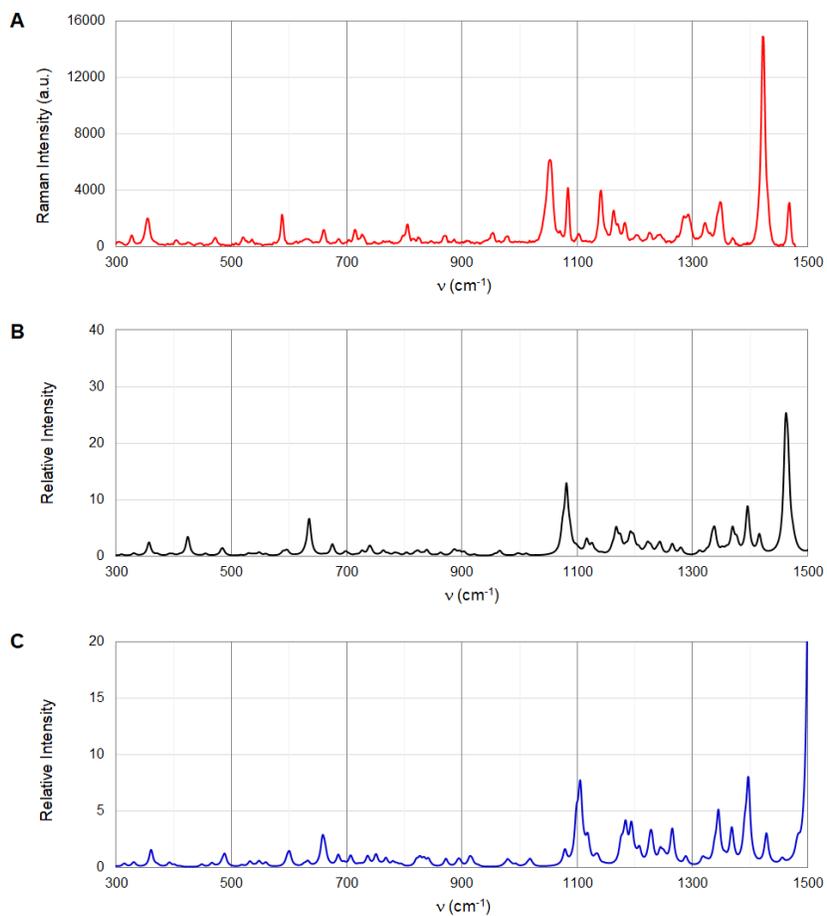


Figure 3. Raman Spectra of 10c

(A) A spectrum (red) measured by using a single crystal at 298 K.

(B) A simulated spectrum (black) based on DFT calculations at the B3LYP/6-31G* level.

(C) A simulated spectrum (blue) based on DFT calculations at the M06-2X/6-31G* level.

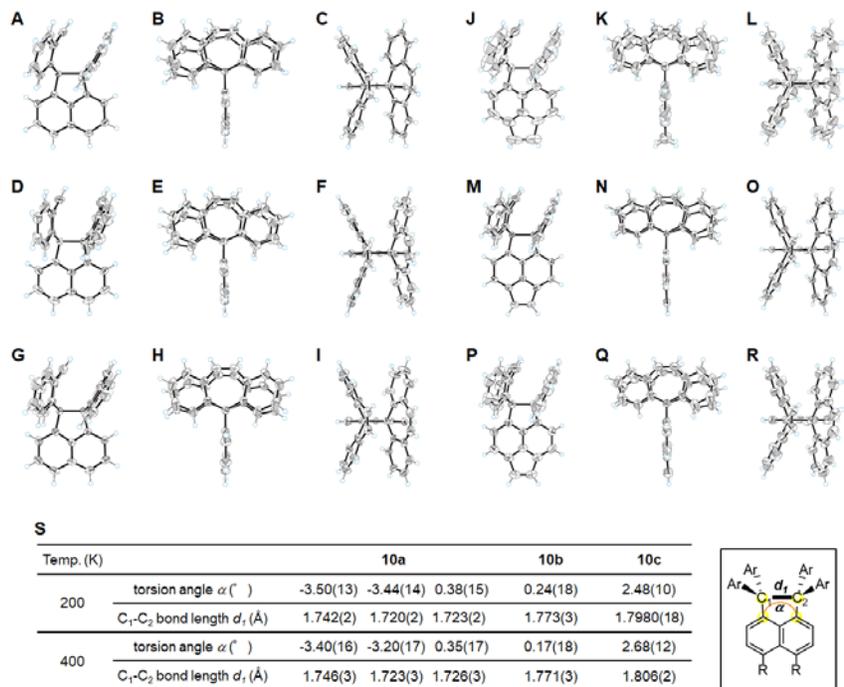


Figure 4. Data Obtained from X-ray Analyses of 10a-10c

(A-I) X-ray structures (front, side, and top views) of mol-1 (A, B, and C), mol-2 (D, E, and F), and mol-3 (G, H, and I) in three crystallographically independent molecules of **10a** at 200 K. Thermal ellipsoids are shown at the 50% probability level.

(J-L) X-ray structures [front (J), side (K), and top (L) views] of **10b** at 200 K. Thermal ellipsoids are shown at the 50% probability level.

(M-O) X-ray structures [front (M), side (N), and top (O) views] of **10c** at 200 K. Thermal ellipsoids are shown at the 50% probability level.

(P-R) X-ray structures [front (P), side (Q), and top (R) views] of **10c** at 400 K. Thermal ellipsoids are shown at the 50% probability level.

(S) Torsion angles α and d_i values of X-ray structures for **10a-10c**.

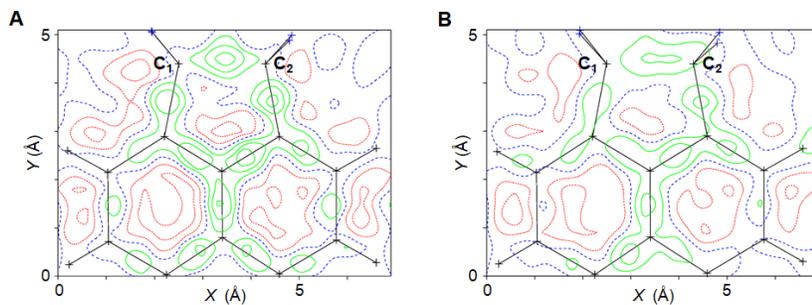


Figure 5. D Maps of 10c

(A) Difference electron density map (D map) around the ultralong C₁-C₂ bond in **10c** at 200 K. The contour interval is 0.05 eÅ⁻³; solid lines are positive values (green) and dotted lines are zero (blue) and negative values (red).

(B) Difference electron density map (D map) around the ultralong C₁-C₂ bond in **10c** at 400 K. The contour interval is 0.05 eÅ⁻³; solid lines are positive values (green) and dotted lines are zero (blue) and negative values (red).

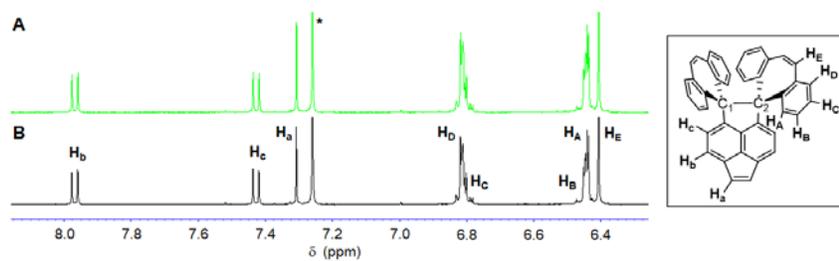


Figure 6. ^1H NMR Spectra of **10c** with an Ultralong $\text{C}_1\text{-C}_2$ Bond

(A) Spectrum of **10c** in CDCl_3 at 296 K after the solution was allowed to stand at ambient temperature for 100 days under air.

(B) Spectrum of **10c** in CDCl_3 at 296 K before standing. Peaks were assigned with the support of the two-dimensional $^1\text{H}\text{-}^1\text{H}$ COSY NMR spectrum and the presence of nuclear Overhauser effects (NOEs) between $\text{H}_\text{A}/\text{H}_\text{c}$, $\text{H}_\text{D}/\text{H}_\text{E}$, and $\text{H}_\text{A}/\text{H}_\text{b}$. *The residual proton signal of the solvent (CHCl_3 , $\delta = 7.26$ ppm).

Scheme 1. Preparation of Dispiro(dibenzocycloheptatriene) Derivatives

