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A Polycyclic Pentamer of Bicyclo[2.2.2]octene. A Hydrocarbon Molecule with a Long C−C Single Bond Connecting Two Cofacially Disposed Cyclopentadiene Rings

Koichi Komatsu,[*,†] Tohru Nishinaga,[†] Ken'ichi Takeuchi,[‡] Hans J. Lindner,[§] and
Jens Richter[§]

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan, Division of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan, and Institut für Organische Chemie, Technische Hochschule Darmstadt, Petersenstrasse 22, D-64287 Darmstadt, Germany

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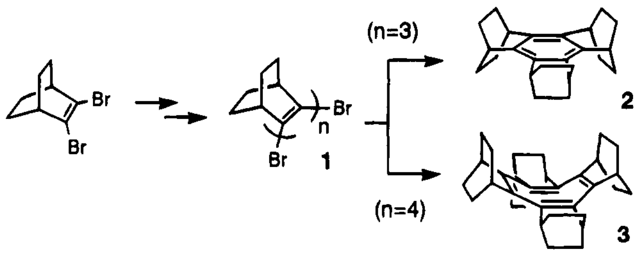
Intramolecular reductive cyclization was examined for the α,ω-dibromide of the bicyclo[2.2.2]oct-2-ene-2,3-diyl pentamer, **1** ($n = 5$). Molecular mechanics calculations indicated that direct C−C bond formation between the two terminal carbons is not feasible due to a long distance and steric hindrance in contrast to the cyclization of trimeric and tetrameric dibromides **1** ($n = 3$ and 4). Reduction of **1** ($n = 5$) with an excessive amount of sodium naphthalenide in THF at −78 °C afforded hydrocarbon **7** in 61% yield. The structure of **7** was determined by X-ray crystallography to be a bicyclo[2.2.2]octane having two bis(bicyclo[2.2.2]octeno)cyclopentadiene rings spiro-connected at the vicinal C-2 and C-3 carbons. The X-ray structure disclosed remarkable elongation (1.627(4) Å) of the σ-bond connecting the two cyclopentadiene rings. Theoretical considerations based on both molecular mechanics and molecular orbital calculations on compound **7** and on the related model compounds imply that the major contributing factor for this bond elongation is the σ−π interaction (C−C hyperconjugation) between the σ-bond and the dienyl π-systems in the cyclopentadiene rings. The elongated σ-bond was readily cleaved by potassium metal to give a cyclohexane substituted by two cyclopentadienide anions at the 1,4−positions.

The use of a certain molecular unit as a building block to construct highly ordered molecules with well-defined structures is an attractive methodology in modern synthetic and structural organic chemistry.[1] We have previously reported on the use of a bicyclo[2.2.2]oct-2-ene (BCO) unit as such a molecular building block.[2] Thus, linear combination of a dibromo-BCO monomer to oligomeric dibromides **1** followed by reductive cyclization at the two ends of **1** ($n = 3$ and 4) has successfully led to the formation of benzene **2** [2a] and cyclooctatetraene (COT) **3** [2b] fully annelated with bicyclic σ-frameworks (Scheme 1).

Although the central π-systems in **2** and **3** are simply the classically known aromatic and polyolefinic rings, they demonstrated unusual properties such as remarkable stabilization at the one- or two-electron oxidized states due to steric and electronic effects of the rigid σ-frameworks surrounding the π-systems.[2a,3,4] In the present paper we report on the two-electron reduction of BCO-pentamer **1** ($n = 5$) and on the novel structure and properties of a polycyclic hydrocarbon which was produced.

Scheme 1



Results and Discussion

Molecular Mechanics Calculations on the Favored Conformations of BCO Oligomers. The dibromide of BCO-pentamer, **1** ($n = 5$), was isolated from a mixture of oligomers **1** ($n = 2−5$), obtained via generation of bicyclo[2.2.2]octyne by lithiation of monomeric dibromide **1** ($n = 1$) followed by LiBr elimination, as has been reported.[2a]

In our previous work, two-electron reduction of the terminal dibromide of BCO trimer **1** ($n = 3$) was shown to give benzene **2** in high yield (89%),[2a] whereas the reduction of tetrameric dibromide **1** ($n = 4$) afforded COT **3** in 20% yield with benzene **2** as the major product (40%).[2b] As to the cyclization mechanism of **1** ($n = 3$) for example, the key reaction was considered to be an intramolecular cyclization of a σ-radical **4** (Scheme 2)

[†] Institute for Chemical Research, Kyoto University.

[‡] Division of Energy and Hydrocarbon Chemistry, Kyoto University.

[§] Institut für Organische Chemie, Technische Hochschule Darmstadt.

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(2) (a) Komatsu, K.; Aonuma, S.; Jinbu, Y.; Tsuji, R.; Hirosawa, C.; Takeuchi, K. *J. Org. Chem.* **1991**, *56*, 195−203. (b) Komatsu, K.; Nishinaga, T.; Aonuma, S.; Hirosawa, C.; Takeuchi, K.; Lindner, H. J.; Richter, J. *Tetrahedron Lett.* **1991**, *32*, 6767−6770.

(3) Nishinaga, T.; Komatsu, K.; Sugita, N.; Lindner, H. J.; Richter, J. *J. Am. Chem. Soc.* **1993**, *115*, 11642−11643.

(4) For the case of the tropylium analogue, see Komatsu, K.; Akamatsu, H.; Jinbu, Y.; Okamoto, K. *J. Am. Chem. Soc.* **1988**, *110*, 633−634. Komatsu, K.; Akamatsu, H.; Aonuma, S.; Jinbu, Y.; Maekawa, N.; Takeuchi, K. *Tetrahedron* **1991**, *47*, 6951−6966.

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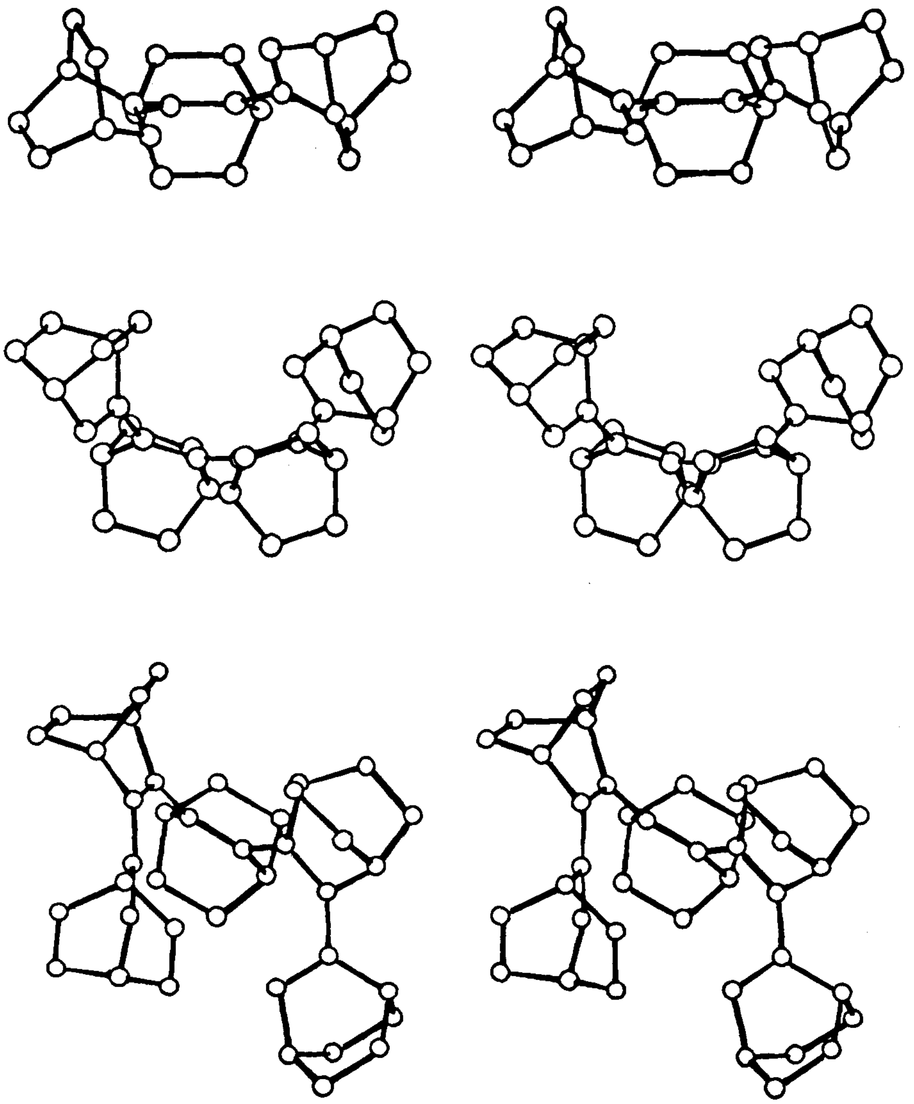
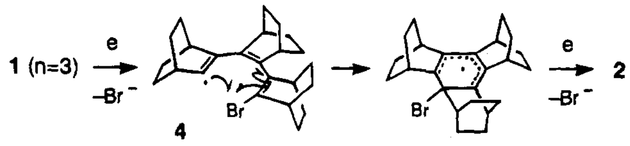


Figure 1. Stereoviews of MM2-minimized structures for the most stable conformers of **5** ($n = 3$), **5** ($n = 4$), and **5** ($n = 5$), from the top. Hydrogens are omitted for clarity.

Scheme 2



formed by "dissociative electron-transfer",[5] i.e., one-electron reduction with concomitant elimination of the bromide ion. In order to rationalize the occurrence of such a cyclization, we examined the conformation of a series of BCO oligomers by molecular mechanics calculations using the MM2 method.[6]

Since some of the parameters needed for full manipulation of bromo-substituted compounds were not available in the MM2 program,[6] calculations were conducted on oligomeric hydrocarbons **5** (Figure 2) instead. The MM2 calculations were carried out to obtain the optimized geometry as well as the steric energy for all the possible conformers of each of the oligomers **5** (n = 3, 4, and 5). The results are shown in Figure 1 and also schematically in Figure 2. Although the rotational barrier is quite small for each of the connecting single bonds,[7] and the molecules should be quite flexible, there seems to be a preference for specific conformations for each of the oligomers due to intramolecular nonbonded interactions between the BCO units.

Though, of course, these hydrocarbon structures can not be simply related to the conformation of dibromides **1**, they might serve as models of the neutral σ-radicals such as **4** in Scheme 2, which are about to undergo the intramolecular cyclization. Thus, the all-*syn* conformation, which is quite close to the structure of benzene **2**, is the most favorable for trimer **5** ($n = 3$), whereas the conformation containing one *anti* fragment is favored for tetramer **5** ($n = 4$). In the case of pentamer **5** ($n = 5$), the BCO unit newly added to **5** ($n = 4$) tends to take the *syn* conformation, although the polyenyl sequence can hardly maintain the π-system planar due to severe steric congestion. (See the Experimental Section for the specific values of dihedral angles.)

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(5) Andrieux, C. P.; Merz, A.; Savéant, J.-M. *J. Am. Chem. Soc.* **1985**, *107*, 6097–6103 and the references cited therein. See also Garst, J. F.; Barbas, J. T. *J. Am. Chem. Soc.* **1974**, *96*, 3239–3246.

(6) The MM2(87) program was obtained from QCPE, Indiana University.

(7) The rotational barrier around the central single bond for the dimer **5** ($n = 2$) was calculated as 3.5 kcal/mol: see Experimental Section.

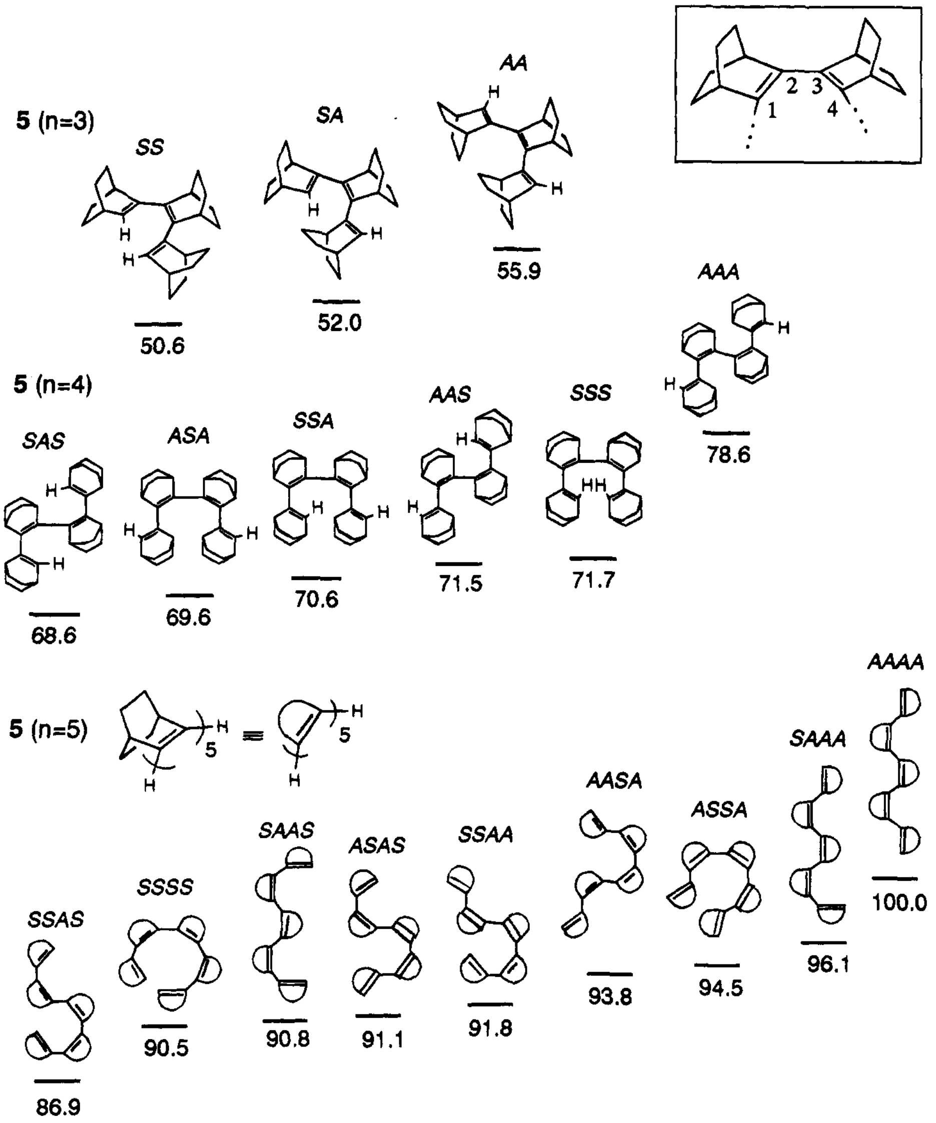
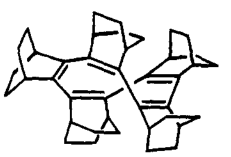


Figure 2. Schematic presentation of the possible conformers and steric energies (kcal/mol) calculated for the MM2-optimized structure of each confomer of **5** ($n = 3, 4, 5$). Combination of the relative conformation with respect to each single bond is shown on each structure: *S* refers to *syn* ($-90° < \theta < 90°$), and *A* to *anti* ($-180° < \theta < -90°$ or $90° < \theta < 180°$), where θ is the dihedral angle ∠1234 shown at the top. For the value of θ calculated for each comformer, see the Experimental Section.

Two-Electron Reduction of the Pentameric Dibromide 1 (n = 5). In contrast to the two-electron reduction of dibromides **1** ($n = 3, 4$), which gave the cyclized hydrocarbons smoothly at room temperature,[2] the reduction of pentamer **1** ($n = 5$) required cooling to -78 °C in order to effect a "clean" reaction to give a hydrocarbon product in substantial yield.

The hydrocarbon isolated as a major product in 61% yield exhibited ^{13}C NMR signals for two types of sp^2 carbons, three types of methine-, five types of methylene-, and one quaternary carbon, and ^{1}H NMR signals for methine singlets and complex methylene signals. The compound also showed an electronic absorption at 274 nm (log ϵ 3.62). From these spectral data, the product cannot be considered to be a 10-membered ring hydrocarbon such as **6**, which might have been formed if the two ends of **1** ($n = 5$) were simply connected by a single bond. Neither were ring-contracted products such as COT **3** nor benzene **2** formed.

The structure of this product was determined by X-ray crystallography to be hydrocarbon **7**, that is, a bicyclo[2.2.2]octane having two spiro-connected cyclopentadiene rings at the vicinal carbons, as shown in Figure 3.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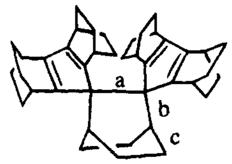

7

Supposing that the cyclization actually took place through a σ-radical with the structure similar to the most stable conformation of **5** ($n = 5$) shown in Figures 1 and 2, the direct ring closure between remote terminal carbons would have been sterically difficult. The formation of **7** most probably proceeded as shown in Scheme 3 by way of tandem double cyclization initiated by the σ-radical formed at one end of the BCO pentamer. This first cyclization can be viewed as an example of radical cyclization of the "5-exo-trig" type according to the classification by Baldwin.[8] The newly formed radical center can then attack the other end of the double bond to furnish two spiro-connected cyclopentadiene rings after further reduction. The second cyclization can alterna-

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[8] Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734–736.

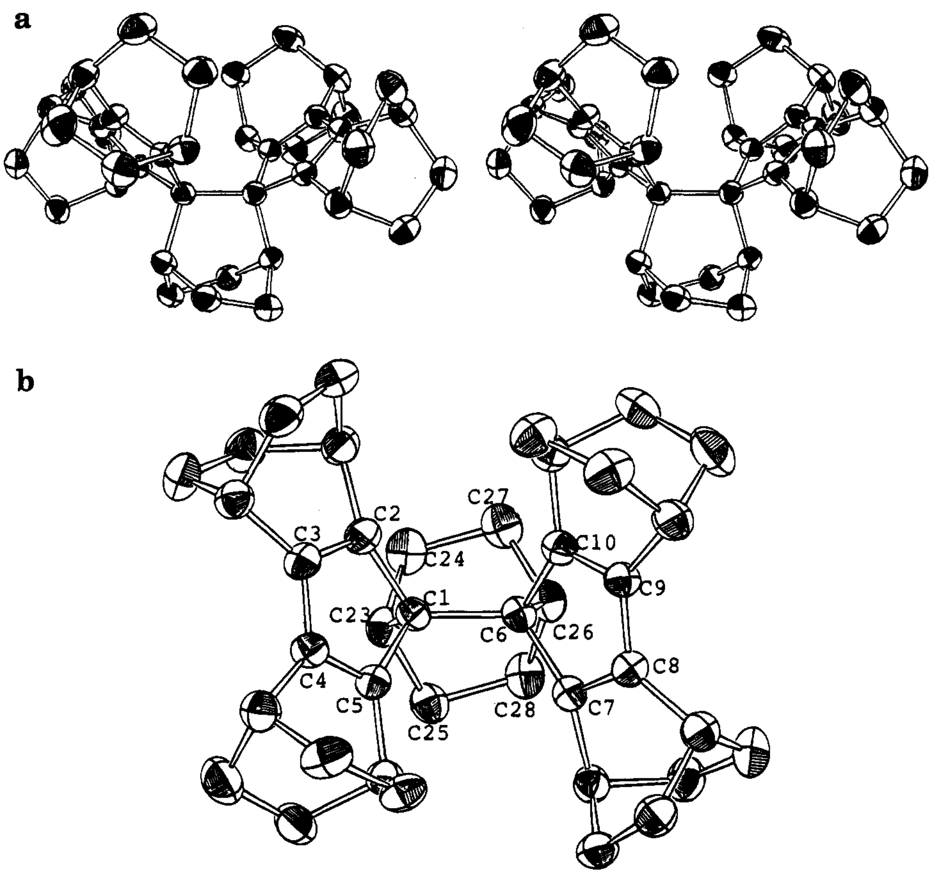
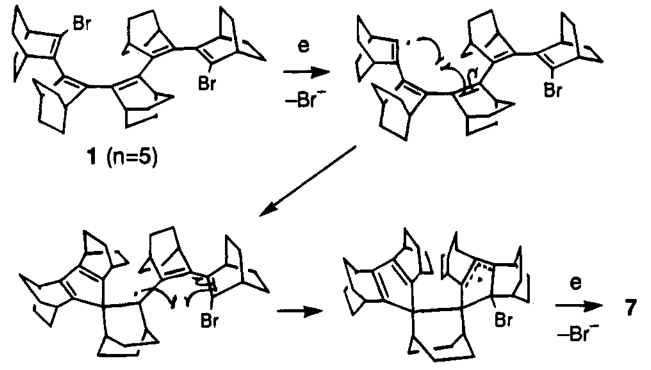


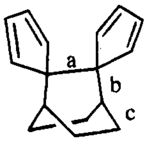
Figure 3. ORTEP drawings of the X-ray structure of **7**: (a) a stereoview of the side view; (b) the top view. Hydrogens are omitted for clarity. Some selected bond lengths (Å) and angles (deg) are: C1−C2, 1.567(5); C2−C3, 1.356(4); C3−C4, 1.447(5); C4−C5, 1.341(5); C5−C1, 1.536(4); C1−C6, 1.627(4); C6−C7, 1.572(5); C7−C8, 1.353(4); C8−C9, 1.439(5); C9−C10, 1.340(5); C10−C6, 1.539(4); C1−C23, 1.581(3); C23−C24, 1.531(5); C24−C27, 1.549(4); C27−C26, 1.526(5); C26−C6, 1.579(3); C1−C2−C3, 109.3(3); C2−C3−C4, 109.9(3); C3−C4−C5, 110.1(3); C4−C5−C1, 110.9(3); C5−C1−C6, 113.6(2); C2−C1−C6, 120.6(2); C1−C6−C10, 113.2(2); C1−C6−C7, 120.0(2); C5−C1−C2, 99.6(2); C7−C6−C10, 99.6(2); C6−C1−C23, 106.6(2); C1−C23−C24, 112.5(2); C1−C23−C25, 110.1(2).

Scheme 3



tively be considered as a disrotatory electrocyclization of the pentadienyl radical.

Structure of the BCO Pentamer 7. As shown in Figure 3, hydrocarbon **7** has a highly congested structure with the two BCO-annelated cyclopentadiene rings fixed in close proximity. In order to reduce the congestion, the two cyclopentadiene rings are skewed with each other and splayed out with the dihedral angle, between the mean planes of cyclopentadiene rings, of 86°. For a much simpler model **8** having no BCO-annelation, the MM2 calculations indicated no such skewing for the five-membered rings and indicated the splaying angle to be reduced (74.0°).



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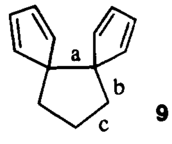

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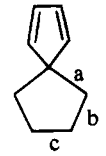

10

The most remarkable feature in the structure of **7** is a significant elongation (1.627(4) Å) of the central single bond (C1−C6) connecting the two cyclopentadiene rings. This bond is much longer than the generally known value of 1.54 Å for single bonds between sp^3-hybridized carbons, and is actually one of the longest C−C single bonds so far reported for cyclophanes,[9] photodimers of polynuclear aromatics,[10] and various other compounds with characteristic structural features.[11,12] The possible factors for the cause of this elongation will be discussed in detail below.

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(9) Gleiter, R.; Eckert-Maksic, M.; Schäfer, W.; Truesdale, E. A. *Chem. Ber.* **1982**, *115*, 2009−2011. Kovac, B.; Allan, M.; Heilbronner, E. *Helv. Chim. Acta* **1981**, *64*, 430−448, and references cited therein. Hanson, A. W. *Acta Crystallogr.* **1977**, *B33*, 2003−2007. Zhou, X.; Liu, R.; Allinger, N. L. *J. Am. Chem. Soc.* **1993**, *115*, 7525−7526.

(10) For example, Anderson, B. F.; Ferguson, J.; Morita, M.; Robertson, G. B. *J. Am. Chem. Soc.* **1979**, *101*, 1832−1840. Ehrenberg, M. *Acta Crystallogr.* **1966**, *20*, 182−186. Choi, C. S.; Marinkas, P. L. *Acta Crystallogr.* **1980**, *B36*, 2491−2493. Dougherty, D. A.; Choi, C. S.; Kaupp, G.; Buda, A. B.; Rudzinski, J. M.; Osawa, E. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1063−1070.

(11) Osawa, E.; Kanematsu, K. In *Molecular Structure and Energetics. Vol. 3. Studies of Organic Molecules;* Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1986; pp 329−369.

Table 1. Comparison of Bond Lengths and Splaying Angles for Various Spirocyclopentadienyl Compounds

compd	method	bond length (Å) *a*			Cp−Cp (deg)[a]
		b	*c*		
7	X-ray	1.627(4)	1.580(3)	1.531(5)	85.9
	MNDO	1.632	1.601	1.563	89.4
	PM3	1.578	1.572	1.533	85.4
	MM2	1.570	1.561	1.549	76.7
8	MNDO	1.591	1.580	1.556	76.9
	STO-3G	1.596	1.569	1.549	76.2
	PM3	1.555	1.548	1.532	76.2
	MM2	1.545	1.545	1.542	74.0
9	MNDO	1.580	1.562	1.540	77.2
	PM3	1.549	1.534	1.522	76.4
	MM2	1.531	1.533	1.541	72.4
10	MNDO	1.560	1.542	1.539	–
	PM3	1.529	1.527	1.526	–
	MM2	1.531	1.538	1.542	–

[a] The splaying-out angle between two spiro-cyclopentadiene rings (the dihedral angle between two planes formed by C1, C2, and C5 of the two cyclopenta-2,4-diene rings).

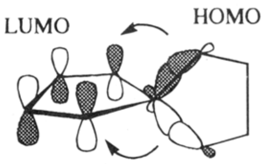
At first sight, the most obvious factor for this bond elongation may seem to be the steric one,[13] that is, the release of severe steric congestion between the two cyclopentadiene moieties with such bulky and rigid frameworks. Whether this is the sole effect for such elongation could be judged from the results of molecular mechanics (MM2) calculations. The calculated structure fairly well reproduced the experimentally observed one *except* that the central σ-bond was calculated to be only 1.570 Å, which is 0.057 Å shorter than the observed value. This difference between the calculated value (by MM2) and the observed value is most probably attributed to an electronic effect which was not fully taken into consideration in the MM2 calculations.[11,12,14]

Actually, the results of semiempirical molecular orbital calculations using MNDO[15] for hydrocarbon **7** gave a value of 1.632 Å for this central σ-bond, which is quite close to the observed one. In contrast, calculations by PM3 method[15b,16] resulted in only a modestly long bond distance of 1.578 Å, and a similar trend was observed for a series of related compounds as summarized in Table 1. For the simpler model **8**, this central bond length was calculated by the MNDO method to be 1.591 Å, which is still considerably long in spite of the absence of any steric congestion. Ab initio molecular orbital calculations (STO-3G)[17] on **8** resulted in a value of 1.596 Å for the same bond, thus supporting the validity of the MNDO result. These values are to be compared with the length of 1.545 Å calculated for the same bond in **8** by MM2, which is nearly 0.05 Å shorter. (See Table 1.)

From these results, it is tempting to assume that a through-bond coupling[12,14] is operating between the two cofacial cyclopentadiene systems to weaken the central bond. However, when we examine the X-ray structure of **7** more carefully, it is noted that the bonds next to the central bond are also elongated (C1−C23, 1.581(3); C6−C26, 1.579(3) Å), whereas other single bonds are in the normal range of the C−C single bond length. This suggests that the bond elongation is originating from a σ−π interaction (C−C hyperconjugation) between the diene systems of the cyclopentadiene rings and the single bond connecting them.

As shown in Table 1, in the case of the more simplified model **9**, i.e., a cyclopentane having spiro-cyclopentadiene rings at the vicinal positions, the central bond was calculated by the MNDO method as 1.580 Å while the next bond was calculated as 1.562 Å. Even in the simpler model **10**, i.e., a cyclopentane with only one spiro-cyclopentadiene, the MNDO calculations showed that the cyclopentane's single bond from the spiro-carbon is 1.560 Å, which is nearly 0.02 Å elongated compared with the rest of the single bonds in the same ring (Table 1). Again, there was observed no such bond-elongation in the results of MM2 calculations for compounds **9** and **10**.

From these results, a σ-bond which is in a geometry nearly parallel to the 2p orbitals of a cyclopentadiene ring appears to be elongated due to C−C hyperconjugation with the 2p orbitals. This is in accord with a prediction from a simple frontier orbital model (**11**) that the major interaction between HOMO of the σ-bonds and LUMO of diene would make the σ-bonds longer. A typical example for such interaction is seen in spiro[2.4]hepta-4,6-diene (**12**) which displays marked elongation and shortening of the σ-bonds in the cyclopropane ring.[18] Then it would be quite reasonable to suppose that the central single bond in **7**−**9** is further elongated due to doubly enhanced hyperconjugation effects caused by the two adjacent cyclopentadiene rings.[19]



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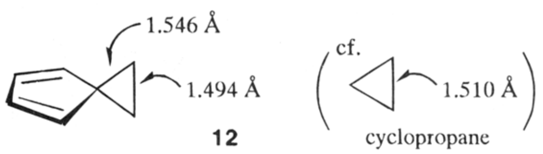

12

cyclopropane

Reactions of the BCO Pentamer 7. Reflecting such a strained structure with an elongated central bond, the hydrocarbon **7** was found to be thermally unstable, decomposing into a mixture of unidentified products by heating in xylene at 150 °C in an ampoule sealed under vacuum.

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(12) Anstead, G. M.; Srinivasan, R.; Peterson, C. S.; Wilson, S. R.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 1378−1385, and references cited therein.

(13) For examples of bond elongation solely due to steric repulsion, see Beckhaus, H.-D.; Kratt, G.; Lay, K.; Geiselmann, J.; Rüchardt, C.; Kitschke, B.; Lindner, H. J. *Chem. Ber.* **1980**, *113*, 3441−3455. Winiker, R.; Beckhaus, H.-D.; Rüchardt, C. *Chem. Ber.* **1980**, *113*, 3456−3476. Beckhaus, H.-D.; Hellmann, G.; Rüchardt, C. *Chem. Ber.* **1978**, *111*, 3764−3779.

(14) Hoffmann, R. *Acc. Chem. Res.* **1971**. *4*, 1−9. Dougherty, D. A.; Schlegel, H. B.; Mislow, K. *Tetrahedron* **1978**, *34*, 1441−1447.

(15) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899−4907. (b) The calculations were conducted using the standard method implemented in the MOPAC 6.0 semiempirical orbital package.

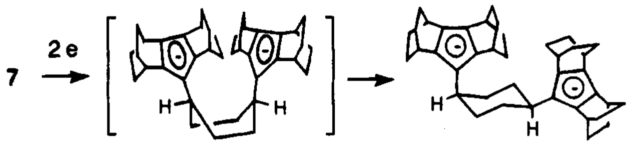
(16) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221−264. The results with AM1 calculations showed a similar tendency.

(17) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A.; *GAUSSIAN 92, Revision C*; Gaussian, Inc., Pittsburgh, PA, 1992.

(18) Staley, S. W.; Howard, A. E.; Harmony, M. D.; Mathur, S. N.; Kattija-Ari, M.; Choe, J-I.; Lind, G. *J. Am. Chem. Soc.* **1980**, *102*, 3639−3640. Harmony, M. D.; Mathur, S. N.; Choe, J-I.; Kattija-Ari, M.; Howard, A. E.; Staley, S. W. *J. Am. Chem. Soc.* **1981**, *103*, 2961−2966. We are indebted to Professor L. T. Scott for calling our attention to this work.

(19) The through-bond coupling (ref 14) between the 2p orbitals of the two cyclopentadiene rings in **7**, if present, would not be significant since the two π-systems are opened up with an angle of 86°, which seems too large to cause the effective interaction.

Scheme 4



13

Hydrocarbon **7** exhibited a nearly reversible oxidation wave at a considerably low potential such as +0.31 V vs Ag/Ag$^+$ [20] upon cyclic voltammetry carried out in dichloromethane. It is hypothesized that the weak central σ-bond is oxidatively cleaved. The electrolyzed solution exhibited a broad 5-line signal by ESR spectroscopy, but its life time was too short to allow detailed examination. Hydrocarbon **7** also readily reacted with oxidizing agents such as antimony pentachloride, silver nitrate, and nitrosonium tetrafluoroborate, but did not afford a product with a well-defined structure.

In contrast, reduction of **7** with potassium metal in THF-d_8 in a vacuum-sealed tube smoothly afforded a solution which exhibited ^{1}H and ^{13}C NMR spectra that are assignable to 1,4-cyclohexylenebis(cyclopentadienide) dianion **13** (Scheme 4), thus chemically confirming the weakness of the elongated central bond.

Conclusion

Two-electron reduction of the α,ω-dibromide of bicyclo[2.2.2]oct-2-ene-2,3-diyl pentamer (**1** (n = 5)) results in the formation of a highly congested hydrocarbon, **7**. From the structure of an MM2 optimized model of the pentamer, the most probable reaction pathway is an intramolecular, tandem radical-cyclization forming two cyclopentadiene rings consecutively. Exceedingly high reactivity of the intermediate radical species would possibly be the primary cause for formation of such an overcrowded molecule. The most characteristic feature of this molecule is elongation of the central σ-bond connecting the two cyclopentadiene rings. This is ascribed not simply to steric congestion but more importantly to the σ–π conjugation (C–C hyperconjugation) of this σ-bond with the two dienyl π-systems. The weakness of this σ-bond is experimentally proven by ready cleavage upon reduction. In summary, this study presented a rare example in which even a σ-bond in a nonstrained medium-sized ring can effectively interact with π-conjugated systems when both moieties are rigidly disposed with each other at an appropriate arrangement for such electronic interaction.

Experimental Section

General experimental procedures and instruments used are described in a previous paper.[21] The pentameric dibromide **1** (n = 5) was prepared as has been reported.[2a]

Reduction of the Pentameric Dibromide 1 (n = 5). To a stirred solution of **1** (n = 5) (215 mg, 0.311 mmol) in THF (25 mL) at −78 °C was added dropwise a solution of about 0.6 M sodium naphthalenide in THF (1.7 mL, 1.0 mmol). Addition of each drop of the naphthalenide solution caused a rapid coloration to deep red-purple. After stirring for 15 min at −78 °C the reaction mixture was quenched with methanol (20 mL) and allowed to warm to room temperature. The white solid that separated was collected by filtration and identified as hydrocarbon **7** (100.5 mg, 61%). Hydrocarbon **7** is unstable under acidic conditions and decomposed on a silica gel column during attempted chromatography. A single crystal of **7** was prepared by very slow recrystallization from benzene: mp 247–248 °C (dec); ^{1}H NMR (C_6D_6, 270 MHz) δ 3.23 (s, 4 H), 2.81 (s, 4 H), 2.26 (br d, J = 8.1 Hz, 4 H), 1.60–0.89 (m, 38 H); ^{13}C NMR (C_6D_6, 67.8 MHz)[22] δ 151.2 (C=), 143.9 (C=), 67.4 (C), 37.3 (CH-), 35.5 (CH-), 29.2 (CH_2), 28.6 (CH-), 27.5 (CH_2), 27.3 (CH_2), 26.4 (CH_2), 25.8 (CH_2); IR (KBr) 3010, 2990, 2960, 2930, 2855, 1485, 1465, 1450, 1355, 1340, 1320, 1180, 1155, 1140, 990, 860, 875, 870, 810, 760 cm^{-1}; UV (THF) λ_{max} 274 (log ϵ 3.62); HRMS calcd for $C_{40}H_{50}$: 530.3910. Found, 530.3918. Anal. Calcd for $C_{40}H_{50}$: C, 90.51; H, 9.49. Found: C, 88.85, 88.87; H, 9.39, 9.53.[23]

Potassium Metal Reduction of 7. A 10-mm diameter Pyrex glass tube, which was connectable to a vacuum line and equipped with a 5-mm diameter NMR tube as a side arm, was prepared. Into the side-arm NMR tube was placed hydrocarbon **7** (3.5 mg, 0.0066 mmol), and potassium metal (70 mg, 1.8 mmol) was added to the Pyrex glass tube, which was then evacuated by a vacuum line. The potassium was sublimed under vacuum by external heating to form a mirror at the upper part of the NMR tube. Then, THF-d_8 (1 mL), which had been dried over sodium–potassium alloy under vacuum, was transferred into the side-arm NMR tube under vacuum, and the NMR tube was sealed off just above the potassium mirror. The THF-d_8 solution of **7** was allowed to react with the potassium mirror in a ultrasonic bath for 1 h. A resulting pale-yellow solution exhibited the following spectra: ^{1}H NMR (THF-d_8 , 270 MHz; OCH_2 signal (3.60 ppm) of THF as an internal standard) δ 3.18 (s, 4 H), 2.91 (s, 4 H), 1.75–0.89 (m, $\geq$42 H); ^{13}C NMR (THF-d_8, 67.8 MHz; CH_2 signal (24.05 ppm) of THF-d_8 as an internal standard) δ 115.3, 112.4, 108.9, 35.3, 34.1, 30.2, 29.5, 29.4, 29.1.

X-ray Structure Determination of 7.[24] A rhombic plate of **7** was mounted on a glass capillary. All measurements were done on a STOE STADI4 diffractometer using graphite monochromated Mo Kα radiation. Cell dimensions and the orientation matrix were obtained from a least squares refinement of 54 reflections in the range of 35° < 2 θ < 42°, measured using the $\pm\omega$ scan technique. The lattice constants were a = 28.374(3) Å, b = 11.248(2) Å, c = 19.456(3) Å and β = 111.394(7)°. A dataset of 5151 reflections was collected at 20 °C using a $\omega/2\theta$ scan in the range of $-29 \leq h \leq 30$, $0 \leq k \leq 12$, and $-20 \leq l \leq 3$. The space group determined for the monoclinic crystal system was $C2/c$ (no.15). For Z = 8, the formula weight 530.90, and a volume of 5782(2) Å^3, a density of 1.220 g/cm^3 was calculated. After solving the structure using the program SHELXS-86[25] the crystal was identified as a twin. The twinning law for this crystal was $h' = h$, $k' = k$, $l' = -(l + h/2)$. The intensities for each part were calculated using $I(h) = a/(2a - 1)I'(h) + (a - 1)/(2a - 1)I'(h')$ and $I(h') = (a - 1)/(2a - 1)I'(h) + a/(2a - 1)I'(h')$ with $a = 0.75$ for all reflections with $h = 2n$. The resulting dataset contains 2740 independent reflections out of 3444. The structure model was refined with the program SHELXL-93[26] using 2727 reflections with $I \geq 2\sigma(I)$. The hydrogen atoms were positioned geometrically with a fixed U_{eq} that was given by the U_{eq} of the atom connected to the hydrogen atom multiplied by 1.2. All other atoms were refined anisotropically. The final R-values were $R1$ = 0.0668, $wR2$ = 0.1668 for 361 variable parameters. The largest electron density peak/hole resulting from the difference fourier calculation was 0.373 and −0.190 e/Å^3, respectively.

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[20] This potential is even lower than the oxidation potential (+0.48 V vs Ag/Ag$^+$) found for COT **3** to give a stable cation radical $\mathbf{3}^{\bullet+}$ in acetonitrile–CH_2Cl_2 (3:1): ref 3.

[21] Kagayama, A.; Komatsu, K.; Nishinaga, T.; Takeuchi, K.; Kabuto, C. *J. Org. Chem.* **1994**, *59*, 4999–5004.

[22] The signal assignment was made based on DEPT measurements.

[23] Repeated analyses on carefully recrystallized samples from different lots did not give satisfactory analytical data, presumably due to ready air oxidation.

[24] The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

[25] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.

[26] Sheldrick, G. M. SHELXL-93 User's Manual, University of Göttingen, 1993: Sheldrick, G. M. *J. Appl. Cryst.* **1994**, in preparation.

MM2 Calculations of Bicyclo[2.2.2]oct-2-ene-2,3-diyl Oligomers 5 (n = 2−5). (a) Dimer 5 (n = 2). MM2 calculations were performed on dimer **5** (n = 2) with the dihedral angle θ ($\angle 1234$; see Figure 2) varied by increments of 10°. The energy-minimized structures were those with θ of 20° ("*syn*" conformer; steric energy (SE) = 33.4 kcal/mol) and 160° ("*anti*"; SE = 33.7 kcal/mol). The SE for the energy-maximum structure with θ = 90° was 36.9 kcal/mol.

(b) Trimer 5 (n = 3). The calculations were conducted for six conformers made from all possible combinations of the most likely values of θ (taken from the above-mentioned results for **5** (n = 2); θ (*syn*) = 20° and θ (*anti*) = 160°) for the two single bonds connecting the BCO units and also for four extra conformers which appeared possible from inspection of a molecular model. All the input structures converged into three conformers as the energy-minimized structures. The values of θ_1, θ_2, and SE for each of the calculated structures are: conformer *ss* (*syn, syn*); θ_1 = 38.4°, θ_2 = 38.4°; SE = 50.6 kcal/mol: *sa* (*syn, anti*); 43.3°, −149.9°; 52.1 kcal/mol: *aa* (*anti, anti*); 149.3°, 152.2°; 55.9 kcal/mol.

(c) Tetramer 5 (n = 4). Similarly, structure optimizations were performed for all six *syn*/*anti* conformers made from the most suitable values of θ for each of the single bond rotamers obtained from the results for **5** (n = 4), and six extra conformers, to give the following energy-minimized structures: conformer *sas*; θ_1 = 38.7°, θ_2 = -148.4°, θ_3 = 38.7°; SE = 68.6 kcal/mol: *asa*; 151.0°, 54.8°, 151.0°; 69.6 kcal/mol: *ssa*; 35.8°, 52.8°, −150.8°; 70.6 kcal/mol: *aas*; 100.8°, 137.2°, −38.9°; 71.5 kcal/mol: *sss*; 28.6°, 58.0°, 24.9°; 71.7 kcal/mol: *aaa*; 163.1°, 159.0°, 163.6°; 78.6 kcal/mol.

(d) Pentamer 5 (n = 5). Exactly the same treatment for all the possible conformers of **5** (n = 5) gave the following results: conformer *ssas*, θ_1 = 30.3°, θ_2 = 54.1°, θ_3 = −155.0°, θ_4 = 34.7°; SE = 86.9 kcal/mol: *ssss*; 14.3°, −87.5°, −87.5°, 14.4°; 90.5 kcal/mol: *saas*; 37.0°, −156.2°, −157.6°, 37.5°; 90.8 kcal/mol: *ssaa*; 21.1°, 57.5°, −161.1°, −141.1°; 91.8 kcal/mol: asas; −168.6°, 58.6°, −157.5°, 34.5°; 91.1 kcal/mol: *aasa*; −147.5°, −163.6°, 59.7°, −163.3°; 93.8 kcal/mol: *assa*; −150.4°, 62.9°, 62.9°, −150.5°; 94.5 kcal/mol: *saaa*; −36.3°, 160.4°, 159.4°, 169.8°; 96.1 kcal/mol: *aaaa*; 160.6°, 165.2°, 164.0°, 163.1°; 100.0 kcal/mol. No energy-minimum was observed for the structure corresponding to conformer *sssa*.

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Supplementary Material Available: ^{1}H NMR and ^{13}C NMR spectra of **7** and of anion **13**, a cyclic voltammogram of **7**, and an ESR spectrum of a radical species generated upon electrolytic oxidation of **7** (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.