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Crystal Structure of a Cyclotetramer from a Strained Cyclic Allene

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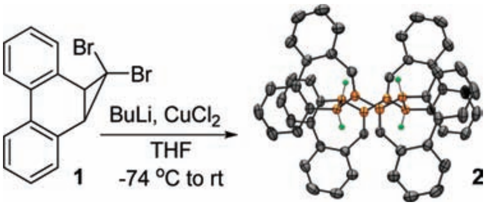
ABSTRACT

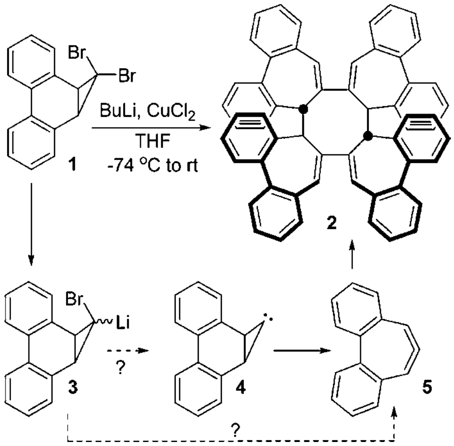


The low-temperature treatment of 1,1-dibromo-1a,9b-cyclopropa[*l*]phenanthrene (1) with butyllithium and copper(II) chloride in THF affords a dibenzoannellated 1,2,4,6-cycloheptatetraene which undergoes a rare cyclotetramerization. The crystal structure of this “formal” 2 + 2 + 2 + 2 cyclotetramer (2) reveals a central eight-membered ring folded in a zigzag fashion with hydrogen atoms and exocyclic double bonds occupying axial positions. B3LYP/6-31+G calculations indicate that the strained cyclic allene is significantly distorted and could be formed by ring expansion of a putative cyclopropylidene intermediate.**

The structure, bonding, reactivity, and strain exhibited by small ring systems containing allenic units have been a subject of much interest to synthetic chemists and theoreticians.[1] An especially useful method for generating such strained cyclic allenes is the Doering−Moore−Skattebøl reaction of *gem*-dihalocyclopropanes with alkyllithiums.[2] Herein we report that the treatment of 1,1-dibromo-1a,9b-cyclopropa[*l*]phenanthrene (**1**)[3] with butyllithium and copper(II) chloride in THF, at −74 °C, affords compound **2**, a cyclotetramer of the dibenzocycloheptatetraene (**5**), in low yield (<2%) (Scheme 1). The X-ray structure of **2**, which represents the first solid state description of an allene cyclotetramer, is also presented.

Cyclotetramerizations of allenes are rare, and to the best of our knowledge, there is just one other report of such a process in the literature.[4] That solitary report indicates that

Scheme 1. Route to Cyclotetramer **2**



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(1) For reviews, see: (a) Christl, M. *Modern Allene Chemistry*; Krause, N., Hashmi, S. K., Eds.; Wiley-VCH Verlag: New York, 2004; Vol. 1, pp 242−356. (b) Balci, M.; Taskesenligil, Y. *Advances in Strained and Interesting Organic Molecules*; Halton, B., Ed.; JAI Press Inc: Stamford, CT, 2000; Vol. 8, pp 43−81. (c) Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111.

(2) (a) Doering, W. v. E.; LaFlamme, P. M. *Tetrahedron* **1958**, *2*, 75. (b) Moore, W. R.; Ward, H. R. *J. Org. Chem.* **1960**, *25*, 2073. (c) Skattebøl, L. *Acta Chem. Scand.* **1963**, *17*, 1683.

(3) Nguyen, J. M.; Thamattoor, D. M. *Synthesis* **2007**, 2093.

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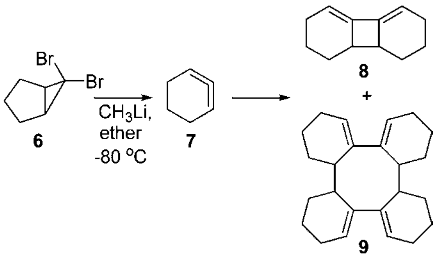
1,2-cyclohexadiene (**7**), generated according to Scheme 2, affords dimer **8** and tetramer **9**. Peculiarly, an analogous approach to the generation of 1,2-cycloheptadiene proved futile,[2c,5] and a computational study by Schleyer and coworkers provided a rationale for this anomaly based on conformational preferences.[6] It is significant, therefore, that this work is among the very few examples[7] of the use of the Doering−Moore−Skattebøl reaction to generate seven-membered cyclic allenes embedded in larger systems.

Scheme 2. Reaction of 1,2-Cyclohexadiene[4]



Slow evaporation of column fractions containing **2** (in 5% ethyl acetate/95% hexanes) afforded diamond-shaped colorless crystals suitable for single-crystal X-ray crystallography. Unlike **9**, which was formed as a mixture of two diastereomers from **6**, only a single diastereomer of **2** was obtained from **1**. Compound **2** crystallizes as a racemate in the *C*2/*c* space group of the monoclinic system ($Z = 4$). The crystal structure of an enantiomer of **2** selected from the unit cell is shown in Figure 1. The central eight-membered ring is folded in a zigzag fashion with hydrogen atoms and exocyclic double bonds occupying axial positions.

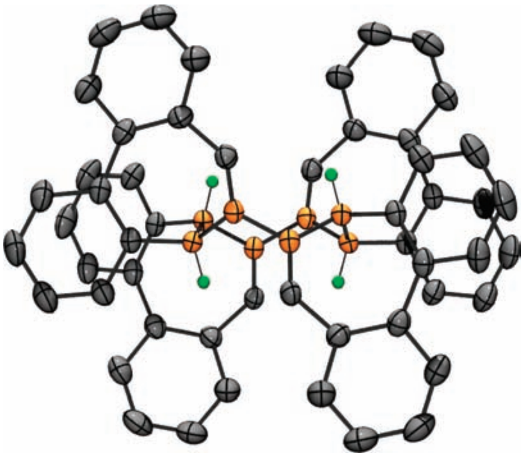
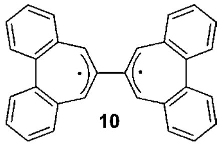


Figure 1. X-ray structure of **2** with all hydrogens, except those on the eight-membered ring, omitted for clarity. The shape of the eight-membered ring is highlighted by the orange-colored carbon atoms, and the hydrogen atoms in green are included to show stereochemistry.

Although **2** may be regarded as a “formal” 2 + 2 + 2 + 2 cycloadduct of **5**, entropic considerations make it most unlikely that it is produced in a single step. By analogy to the mechanism advanced for the formation of **9** from **7**,[4] it is more likely that **5** first dimerizes to the bisallyl intermediate **10**, which then undergoes further dimerization to afford **2**.



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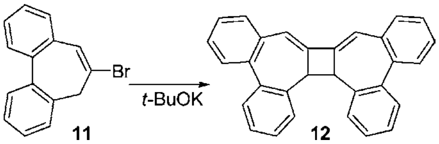
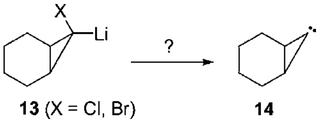
It is also noteworthy that a prior attempt at generating **5** by the base-promoted dehydrohalogenataion of **11** produced dimer **12**.[8] The formation of **12**, which is analogous to the dimerization of **7** to **8**, could occur by a ring closure in **10**. Under our conditions, however, we have not observed **12** in the product mixture.



Another question of mechanistic interest concerns the origin of **5**. Does the initially formed lithiated species **3** directly afford **5**, or is there an alternate or concomitant pathway involving the free carbene **4**? A similar question has generated some controversy in the related systems **13** and **14**, and it appears that the reaction conditions play an important role in influencing formation of the free carbene.[6,9,10] The presence of substituents can also affect such a process.[11]



This issue is debatable in our system as well. Although we have no evidence to support or refute the formation of **5** directly from **3**, carbene **4** might be indeed generated in the reaction as evident from the THF insertion product **15**

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(4) Moore, W. R.; Moser, W. R. *J. Am. Chem. Soc.* **1970**, *92*, 5469.

(5) Köbrich, G.; Goyert, W. *Tetrahedron* **1968**, *24*, 4327.

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(7) (a) Azizoğlu, A.; Demirkol, O.; Kilic, T.; Yildiz, Y. K. *Tetrahedron* **2007**, *63*, 2409. (b) Azizoğlu, A.; Özen, R.; Hökelek, T.; Balci, M. *J. Org. Chem.* **2004**, *69*, 1202.

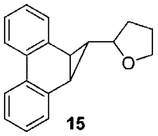
(8) Winchester, W. R.; Jones, W. M. *Organometallics* **1985**, *4*, 2228.

(9) For the chemistry of **13** (X = Cl) see: Köbrich, G.; Goyert, W. *Tetrahedron* **1968**, *24*, 4327.

(10) For two different accounts of the reactions of **13** (X = Br), see: (a) Moore, W. R.; Ward, H. R.; Merritt, R. F. *J. Am. Chem. Soc.* **1961**, *83*, 2019. (b) Warner, P. M.; Herold, R. D.; Chu, I.; Lessman, J. *J. Org. Chem.* **1988**, *53*, 942.

(11) See, for example: (a) de Meijere, A.; Faber, D.; Heinecke, U.; Walsh, R.; Muller, T.; Apeloig, Y. *Eur. J. Org. Chem.* **2001**, 663–680. (b) Azizoglu, A.; Balci, M.; Mieusset, J.-L.; Brinker, U. H. *J. Org. Chem.* **2008**, *73*, 8182–8188.

isolated from the product mixture. Furthermore, we have found that the reaction depicted in Scheme 1 is also sensitive to the conditions employed. No formation of the cyclotetramer **2** was observed when the reaction was quenched at −74 °C or when $CuCl_2$ was excluded. It appears that **2** is produced only upon warming the reaction mixture. Carrying out the reaction at 0 °C, however, leads to insoluble polymeric material and no **2**.



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Calculations performed at the B3LYP/6-31+G** level, with zero-point vibrational energy corrections included, indicate that the carbene **4** is 48.8 kcal/mol higher in energy than the allene **5**.[12] The barrier for the conversion of **4** into **5** was estimated to be 7.0 kcal/mol. As **5** is a dibenzoannelated derivative of 1,2,4,6-cycloheptatetraene (CHT), a comparison of its structure to CHT, also optimized at the B3LYP/6-31+G** level, was made (Figure 2).[13] The C7−C1−C2 angle (146.7°) of the allene unit in **5** is only slightly wider than the corresponding angle of 145.6° in CHT. The H11−C7−C2−H10 dihedral of 91.7° in **5**, however, is closer to that of a normal acyclic allene and considerably larger than the H9−C7−C2−H8 dihedral of 81.8° in CHT. The C6−C7−C2−C3 dihedral of 57.3° in allene **5** is also significantly wider than the corresponding angle of 50° in CHT. The two phenyl rings in **5** are twisted away from each other as indicated by the C8−C5−C4−C9 dihedral angle of 37.8°.

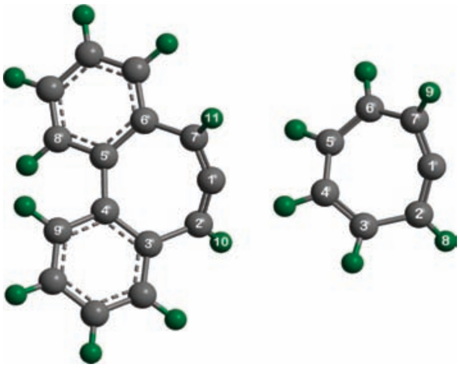

Figure 2. B3LYP/6-31+G** optimized structures of **5** (left) and 1,2,4,6-cycloheptatetraene (right).

In conclusion, we have reported the first crystal structure of a cyclotetramer obtained from a strained cyclic allene. A comparison of the computed geometry of this allene, a dibenzocycloheptatetraene derivative, to the parent CHT is also provided.

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Supporting Information Available: Experimental procedure for the synthesis of **2** and its ^1H and ^{13}C NMR spectra, a crystallographic information file (CIF) for **2**, and computed coordinates and energies for **4**, **5**, **TS** (**4** to **5**), and 1,2,4,6-cycloheptatetraene. This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] For an earlier semi-empirical calculation of **5**, see: Tyner, R. L.; Jons, W. M.; Öhrn, Y.; Sabin, J. R. *J. Am. Chem. Soc.* **1974**, *96*, 3765.

[13] For detailed calculations of CHT, see: (a) Matzinger, S.; Bally, T.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 1535. (b) Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1996**, *61*, 7022. (c) Schreiner, P. R.; Karney, W. L.; Schleyer, P. v. R.; Borden, W. T.; Hamilton, T. P.; Schaefer, H. F. *J. Org. Chem.* **1996**, *61*, 7030.