Precursors to Endohedral Metal Fullerene Complexes: Synthesis and X-ray Structure of a Flexible Acetylenic Cyclophane $C_{60}H_{18}$

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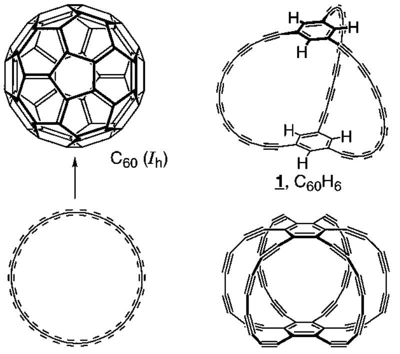
The rational synthesis of stable endohedral metal fullerene complexes poses a major challenge to current synthetic methodologies. We are particularly interested in C_{60} endohedral complexes because C_{60} itself has delivered the most interesting physical properties among the empty fullerenes.[1] While lanthanide endohedral complexes of higher fullerenes (e.g. La@C_{82}) have been available for some time by resistive evaporation methods, analogous C_{60} complexes do not seem to be isolable.[2] Endohedral complexes of C_{60} with noble gases (e.g. He@C_{60}) have been prepared by insertion into empty fullerenes under high pressure and temperature.[3] These methods are limited by the choice of guest atom, fullerene size, and very low yields.

We are proposing an unconventional approach to fullerene synthesis from polyalkynyl precursors such as **1** and **2**.[4] This approach is based on the remarkable propensity of cyclo[*n*]-carbons to rearrange to fullerenes in the gas phase (e.g. **3** converting to C_{60}).[5−7] Even though the mechanism of this rearrangement is complex, we envision 60-carbon polyacetylenic cyclophanes such as **1** and **2** analogously forming C_{60} after being generated from more stable precursors under flash vacuum pyrolytic conditions or even in solution.[8,9] A metal guest included in their cavity should be trapped endohedrally when rearrangement occurs. We are reporting the synthesis, X-ray structure, and preliminary mass spectroscopic study of cyclophane **7** in our first approach to the rational synthesis of fullerenes.



C_{60} (I_h)

1, $C_{60}H_6$

3, C_{60} (D_{30h})

2, C_{60} (D_{6h})

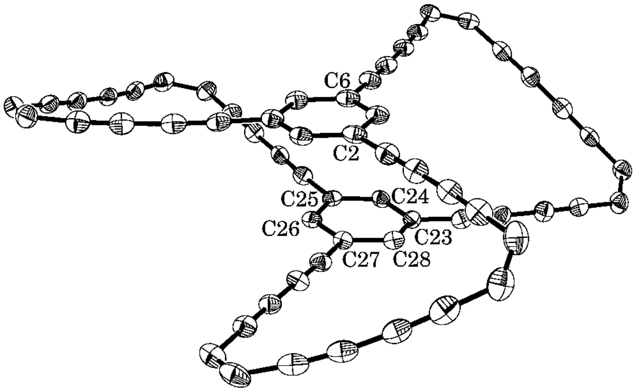
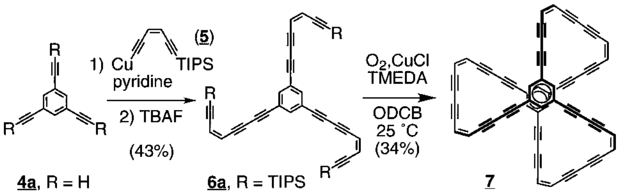


Figure 1. ORTEP plot of the crystal structure of **7**.



4a, R = H
4b, R = Br

6a, R = TIPS
6b, R = H

7
($C_{60}H_{18}$)

The short convergent route to cyclophane **7** was devised by application of straightforward alkynylation procedures. The tris(bromoalkyne) **4b** was prepared from 1,3,5-triethynylbenzene (**4a**)[10] by bromination with NBS.[11] The copper acetylide **5** was obtained by selectively deprotecting 1-(triisopropylsilyl)-6-(trimethylsilyl)-3-hexen-1,5-diyne[12] with K_2CO_3/MeOH, followed by deprotonation (LHMDS, THF) and addition of CuBr. A three-fold coupling of **5** to **4b** in pyridine[13] yielded the stable intermediate **6a** which was deprotected (TBAF) to give the unstable triyne **6b**. Cyclization of **6b** under Hay conditions in *o*-dichlorobenzene (ODCB) afforded the bright yellow cyclophane **7** in 34% yield. Cyclophane **7** decomposes over a period of weeks in the crystalline state but is stable indefinitely in dilute solutions (e.g. CH_2Cl_2) if kept in the dark.

After considerable effort, crystals suitable for X-ray diffraction were grown by vapor phase diffusion of heptane into a solution of **7** in ODCB (Figure 1). Analysis of the crystal structure[14] reveals that the two benzene rings of cyclophane **7** are not stacked on top of each other, but rather are offset by

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[1] Hirsch, A. *The Chemistry of the Fullerenes*; Thieme Verlag: Stuttgart, 1994.

[2] Edelmann, F. T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 981−985 and references therein.

[3] Saunders, M.; Cross, R. J.; Jiménez-Vázquez, H. A.; Shimshi, R.; Khong, A. *Science* **1996**, *271*, 1693−1697.

[4] Most approaches to C_{60} reported so far rely on the synthesis of bowl-shaped fragments such as corannulene, see: (a) Abdourazak, A. H.; Marcinow, Z.; Sygula, A.; Sygula, R.; Rabideau, P. W. *J. Am. Chem. Soc.* **1995**, *117*, 6410−6411. (b) Faust, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1429−1432 and references cited therein.

[5] (a) Rubin, Y.; Kahr, M.; Knobler, C. B.; Diederich, F.; Wilkins, C. L. *J. Am. Chem. Soc.* **1991**, *113*, 495−500. (b) McElvany, S. W.; Ross, M. M.; Goroff, N. S.; Diederich, F. *Science* **1993**, *259*, 1594−1596. (c) Goroff, N. S. *Acc. Chem. Res.* **1996**, *29*, 77−83.

[6] von Helden, G.; Gotts, N. G.; Bowers, M. T. *Nature* **1993**, *363*, 60−63.

[7] (a) Clemmer, D. E.; Jarrold, M. F. *J. Am. Chem. Soc.* **1995**, *117*, 8841−8850. (b) Hunter, J.; Fye, J.; Jarrold, M. F. *Science* **1993**, *260*, 784−786.

[8] The AM1 calculated heat of formation of the acetylenic precursor **2** is 562 kcal/mol (9.4 kcal/mol per carbon) higher than its isomer C_{60}.

[9] For the remarkable "zipper" rearrangement of cyclic *o*-ethynylbenzenes, see: Bradshaw, J. D.; Solooki, D.; Tessier, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1994**, *116*, 3177−3179.

[10] Weber, E.; Hecker, M.; Koepp, E.; Orlia, W.; Czugler, M.; Csöregh, I. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1251−1257.

[11] Hofmeister, H.; Annen, K.; Laurent, H.; Wiechert, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 727−729.

[12] Lu, Y. F.; Harwig, C. W.; Fallis, A. G. *J. Org. Chem.* **1993**, *58*, 4202−4204.

[13] Miller, J. A.; Zweifel, G. *Synthesis* **1983**, 128−130.

[14] Compound **7** ($C_{60}H_{18}\cdot 3o\text{-}C_6H_4Cl_2$; $M_r = 1179.81$) crystallized in the orthorhombic space group *Pbca* with cell dimensions of $a = 35.320(5)$ Å, $b = 40.488(7)$ Å, and $c = 8.458(2)$ Å; $V = 12095(4)$ Å^3, and an occupation of $Z = 8$ in the unit cell. Data were collected at 110 K on a AFC5R Rigaku diffractometer using graphite-monochromated Cu Kα radiation, to a maximum $2\theta = 120°$, giving 10 054 unique reflections; the structure was solved by direct methods (SHELX86) and refined with full matrix least squares, yielding $R = 0.062$, $R_w = 0.080$ for 5383 independent reflections with $I > 3\sigma(I)$.

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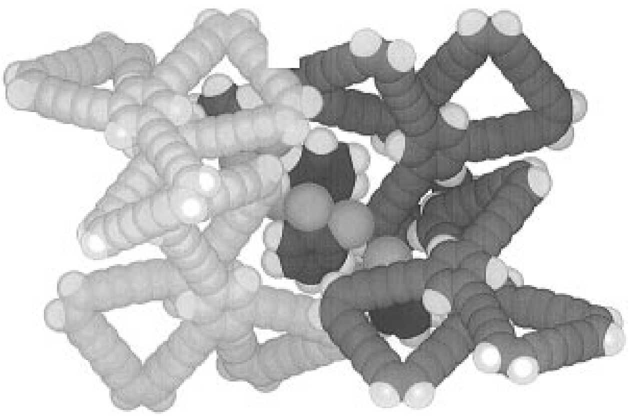


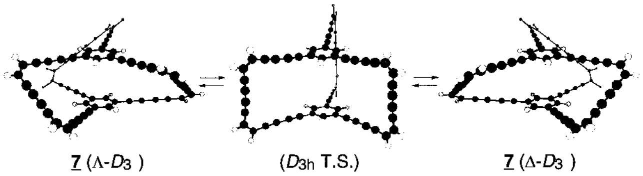
Figure 2. Space-filling model for a partial packing diagram showing two pairs of enantiomeric units of **7** and four ODCBs: light gray = right handed, dark gray = left handed.

~1.32 Å along the C23−C26 axis (offset distances between C2−C28 and C6−C24 are 1.254 and 1.386 Å, respectively). The two pairs of carbons C2−C27 and C6−C25 are essentially sitting on top of each other as a result. The angle between the mean planes of the two benzene rings is 5.0°. The distances between the two planes, as defined by the normal from C2 and C6 to the opposite plane, are 3.323 and 3.250 Å, essentially within van der Waals distances. In addition, the butadiynyl moieties are bent as much as 5° from their ideal linearity, which imparts C_1 symmetry to the whole structure in the crystalline state. The fact that the two benzene rings are not superimposed may be due to crystal-packing forces combined with electrostatic/π-stacking effects. The distortion of **7** in the solid state from more energetically favorable structures found by minimization is not surprising due to the relative flexibility of alkynes.

Cyclophane **7** has a helical chiral nature which is revealed in its ORTEP representation and in the partial view of the crystal-packing structure (Figures 1 and 2).[15] Each pair of like-handed helices stack along the *z*-axis in a herringbone manner, but the like-handed helices are separated from the opposite-handed helices by a channel of ODCBs. Thus an interesting aspect of the crystal is that each helix appears to recognize its like-handed partner. An intriguing possibility with this system is that derivatization at the alkene positions with an appropriate long-chain alkyl group will support the formation of chiral columnar arrangements giving rise to interesting liquid crystalline properties. Another aspect of the crystallization process that intrigued us was that of the many solvent systems used, *only* ODCB produced well-formed crystals so far. The reason for this presumably lies in the complex cocrystallization scheme that can be seen from the arrangement of ODCBs in the lattice. Although one ODCB is included in the space between the like-handed cyclophanes, the middle two form a channel which extends along the *z*-axis throughout the crystal lattice.

We have determined by computation whether cyclophane **7** should be separable into its enantiomeric forms. Racemization of the enantiomeric forms should proceed *via* the dynamic process in Table 1 resulting from rotating the two arene planes in opposite directions, producing a transition state with D_{3h} symmetry.[18] Using semiempirical and molecular mechanics methods, the energy of the transition state was located 3−6 kcal/mol higher in energy than that of the minimized, relaxed enantiomeric forms. Thus even at low temperatures, the racemization of the flexible cyclophane must occur very rapidly.

Table 1. Calculated Barriers (kcal/mol) for the Racemization of **7**



AM1[16]	PM3[16]	CVFF[17]	CFF91[17]
+3.28	+2.81	+6.13	+3.37

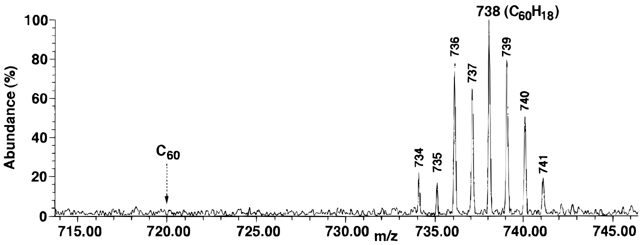


Figure 3. MALDI-TOF negative ion mass spectrum of **7**.

An important question to answer is whether the cyclophane **7** can be induced to rearrange to C_{60} in the gas phase. MALDI-FTMS and APCI negative ion mass spectrometric studies on **7** have revealed a cluster of peaks around the molecular ion $C_{60}H_{18}$ at *m/z* 738 (Figure 3). The most abundant ion corresponds to the parent ion **7**, with the higher *m/z* peaks in the approximate relative abundance expected for natural ^{13}C incorporation in $C_{60}H_{18}$ and subsequent dehydrogenated species. The lower mass peaks from *m/z* 734 to 737 indicate that **7** undergoes dehydrogenation at least down to $C_{60}H_{14}$; however no peak for C_{60} was detected in the experimental conditions examined so far. The reluctance of **7** to lose hydrogen seems at first surprising, since its thermal chemistry must be dictated by its enediyne nature giving rise to aromatic 1,4-diyls *via* Bergman cyclization.[19] However, this system may be somewhat too flexible to produce controlled pathways for bond formation. Further studies will be directed at the preparation of halogenated derivatives of **7** capable of generating the more rigid precursor **1**.

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Supporting Information Available: Experimental procedures, ^1H and ^{13}C NMR spectra for **4b**, **6a**, and **7**, X-ray structure of **7**, fully labeled view of the structure, tables of atomic coordinates, equivalent isotropic thermal parameters, bond angles, and bond lengths (22 pages). Ordering information is given on any current masthead page.

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(15) For chiral cyclophanes, see: Forman, J. E.; Barrans, R. E.; Dougherty, D. A. *J. Am. Chem. Soc.* **1995**, *117*, 9213−9228 and references therein.

(16) SPARTAN version 4.0.1; Wavefunction Inc., 18401 Von Karman Avenue, Suite 370, Irvine, CA 92715.

(17) Biosym *Insight II* molecular modeling package.

(18) AM1 analysis of the vibrational modes produced a D_{3h} geometry with one imaginery frequency.

(19) Wang, K. K. *Chem. Rev.* **1996**, *96*, 207−222.