

Preparation of a [60]Fullerene Derivative Containing a Fused Seven-Membered Ring

Soomi Pyo, Lianhe Shu, Luis Echegoyen*

Department of Chemistry, University of Miami, Coral Gables, FL 33124, USA

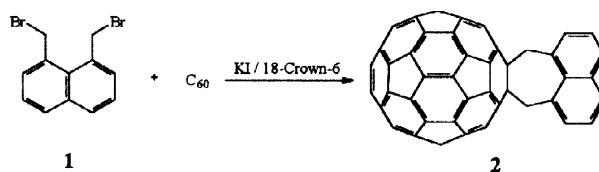
Received 5 June 1998; accepted 10 August 1998

Abstract: [60]Fullerene reacts with 1,8-bis(bromomethyl)naphthalene in the presence of KI/18-crown-6 to form a C₆₀ derivative with a seven-membered ring fused to a [6,6] junction.

© 1998 Elsevier Science Ltd. All rights reserved.

The double bonds at [6,6] junctions of C₆₀ are known to be electron-deficient and able to react with a variety of reagents.¹ Multiple cycloaddition reactions at these [6,6] bonds have led to a variety of C₆₀ derivatives with fused three-, four-, five- and six-membered rings.² The reactions of C₆₀ with *ortho*-quinodimethane intermediates have been intensively investigated, and these provide extremely stable [4+2] adducts in relatively high yields. Müllen *et al.*³ were the first to report the *Diels-Alder* reactions of C₆₀ with *ortho*-quinodimethane intermediates generated from the reaction of I with 1,2-bis(bromomethyl)benzene and other analogous bis(bromomethyl)-aromatic compounds. Since then, many others have used this reaction to prepare new derivatives of C₆₀.⁴ In this paper, we report the somewhat unexpected reaction of 1,8-bis(bromomethyl)naphthalene (1) with C₆₀ in the presence of KI and 18-crown-6 to yield a C₆₀ derivative with a seven-membered ring fused at a [6,6] junction. To the best of our knowledge such a fullerene structure has never been previously reported and there is no precedent for such an unusual cycloaddition reaction (Scheme 1).

The reaction was conducted in refluxing benzene under an argon atmosphere for 24 hours. The product was obtained by flash column chromatography on silica gel. The isolated yield was 75% based on reacted C₆₀ (38% based on initial C₆₀).⁵



Scheme 1

The structure of the product was determined by spectral analysis as described below. The FAB MS shows the M⁺+1 peak at 875 as well as a base peak at 720 which arises from the loss of the addend. The high resolution mass spectrum (HRMS) gives the molecular weight at 874.078 for C₇₂H₁₀, which corresponds exactly to the calculated value. The UV-VIS spectrum in dichloromethane is similar to those of fullerene derivatives with a [6,6] addition pattern and shows the characteristic absorption at 433 nm. The ¹H-NMR spectrum (400 MHz, in CS₂/CDCl₃=3/1) shows the aromatic protons at 7.48 and 7.87 ppm as two multiplets, and the methylene protons appear as an AB quartet at 6.24 and 4.62 ppm (Figure). Under identical experimental

conditions, the methylene protons of compounds **3** and **4** appear around 4.4–5.0 ppm as AB quartets at room temperature.⁴ In compound **2**, the splitting of the AB quartet is *ca* 1.6 ppm, somewhat unusual when compared to other *ortho*-quinodimethane C₆₀ adducts. Protons and carbon atoms which are close to a five-membered ring on the surface of the C₆₀ are shifted significantly downfield.⁶ For example, in the fulleroid (C₆₁H₂), the proton which lies above the five-membered ring is 3.48 ppm downfield shifted relative to the other methano proton.⁷ In compound **2**, the three aromatic carbons in the seven-membered ring are coplanar. This makes the configuration of the seven-membered ring relatively rigid and in this configuration, the protons closer to the fullerene skeleton give rise to the downfield-shifted signal. This is supported by results from calculations, which show that one of the hydrogens in **2** lies very close to a five-membered ring on the fullerene surface, more so than in **3** or **4**.

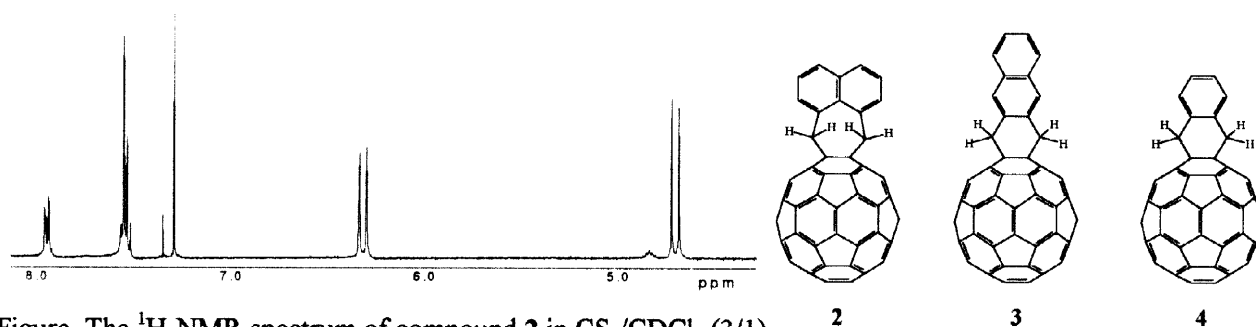
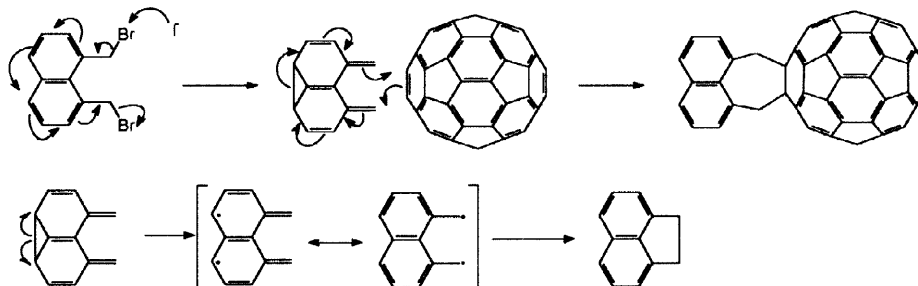


Figure The ¹H-NMR spectrum of compound **2** in CS₂/CDCl₃ (3/1).

The ¹³C-NMR spectrum consists of 36 inequivalent carbon resonances.⁸ Those peaks at 126.21, 128.90, 129.35, 131.74, 134.61 and 135.77 ppm correspond to the naphthalene ring. The signal at 51.22 ppm is due to the methylene carbons. The resonance of the carbon at the addition site is located at 67.53 ppm, which means that the addition takes place at a [6,6] bond. The remaining 28 peaks are assignable to the fullerene skeleton. The number of signals is consistent with a C_s symmetric structure, which predicts 32 lines for the C₆₀ core.

As shown in Scheme 2, a cycloaddition mechanism is suggested for the formation of compound **2**. A related reactive intermediate with a three-membered ring attached to naphthalene was proposed earlier by Rees *et al.*⁹ Because of the strain of the three-membered ring, the intermediate is very unstable and undergoes rearrangement to another reactive intermediate, naphthoquinodimethane, which was reported by Ouchi *et al.*¹⁰ In our experiment, when the reaction was run in toluene, the yield of compound **2** was very low, and 1,8-dimethylnaphthalene and acenaphthene were detected by GC-MS. However, when the reaction was done in dry benzene, the yield of the fullerene product increased and those of the by-products decreased. This is consistent with the mechanism, since the diradical (naphthoquinodimethane) can easily couple or extract hydrogen atoms from toluene.



Scheme 2

Compound **2** was analyzed electrochemically using a 1 mm platinum working electrode under an argon atmosphere.¹¹ The results are presented in Table, along with those for C₆₀ for comparison.¹² The CV of compound **2** shows that the first three reductions are reversible and, as typical for C₆₀ adducts, it is more difficult to reduce than the parent fullerene by more than 90 mV. All reductions appear to be fullerene-based.

Table E_{1/2} Values of C₆₀ and Compound **2** vs. Fc/Fc⁺ (E_{1/2} (mV), ΔE (mV)).

Compound	E ₁	E ₂	E ₃	E ₄	E ₅
C ₆₀	-1050(110)	-1450(100)	-1950(90)	-2420(80)	-2920(110)
2	-1150(60)	-1540(80)	-2090(70)	-2550(60)	

Quantum chemical calculations were performed for compound **2**, **3** and **4** using the PM3 semi-empirical method in the Spartan program.¹³ The molecular geometries of compounds **2**, **3** and **4** were optimized for comparison. The calculations show that compound **2** has a lower binding energy than other *ortho*-quinodimethane fullerene adducts by ~4.0 kcal/mol.

ACKNOWLEDGMENT The authors wish to acknowledge the National Science Foundation, grant CHE-9313018, for generous support.

REFERENCES AND NOTES

- (a) Hirsch, A. *The Chemistry of the Fullerenes* **1994**, Thieme, New York. (b) Hirsch, A. *Synthesis* **1995**, 895-913. (c) Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317-323.
- (a) Hoke II, S. H.; Molstad, J.; Dilettato, D.; Jennifer, J.; Carlson, D.; Kahr, B.; Cooks, R. G. *J. Org. Chem.* **1992**, *57*, 5069-5071. (b) Komatsu, K.; Murata, Y.; Sugita, N.; Takeuchi, K.; Wan, T. S. M. *Tetrahedron Lett.* **1993**, *34*, 8473-8476. (c) Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1993**, *115*, 1605-1606. (d) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798-9799. (e) Giovane, L. M.; Barco, J. W.; Yadav, T.; Lafleur, A. L.; Marr, J. A.; Howard, J. B.; Rotello, V. M. *J. Phys. Chem.* **1993**, *97*, 8560-8561. (f) An, Y.-Z.; Anderson, J. L.; Rubin, Y. *J. Org. Chem.* **1993**, *58*, 4799-4801. (g) Tsuda, M.; Ishida, T.; Nogami, T.; Kurono, S.; Ohashi, M. *J. Chem. Soc., Chem. Commun.* **1993**, 1296-1298. (h) Prato, M.; Suzuki, T.; Foroudian, H.; Li, Q.; Khemani, K.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 1594-1595. (i) Tsuda, M.; Ishida, T.; Nogami, T.; Kurono, S.; Ohashi, M. *Tetrahedron Lett.* **1993**, *34*, 6911-6912. (j) Hoke II, S. H.; Molstad, J.; Yang, S. -S.; Carlson, D.; Kahr, B. *J. Org. Chem.* **1994**, *59*, 3230-3231. (k) Bidell, W.; Douthwaite, R. E.; Green, M. L. H.; Stephens, A. H. H.; Turner, J. F. C. *J. Chem. Soc., Chem. Commun.* **1994**, 1641-1642. (l) Kraus, A.; Gügel, A.; Belik, P.; Walter, M.; Müllen, K. *Tetrahedron* **1995**, *51*, 9927-9940. (m) Linssen, T. G.; Dürr, K.; Hanack, M.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, 103-104. (n) Torres-Garcia, G.; Luftmann, H.; Wolff, C.; Mattay, J. *J. Org. Chem.* **1997**, *62*, 2752-2756.
- (a) Belik, P.; Gügel, A.; Spickermann, J.; Müllen, K. *Angew. Chem. Int. Engl. Ed.* **1993**, *32*, 78-80. (b) Gügel, A.; Kraus, A.; Spickermann, J.; Belik, P.; Müllen, K. *Angew. Chem. Int. Engl. Ed.* **1994**, *33*, 559-561.
- Nakamura, Y.; Minowa, T.; Tobita, S.; Shizuka, H.; Nishimura, J. *J. Chem. Soc., Perkin Trans. 2* **1995**,

2351-2357.

5. *General procedure* A mixture of 72.0 mg (0.1 mmol) of C₆₀, 94 mg (0.3 mmol) of 1,8-bis(bromomethyl)naphthalene, 100 mg (0.6 mmol) of KI and 264 mg (1 mmol) of 18-crown-6 was dried under vacuum for 5 hours. Then 50 mL of dry benzene (refluxed over sodium for 6 hours) was transferred to the flask under vacuum. This solution was kept stirring at reflux under argon for 24 hours. Then the solvent was evaporated. The solid was washed three times with acetone and then dissolved in CS₂. Isolation of the solution on silica gel with hexane/CS₂ (2/1) afforded 33.5 mg of the product and 35.0 mg of C₆₀. The isolated yield was 75% based on converted C₆₀ (38% based on starting C₆₀).
6. (a) Pasquarello, A.; Schlüter, M.; Haddon, R. C. *Science* **1992**, *257*, 1660-1661. (b) Prato, M.; Lucchini, V.; Maggini, M.; Stimpfl, E.; Scorrano, G.; Eiermann, M.; Suzuki, T.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 8479-8480.
7. (a) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7301-7302. (b) Smith III, A. B.; Strongin, R. M.; Brard, L.; Frust, G. T.; Romanow, W. J.; Owens, K. G.; King, R. C. *J. Am. Chem. Soc.* **1993**, *115*, 5829-5830. (c) Prato, M.; Suzuki, T.; Wudl, F.; Lucchini, V.; Maggini, M. *J. Am. Chem. Soc.* **1993**, *115*, 7876-7877.
8. ¹³C NMR (100 MHz, in CS₂/CDCl₃=3/1 with 0.01 M of Cr(acac)₃ as relaxation reagent) δ_C 51.22, 67.53, 126.21, 128.90, 129.35, 131.74, 134.61, 135.77, 136.26, 137.49, 139.94, 140.14, 141.42, 141.62, 141.94, 141.98, 142.14, 142.38, 142.47, 142.98, 143.08, 144.54, 144.60, 144.96, 145.07, 145.16, 145.21, 145.36, 145.51, 145.76, 146.06, 146.22, 146.34, 147.56, 156.12, 157.72 ppm.
9. Rees, C. W.; Storr, R. C. *Chem. Commun.* **1965**, 193-194.
10. (a) Ouchi, A.; Koga, Y.; Adam, W. *J. Am. Chem. Soc.* **1997**, *119*, 592-599. (b) Ito, O.; Alam, M. M.; Koga, Y.; Ouchi, A. *J. Photochem. Photobiol. A* **1996**, *97*, 19-23. (c) Adam, W.; Ouchi, A. *Tetrahedron Lett.* **1992**, *33*, 1875-1878. (d) Ouchi, A.; Yabe, A. *Tetrahedron Lett.* **1992**, *33*, 5359-5362. (e) Ouchi, A.; Yabe, A. *Tetrahedron Lett.* **1990**, *31*, 1727-1730. (f) Haider, K.; Platz, M. S.; Despres, A.; Lejeune, V.; Migirdicyan, E.; Bally, T.; Haselbach, E. *J. Am. Chem. Soc.* **1988**, *110*, 2318-2320. (g) Mitchell, J. C.; Heaton, S.; Porter, N. A. *Tetrahedron Lett.* **1984**, *25*, 3769-3772.
11. Voltammetric experiments were done using a BAS-100W electrochemical analyzer, interfaced with a Hewlett-Packard Color Pro Plotter. A platinum electrode (1 mm in diameter) was the working electrode and a silver wire was used as a reference. TBAPF₆ (tetrabutylammonium hexafluorophosphate) from Fluka was used as a supporting electrolyte after being recrystallized twice from ethanol and water (95/5) and dried in a vacuum. A mixture of acetonitrile and toluene (15/85) was used as the solvent under argon. Ferrocene was added as an internal potential reference.
12. Xie, Q.; Pérez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978-3980.
13. (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209-220. (b) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221-264.