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1,2-Methanobuckminsterfullerene ($C_{61}H_2$), the Parent Fullerene Cyclopropane: Synthesis and Structure

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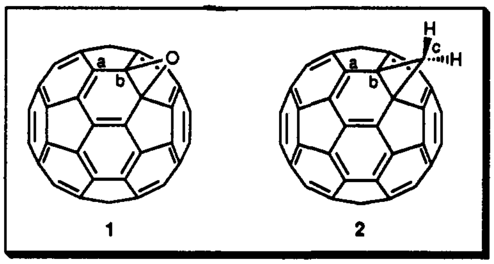
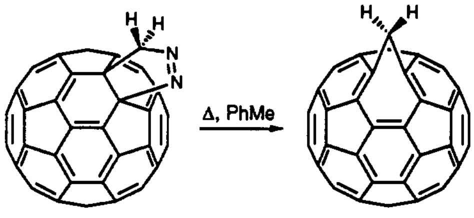
Recently we reported the synthesis, isolation, and characterization of **1**, the first fullerene epoxide ($C_{60}O$).[1] We describe herein the generation and structure elucidation of 1,2-methanobuckminsterfullerene (**2**, $C_{61}H_2$), the parent fullerene cyclopropane. Our work complements the studies of Wudl et al.,[2] who prepared pyrazoline **3**, by addition of diazomethane to a 6,6 "short" bond of C_{60}. They then discovered that thermolysis of **3** in toluene furnished the rearranged fulleroid **4**, embodying an annulene moiety formally derived from methylene insertion into a 6,5 "long" bond.[3]



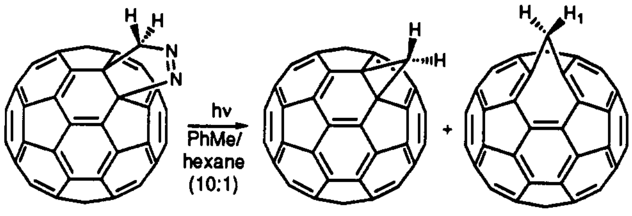
1 **2**



3 **4**

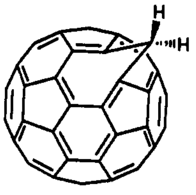
Intrigued by this result, we explored the photolysis of **3**. After treatment of C_{60} in toluene with ethereal diazomethane (1 equiv) at 0 °C, chromatography on silica furnished solutions of pure **3**, which were employed in the next reaction.[4] Irradiation through Pyrex[5] followed by filtration through silica (1:1 hexanes/toluene) afforded a 3:4 mixture of **2** and **4** as the sole isolable products (ratio determined by HPLC; 21% combined yield) (Scheme I). Isomer separation via reverse-phase HPLC[6] gave pure **2** as a dark reddish-brown solid which in toluene forms a pink solution.

Scheme I



3 **2** **4**

Laser desorption time of flight (LDToF) mass spectra of both **2** and **4** show parent ions at 734 amu as well as a less intense peak at 720 amu (C_{60}) (Figure 1a). The 500-MHz ^1H NMR spectrum of **2** comprises a singlet at 3.93 ppm, indicative of a highly symmetric structure. In contrast, the spectrum of **4** contains doublets at 2.87 and 6.35 ppm.[2] Based on observations by Wudl we tentatively assign the downfield doublet to proton H_1, which lies above the annulene triene moiety; other fulleroid derivatives exhibit similar deshielding.[2,7] The 3.93-ppm singlet for **2** therefore excludes the isomeric [10]annulene structure **5**. Interestingly, ^1H NMR analysis also reveals that a trace of **2** is generated in the formation of **4** via thermolysis of **3**.[8]



5

The ^{13}C NMR spectrum of isotopically enriched material (12–13% ^{13}C)[9] contains 18 peaks (Figure 1d) whereas the spectrum of **4** consists of 32 lines, again indicative of a more symmetric structure for **2**.[10] Sixteen of the resonances for **2** fall between 136.5 and 149.5 ppm; the remaining peaks at 30.4 and 71.0 ppm are assigned to the methylene carbon (confirmed by a ^{13}C DEPT experiment) and the two skeletal cyclopropane carbons. Diederich and co-workers have likewise observed chemical shifts in the 70–80-ppm range for their recently reported fullerene cyclopropanes.[3b] No corresponding resonance is found in the ^{13}C NMR spectrum of annulene **4**.

Further support for the assigned structure derives from the J_{CH} and $J_{C_{bc}}$ coupling constants obtained from isotopically enriched material (12–13% $^{13}C_{60}$, 20% $^{13}CH_2$). The values for **2** (166.5 and 20 Hz, respectively) are characteristic of cyclopropanes (160–170 and 10–22 Hz);[11,12] those for **4** (145.0, 147.8, and 32 Hz, respectively) are typical of methano-bridged annulenes.[11] In addition, the $^{13}C_a$–$^{13}C_b$ couplings in **1** and **2**, determined via 1D

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(1) Creegan, K. M.; Robbins, J. L.; Robbins, W. K.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M.; Smith, A. B., III; McCauley, J. P., Jr.; Jones, D. R.; Gallagher, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 1103–1105.

(2) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7301–7302.

(3) (a) The [6,6] carbon-bridged fulleroids (Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, Ö. *Science* **1991**, *254*, 1186–1188) have been reformulated as the corresponding cyclopropanes, in accord with the results of Vasella and Diederich[3b] (Professor F. Wudl, private communication). (b) Vasella, A.; Uhlmann, P.; Waldraff, C. A. A.; Diederich, F.; Thilgin, C. *Angew. Chem.. Int. Ed. Engl.* **1992**, *31*, 1388–1390.

(4) Following elution of unreacted C_{60} with 10:1 hexane/toluene, the solvent polarity was gradually increased to 10:1 toluene/hexane, affording pure **3** as a brown solution.

(5) A 450-W medium-pressure Hanovia lamp was suspended in a quartz well cooled with tap water. The solution of **3** (0.25 mM in toluene) in a Pyrex test tube was held adjacent to the well and irradiated at room temperature for 25 min.

(6) Dynamax 60-A C-18 column, 50% MeOH/toluene, 10 mL/min monitored at 325 nm; retention times for **2** and **4** were 19.8 and 21.5 min, respectively.

(7) Wudl, F. *Acc. Chem. Res.* **1992**, *25*, 157–161.

(8) See supplementary material available for ref 2.

(9) Johnson, R. D.; Meijer, G.; Salem, J. R.; Bethune, D. S. *J. Am. Chem. Soc.* **1991**, *113*, 3619–3620.

(10) (a) ^{13}C chemical shifts for **2** in CS_2/acetone-d_6: 149.5, 145.40, 144.95, 144.86, 144.46,[10b] 144.08, 143.48, 142.92,[10b] 142.82, 142.79, 142.51, 141.94, 140.88, 136.50, 71.04, 30.45 ppm. (b) Represents two close or overlapping resonances.

(11) Arnz, R.; W. de M. Carneiro, J.; Klug, W.; Schmickler, H.; Vogel, E.; Breuckmann, R.; Klärner, F.-G. *Angew. Chem.. Int. Ed. Engl.* **1991**, *30*, 683–686.

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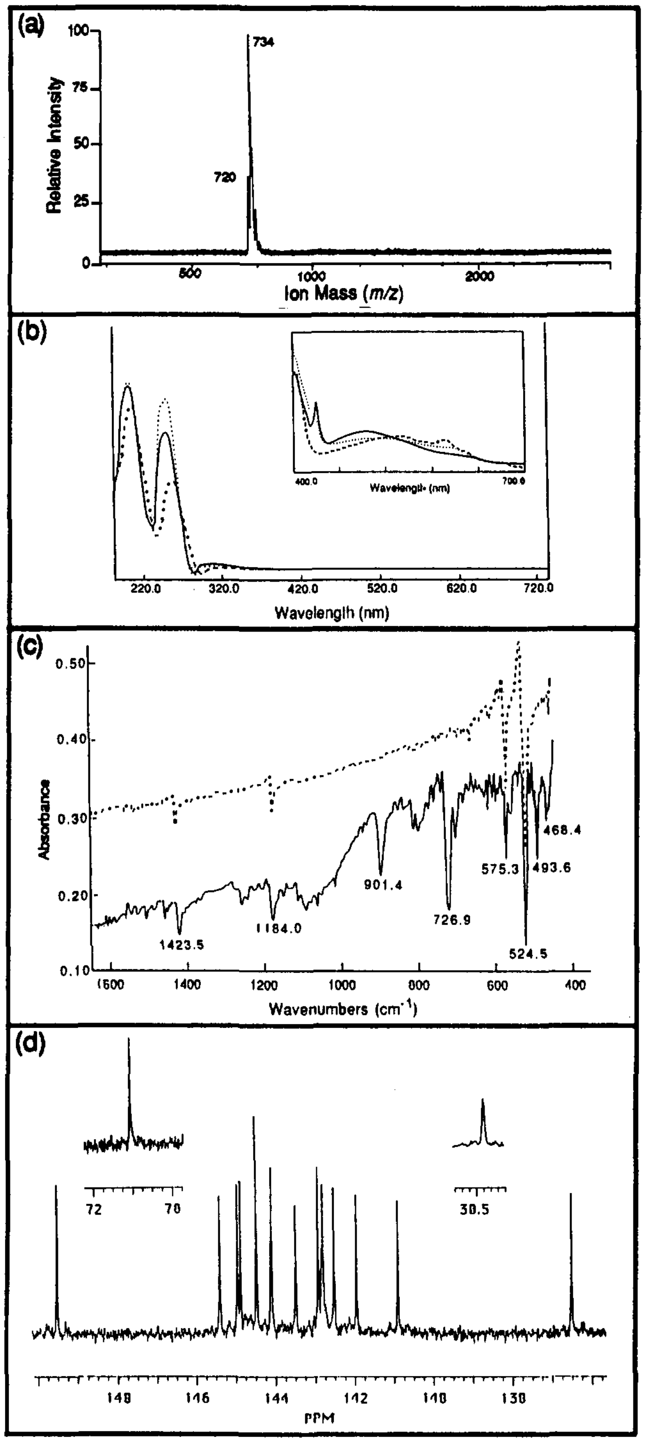
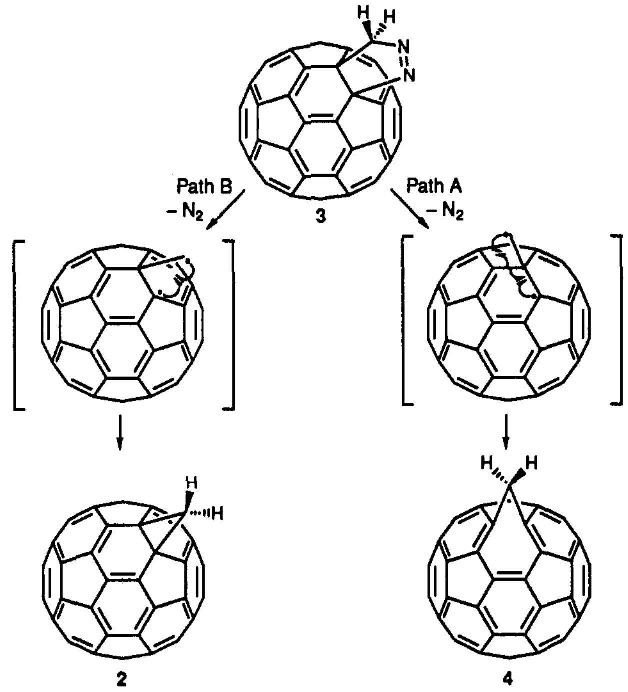


Figure 1. (a) LDToF mass spectrum of **2** ($C_{61}H_2$). (b) UV–vis spectra of C_{60} (- - -), **2** (—), and **4** (···) from 190 to 720 nm in hexane [inset: fine structure spectra of C_{60} (- - -), **2** (—), and **4** (···) from 400 to 700 nm in toluene]. (c) FTIR spectrum of C_{60} (- - -) and **2** (—), KBr pellet. (d) ^{13}C NMR spectrum of **2** in CS_2/acetone-d_6.

Scheme II



INADEQUATE experiments, proved to be 59 and 53 Hz, respectively.[13] Hawkins et al.[14] have demonstrated the utility of ^{13}C–^{13}C coupling constants for estimating bond lengths and hybridization in fullerenes. The data for **1** and **2** indicate that the C_a–C_b bonds in both compounds are very similar, thereby linking the epoxide and cyclopropane structures and excluding the oxo and methano annulene isomers as possible formulations for these substances.

The UV–visible spectrum of **2** has maxima at 426.0, 325.0, 259.0, and 219.0 nm; an overlay of the UV traces (hexane) of C_{60}, **1**, and **2** demonstrates their similar electronic nature (Figure 1b).[1] The FTIR spectrum of **2** exhibits eight major peaks: 1424, 1184, 901, 727, 575, 525, 494, and 468 cm^{-1} (Figure 1c). In contrast, the IR spectrum of **4**[2] displays >12 major peaks, indicative of lower symmetry.

We propose the mechanism shown in Scheme II for the photolysis of **3**. Importantly, individual photolysis of **2** and **4** (0.25 M in toluene) for up to 40 min did not lead to their interconversion.[15] Likewise thermolysis of **2** (toluene at reflux, 3 h) failed to generate **4**.

In conclusion, we have prepared, characterized, and assigned the structure of new fullerene cyclopropane **2**, the methano analog of buckminsterfullerene epoxide **1**. NMR coupling constants were employed to differentiate closed (fullerene) and open (fulleroid) isomers. We are currently exploring the chemical and physical properties of the [6,6] fullerene cyclopropanes.

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Supplementary Material Available: Detailed procedure for the preparation of **2** and tables of IR and NMR data (3 pages). Ordering information is given on any current masthead page.

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(12) (a) Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1967**, *89*, 5962–5963. (b) Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 6021–6025. (c) Rol, N. C.; Clague, A. D. H. *Org. Magn. Reson.* **1981**, *16*, 187–194. (d) Stöcker, M. *Org. Magn. Reson.* **1982**, *20*, 175–179.

(13) Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J. Manuscript in preparation.

(14) Hawkins, J. M.; Loren, S.; Meyer, A.; Nunlist, R. *J. Am. Chem. Soc.* **1991**, *113*, 7770–7771.

(15) The isolation and characterization of the photolysis products will be reported in due course.