# *Communications*

The Reaction of Buckminsterfullerene with Diazotetrazole. Synthesis, Isolation, and Characterization of $(C_{60})_2C_2$

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A current challenge of fullerene chemistry[1] is the synthesis, isolation, and characterization of new molecular carbon allotropes. Recent investigations include the formation of gas-phase clusters[2] as well as the solution-phase production of methanofullerene−acetylene hybrids[3] and all-carbon dimers.[4,5] Dimeric all-carbon fullerenes with appropriate bridging moieties might exhibit novel intercage electronic interactions or serve as precursors to coalesced fullerenes. Herein, we report the first isolation and characterization of the dimeric allotrope $(C_{60})_2C_2$ (**1**) obtained via a new reaction of [60]fullerene with the atomic carbon precursor diazotetrazole, **2**[6] (Scheme 1).

1 $(C_{60})_2C_2$
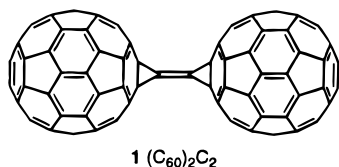
Initially reported by Thiele in 1892,[7] Shevlin discovered a facile preparation of **2** and demonstrated that this highly energetic molecule readily formed carbon atoms upon thermolysis.[6] In the presence of olefins, atomic carbon produces cyclopropylidenes.[8] We reasoned that the decomposition of **2** in the presence of C_{60} could thus lead to direct formation of **3** (Scheme 1). Intermediate **3** has been previously proposed as a precursor to $(C_{60})_2C_2$ (**1**) and $(C_{60})_2C$ (**4**). It was produced via the methanofullerene $C_{61}Br_2$, during

Scheme 1
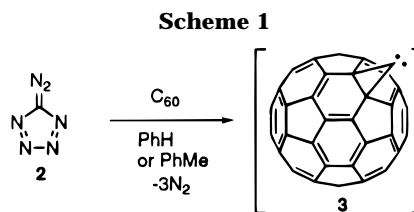
pioneering studies by Osterodt and Vögtle in which **1** and **4** were detected by mass spectrometry.[9]

4 $(C_{60})_2C$
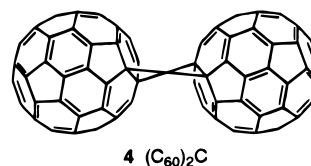
Formation of **2** was achieved via diazotization of 5-aminotetrazole (0.082 g, 0.79 mmol, 11 equiv) with isoamyl nitrite (0.1 mL, 0.74 mmol, 11 equiv) and concentrated HCl (0.4 mL) in THF (1.5 mL).[6] The resultant solution was heated in the presence of C_{60} (0.050 g, 0.069 mmol) dissolved in benzene or toluene (40 mL) to reflux. At least 14 fullerene products were observed via HPLC analysis.[10] We also obtained similar product distributions either by photolysis (Hanovia mercury lamp, medium pressure, quartz filter, rt, 30 min) or upon allowing the solutions to stand at ambient temperature for 12 h.

Since fullerene dimers exhibit relatively long HPLC retention times compared to [60]fullerene and most of its monoadducts,[1,5,11] our main initial focus concerned the isolation and characterization of the latest eluting material. Conversion of [60]fullerene to the product with the longest retention time, a black solid that forms a golden-yellow solution in toluene, has been highly capricious to date for reasons that are presently not clear. The HPLC-isolated yields range from <1 to 3%.

The laser-desorption time-of-flight (LD-TOF) mass spectrum (Figure 1a) of the isolated product displays a parent peak for $(C_{60})_2C_2$ (1465.3 amu calcd, 1466.6 obsd)[12] as well as two highly prominent fragments corresponding to C_{62} (743.9 amu) and C_{60} (719.4 amu). The use of the matrix 9-nitroanthracene[9] did not produce any significant change in the mass spectrum.

The UV−vis spectrum is shown in Figure 1b. Two intense, characteristic fullerene absorptions are present at 210 and 260 nm (Figure 1b, inset). There are no clear

(1) (a) Hirsch, A. *The Chemistry of the Fullerenes*; Thieme: New York, 1994. (b) Taylor, R. *The Chemistry of Fullerenes*; World Scientific: Singapore, 1995.

(2) For example: McElvany, S. W.; Callahan, J. H.; Ross, M. M.; Lamb, L. D.; Huffman, D. R. *Science* **1993**, *260*, 1632.

(3) Isaacs, L.; Seiler, P.; Diederich, F. *Angew Chem., Int. Ed. Engl.* **1995**, *34*, 1466.

(4) For example: Wang, G.-W.; Komatsu, K.; Murata, Y. Yasujiro, S. *Nature* **1997**, *387*, 583.

(5) Gromov, A.; Ballenweig, S.; Giesa, S.; Lebedkin, S.; Hull, W. E.; Krätschmer, W. *Chem. Phys. Lett.* **1997**, *267*, 460.

(6) Shevlin, P. B. *J. Am. Chem. Soc.* **1972**, *94*, 1379. **WARNING!!!** Diazotetrazole is a highly explosive compound that should be handled with extreme precaution and produced only on a small scale!

(7) Thiele, J. *Justus Liebigs Ann. Chem.* **1892**, *59*, 270.

(8) Dewar, M. J. S.; Nelson, D. J.; Shevlin, P. B.; Biesiada, K. A. *J. Am. Chem. Soc.* **1981**, *103*, 2802.

(9) Osterodt, J.; Vögtle, F. *J. Chem. Soc., Chem. Commun.* **1996**, 547.

(10) Cosmosil Buckyprep column, 4.6 × 250 mm, 10% hexane/toluene mobile phase, flow rate1 mL/min, monitored at λ = 325 nm. Retention times: C_{60} = 15.0 min, $(C_{60})_2C_2$ (**1**) = 63.0 min. For semipreparative purposes, a 100% toluene mobile phase was employed. Retention times: C_{60} = 8.0 min, $(C_{60})_2C_2$ (**1**) = 20.2 min.

(11) (a) Lebedkin, S.; Ballenweig, S.; Gross, J.; Taylor, R.; Krätschmer W. *Tetrahedron Lett.* **1995**, *36*, 4971. (b) Smith, A. B., III; Tokuyama, H.; Strongin, R. M.; Furst, G. T.; Romanow, W. J.; Chait, B. T.; Mirza, U. A.; Haller, I. *J. Am. Chem. Soc.* **1995**, *117*, 9359.

(12) PerSeptive Biosystems Voyager linear laser-desorption time-of-flight mass spectrometer equipped with nitrogen laser (337 nm): instrument error = 0.1%.
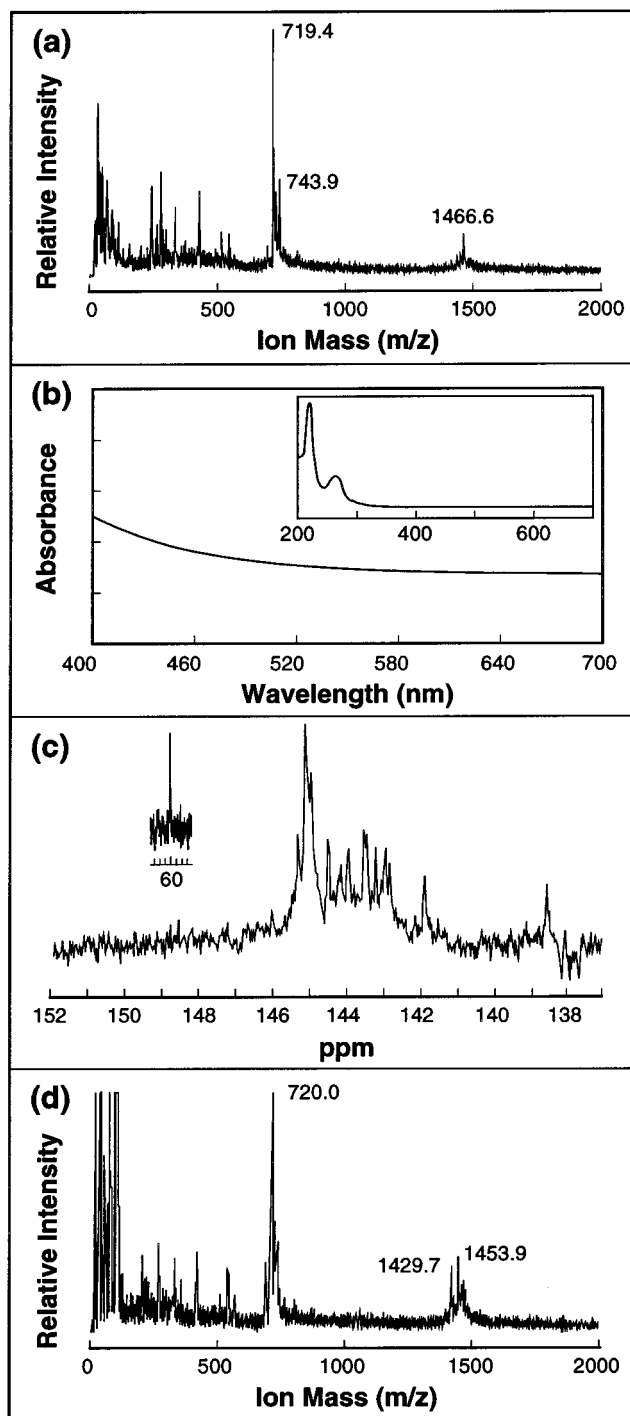
Figure 1. (a) LD-TOF mass spectrum of **1** ($(C_{60})_2C_2$). (b) UV-vis spectrum of **1** from 400 to 700 nm in toluene [inset: spectrum of **1** from 200 to 700 nm in hexane]. (c) ^{13}C NMR spectrum of **1** in $C_6D_4Cl_2$. (d) LD-TOF mass spectrum of $(C_{60})_2C$ and C_{119} (**4**).

absorptions in the region 400−700 nm. Typically, C_{60} monoadducts display highly distinctive bands in the visible region;[1] however, greatly diminished fine structure is well-precedented in the oxo- and methylene-bridged dimeric fullerene analogues, $C_{120}O$[11] and $C_{121}H_2$,[11b] respectively.

The 100 MHz ^{13}C NMR spectrum affords evidence for the proposed D_{2h} symmetry of $(C_{60})_2C_2$, formed via dimerization of **3**. After several attempts, we finally[13] acquired a spectrum with adequate signal/noise ratio on a small (0.1 mg) sample synthesized from 10−15% carbon-13-enriched C_{60}. The ^{13}C-labeled NMR sample coelutes at 20.2 min from the

HPLC with nonlabeled samples that consistently produce the $(C_{60})_2C_2$ parent peak in the mass spectrometer. Prolonged NMR acquisition times and poor solubility precluded our use of 1,2-dichlorobenzene-d_4 as lock solvent. The spectrum (Figure 1c) exhibits 15 of the 16 expected resonances (in the region 136−150 ppm); however, we assign two resonances as overlapping (intense peak at 145.1 ppm). We assign the single upfield resonance (60.1 ppm), integrating to four carbons, to the skeletal cyclopropane carbons. The cyclopropylmethylene bridging carbons, at natural abundance, are not observed.

Other products formed in the reaction of **2** and C_{60} include those found in fractions isolated from a cluster of peaks with HPLC retention times[10] centered at 11 min (100% toluene mobile phase). The LD-TOF mass spectrum of this material (Figure 1d) exhibits formation of the recently isolated C_{119}[5] (1429.3 amu calcd, 1429.7 obsd) as well as sought-after allotrope $(C_{60})_2C$ (1453.3 amu calcd, 1453.9 obsd), **4**. One current challenge is determining the origin of C_{119} and $(C_{60})_2C$, i.e., whether they are produced in the mass spectrometer from isolable precursors or can be directly obtained via the reaction of C_{60} and **2**.

Mass spectrometric analysis indicates the presence, also in fractions of material centered at 11 min, of either $C_{61}(C_6H_6)$, **5**, or $C_{61}(C_7H_8)$, **6**, whose selective appearance is dependent on the choice of benzene or toluene as reaction solvent, respectively.[14] Importantly, the formation of **5** and **6** offers further evidence of the reaction intermediate **3**, the monomer of **1**. The formation of **5** or **6** could occur via carbene addition or insertion of **3** to solvent.[15,16]

In conclusion, we have performed the first synthesis of $(C_{60})_2C_2$ (**1**) in isolable amounts. We have presented spectroscopic evidence consistent with a dimeric D_{2h}-symmetric structure. The reaction of C_{60} with diazotetrazole also leads to several other products observed by mass spectrometry, including the carbon allotropes C_{119} and $(C_{60})_2C$ as well as $C_{61}(C_6H_6)$ and $C_{61}(C_7H_8)$. The further study of the isolation, characterization, and properties of the products arising from the interaction of C_{60} and diazotetrazole is ongoing in our laboratory.

(13) The ^{13}C NMR spectrum was acquired with 1 020 499 scans, a 0.5 s relaxation delay, and 0.1 equiv of Cr[acac]$_3$ spin relaxant in the sample solution.

(14) Although mass spectrometric evidence for the formation of **5** and **6** is conclusive (see Supporting Information), preliminary ^1H and ^{13}C NMR studies indicate that these materials are minor components of the HPLC fraction isolated at 11.0 min (100% toluene mobile phase). Studies towards the isolation and precise structure assignment of **5** and **6** as well as the major component(s) of the material eluting at 11.0 min are in progress.

(15) We cannot exclude the possibility of the formation of a dipolar cycloadduct of **2** [or tetrazole carbene (N_4C:) adduct] and C_{60}. Studies directed toward the isolation and characterization of this putative material will be reported in due course.

(16) Alternatively, the [60]fullerene + carbon + solvent products might potentially arise via initial reaction of atomic carbon with benzene or toluene followed by trapping by [60]fullerene.