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Isolation of Fullerene Products from Flames: Structure and Synthesis of the C_{60}-Cyclopentadiene Adduct

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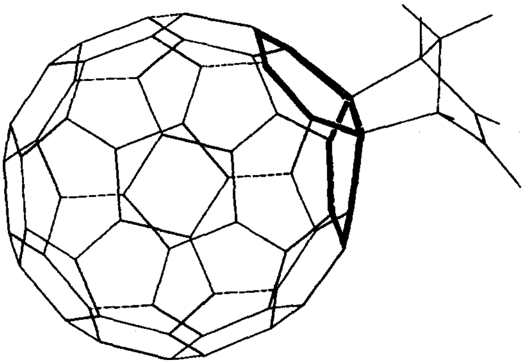
Abstract: A C_{60}-C_5H_6 adduct was isolated from a low pressure benzene flame. The structure of this product is identical to the Diels-Alder adduct of C_{60} and cyclopentadiene as established through independent synthesis. This product was determined to be adduct 1 through ^{13}C and proton NMR, as well as infrared and mass spectrometry.

The discovery that fullerenes can be produced in flames provides a potentially powerful new route to these molecules.[1] In the course of optimizing this process, a relatively unstable product was observed. Isolation of this compound using preparative HPLC provided a solid, which was golden brown in solution, which cleanly converted to C_{60} at temperatures over 95°C. Due to the thermal instability of this material, initial reports based on mass spectroscopic determination postulated an isomeric C_{60} structure for this molecule.[2] Later studies strongly suggested the formula to be $C_{65}H_6$, or $C_{60}\cdot C_5H_6$.[3]

In order to provide a possible mechanism for formation of the postulated $C_{60}C_5H_6$, byproduct, as well as macroscopic quantities of this reagent, C_{60} was reacted with cyclopentadiene.[4] Dropwise addition of freshly distilled cyclopentadiene (0.8 mg, 12 μmol) in benzene (1 mL) to a solution of C_{60} (7.2 mg, 10 μmol) in benzene (0.5 mL) at 20°C caused an immediate color change of the solution, from deep purple to golden brown. Removal of solvent provided a brown solid, which was purified by column chromatography (SiO_2, hexane-CH_2Cl_2 gradient) to yield 4.2 mg (74%) of brown solid, identical by HPLC, UV-vis and ^1H NMR to the previously isolated combustion product.

Proton NMR of the adduct was consistent with the bicyclic Diels-Alder product of C_{60} and cyclopentadiene.[5] In order to verify this structural assignment, we obtained ^{13}C NMR spectra of the cycloadduct.[6] The presence of 33[7] lines (with one of double intensity) agrees with the expected C_S symmetry of the molecule formed by addition across the C_6-C_6 ring fusion.[8]

Kinetic and thermodynamic properties of cycloaddition-cycloreversion reactions of this and other C_{60}-diene systems, as well as the applications of these processes in materials science, are currently under investigation.



C_{60}-Cyclopentadiene addition product 1, with C_6-C_6 ring system highlighted. Structure was determined using the MM3 forcefield

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References and Notes

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4. The reaction of C_{60} with cyclopentadiene to give the poly-(cyclopentadienyl) adduct has been published. No mention was made of the regiochemistry of these additions, or the isolation of a mono-cyclopentadienyl adduct. Wudl, F.; Hirsch, A.; Khemani, K. C.; Suzuki, T.; Allemand, P. M.; Koch, A.; Eckert, H.; Srdanov, G.; Webb, H. M. *ACS Symp. Ser.,* **1992,** *481*(Fullerenes), 161-75
5. ^{1}H NMR (250 MHz, $Cl_2DCCDCl_2$), ppm downfield from TMS: δ7.09 (t, *J*=1.5 Hz, 2H); 4.51 (t, *J*=1.5 Hz, 2H); 3.42 (d, *J*=9.66 Hz, 1H); 2.52 (app. d, *J*=9.6, 2H).
6. ^{13}C NMR (125 MHz, $C_6H_6/Cl_2DCCDCl_2$, 0.035 M $Cr(acac)_3$), broadband decoupling, ppm downfield from TMS: δ157.2; 155.4; 147.6; 146.9; 146.75; 146.65; 146.5; 146.45; 146.35; 145.95 (1/2 inten.) ; 145.85 ; 146.75 (2x inten.); 145.7; 145.1; 144.9; 143.45; 143.10; 143.05; 143.0; 142.55; 142.50; 142.40; 142.3; 142.2; 140.8 (1/2 inten); 140.75 (1/2 inten) ; 140.4; 140.15; 138.25; 138.2; 137.85; 100.5; 30.5
7. 34 lines are expected, however one may be obscured by solvent.
8. Previously reported cycloadditions have occurred across the C_6-C_6 ring fusion. For examples see: Suzuki, T.; Li, Q.; Khemani, C.; Wudl, F. *J. Am. Chem. Soc.* **1992,** *114,* 7301-7302. Hawkins, J.M.; Loren, S.; Meyer, A.; Nunlist, R. *J. Am. Chem. Soc.* **1991,** *113,* 7770-7771. The alternative reaction across the C_6-C_5 fusion also produces a product with C_s symmetry, so it cannot be excluded on the basis of simple ^{13}C or ^{1}H NMR methods.

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