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LDRD Final Report on Fullerene-Based Materials Research and Development

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LDRD Final Report on Fullerene-Based Materials Research and Development

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Abstract

The chemistry and physical properties of fullerenes, the third, molecular allotrope of carbon, have been studied using both experimental and computational techniques. Early computational work investigated the stability of fullerene isomers and oxides, which was followed by extensive work on hydrogenated fullerenes. Our work led to the first synthesis of a polymer containing C₆₀ and the synthesis of the simplest hydrocarbon derivatives of C₆₀ and C₇₀. The excellent agreement between theory and experiment (± 0.1 kcal/mol in the relative stability of isomers) has provided insight into the chemical nature of fullerenes and has yielded a sound basis for prediction of the structure of derivatized fullerenes. Such derivatives are the key to the preparation of fullerene-based materials.

This work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000.

LDRD Final Report on Fullerene-Based Materials Research and Development

Introduction

This LDRD (Laboratory Directed Research and Development) project was funded for three years beginning in October 1991 (FY92) and was designed as a multidisciplinary approach to the chemistry and physics of fullerenes -- new molecules with essentially unknown properties. Materials built from this new allotrope of carbon (after graphite and carbon) were predicted early to impact several areas, including porous materials, CVD diamond deposition, structural materials, electronic and optical materials, pharmaceuticals, etc. At that time the cost of C₆₀ (\$2000/gm) was prohibitive for anything but initial studies; however, the price of C₆₀ is now < \$50/gm and is still dropping. Our efforts included work on tribology, porous materials, optical properties, but especially targeted the chemistry of the fullerenes because derivatization was, and still is, seen as the key to practical applications of C₆₀ and C₇₀.

The efforts of the principal investigators and collaborators at three universities and AT&T Bell Laboratories has led to 19 manuscripts, most of which have been published in peer reviewed journals. These manuscripts describe in detail the efforts funded under this LDRD. The abstracts of each manuscript is presented below along with a complete citation to the full text.

Abstracts of Published Manuscripts

"Imperfect Fullerene Structures: Isomers of C₆₀"

K. Raghavachari and C. M. Rohlfiing
J. Phys. Chem. **1992**, 96, 2463-6.

The structures and energies of several alternative isomeric structures of C₆₀ spheroids have been computed with semiempirical (MNDO) and ab initio Hartree-Fock molecular orbital techniques. Unlike the ideal icosahedral structure, these isomers are characterized by the presence of two or more pairs of adjacent pentagonal rings. The energy contributions of these adjacent pentagonal defects are roughly additive, with each defect making the structure less stable by $\cong 1$ eV. The lowest energy alternative isomer of C₆₀ has C_{2v} symmetry and lies $\cong 2$ eV higher in energy than the icosahedral ground-state structure.

"Defective Buckyballs: Alternative Structural Isomers of C₆₀"

K. Raghavachari and C. M. Rohlfiing
Materials Research Society Symp. Proc. **1992**, 247, 327-332.

Alternative isomeric structures of C₆₀ spheroids have been investigated using semiempirical and ab initio quantum chemical techniques. Unlike the icosahedral ground state, these isomers are characterized by the presence of pentagonal rings adjacent to each other. The lowest energy alternative isomer of C₆₀ has two such pairs of edge-sharing pentagons and lies $\cong 2$ eV higher in energy than the ground state. Isomers containing three and four pairs of adjacent pentagons have also been studied in detail. Overall, the energy contributions of these adjacent pentagonal defects are additive, with each defect making the structure less stable by $\cong 1$ eV.

"Ground state of C₇₀O: oxygen bridging at the equatorial belt"
K. Raghavachari and C. M. Rohlfing
Chem. Phys. Lett. **1992**, *197*, 495-8.

Semi-empirical (MNDO) and ab initio Hartree-Fock (3-21G) calculations on the structures and stabilities of C₇₀O are reported. We have characterized eight isomers of C₇₀O formed by an oxygen atom bridging each of the eight distinct C-C bonds in C₇₀. The ground state isomer corresponds to oxygen bridging across an equatorial C-C bond in C₇₀ which opens out to a distance of ≈ 2.2 Å. This structure is different from the bridged paracyclene-like isomer proposed previously for C₇₀O. Comparison is made between C₇₀O and C₆₀O.

"Semi-empirical calculations of the isomeric C₆₀ dihydrides"
C. C. Henderson and P. A. Cahill
Chem. Phys. Lett. **1992**, *198*, 570-6.

The reduction of C₆₀ to C₆₀H₂ may result in the formation of 23 distinct, energetically non-equivalent isomers, of which three are meso. The heats of formation of these isomers were calculated at spin-restricted and spin-unrestricted semi-empirical levels using PM3 parameters. Our results indicate that at most two of the 23 isomers are likely to be significantly populated at thermal equilibrium at room temperature. The relative energies of the three lowest-energy isomers at the spin-unrestricted level are 0 kcal/mol for substitution across 6,6-ring fusion, +2.5 kcal/mol for substitution 1,4 across a 6 ring and +9.1 kcal/mol for substitution 2,6 across a naphthalene ring subunit. A concise nomenclature for designating substitutional patterns on C₆₀ and fullerenes in general is proposed.

"Synthesis of a C₆₀-Xylylene Copolymer"
D. A. Loy and R. A. Assink
J. Am. Chem. Soc. **1992**, *114*, 3977-8.

A polymeric fullerene material was prepared by reacting C₆₀ with xylylene from the thermolysis of paracyclophane. The polymer characterized using solid state ¹³C NMR, IR, and TGA.

"C₆₀H₂: Synthesis of the Simplest C₆₀ Hydrocarbon Derivative"
C. C. Henderson and P. A. Cahill
Science **1993**, *259*, 1885-7.

The reaction of C₆₀ with BH₃:tetrahydrofuran in toluene followed by hydrolysis yielded C₆₀H₂. This product was separated by high-performance liquid chromatography and characterized as the addition product of H₂ to a 6,6-ring fusion (1a1b isomer). The ¹H nuclear magnetic resonance (NMR) spectrum of the product remained a sharp singlet between -80° and +100°C, which suggests a static structure on the NMR time scale. Hydrolysis of the proposed borane addition product with acetic acid-d, or D₂O yielded C₆₀HD, and its ³J_{HD} coupling constant is consistent with vicinal addition. The observation of a single C₆₀H₂ isomer is in complete agreement with earlier calculations that indicated that at most 2 of the 23 possible isomers of

C₆₀ would be observable at equilibrium at room temperature. These results suggest that organoborane chemistry may be applied to further functionalization of fullerenes.

"Theoretical studies of selected C₆₀H₂ and C₇₀H₂ isomers
C. C. Henderson, C. M. Rohlfiing, P. A. Cahill
Chem. Phys. Lett. **1993**, 213, 383-8

Semi-empirical MNDO methods predict that 2 of 23 structurally distinct C₆₀H₂ isomers and 4 of 143 C₇₀H₂ isomers have particularly low heats of formation. These isomers represent either 1,2-addition across a 6:6 ring fusion or 1,4-addition across a 6-ring, with both hydrogens externally bound. Fully optimized ab initio structures are computed for these low-lying isomers at the Hartree-Fock level using 3-21G and 6-31G* basis sets. For C₆₀H₂, all three methods agree on the isomer ordering, and the lowest energy structure is also the only one that has been observed experimentally. The energy separations among the lowest four C₇₀H₂ isomers are found to be quite small, but only the ab initio ordering is consistent with experimental results.

"Isomers of C₇₈. Competition between electronic and steric factors"
K. Raghavachari and C. M. Rohlfiing
Chem. Phys. Lett. **1993**, 208, 436-40.

Ab initio Hartree-Fock (3-21G and 6-31G*(5d)) calculations on the structures and stabilities of the low-energy isomers of C₇₈ are reported. The energy ordering of the isomers can be interpreted in terms of two different physical effects: an electronic factor which maximizes the resonance stabilization energy and a steric factor which minimizes the strain energy. The nature of the three most stable isomers (C_{2v}, C'_{2v}, and D₃) seen in two different experiments can be understood in terms of competition between these two opposing effects.

"Electrochemical Properties of C₆₀H₂ and C₇₀H₂"
P. Boulas, F. D'Souza, C. C. Henderson, P. A. Cahill, M. T. Jones, K. M. Kadish
J. Phys. Chem. **1993**, 97, 13435-7.

The electrochemistry of C₆₀H₂ and the 1,9- and 7,8-isomers of C₇₀H₂ were investigated in DMF/toluene mixtures and the resulting data compared to that of the parent C₆₀ and C₇₀ fullerenes under the same solution conditions. Each dihydrogen derivative is reduced via a series of one-electron transfers. The C₆₀H₂ undergoes four reversible reductions which occur at E_{1/2} = -1.02, -1.46, -2.07, and -2.58 V vs. Fc/Fc⁺. The two electroreduced isomers of C₇₀H₂ are less soluble than electroreduced C₆₀H₂, and only three reductions are seen for these compounds in a toluene/DMF mixture. These occur at E_{1/2} = -1.04, -1.48, and -1.96 V vs Fc/Fc⁺ for the 7,8-isomer and at E_{1/2} = -1.03, -1.52, and -1.93 V vs Fc/Fc⁺ for the 1,9-isomer. The electronic effect of these two different structural isomers is not reflected in their electrochemistry since almost identical E_{1/2} values are obtained for each reduction process. The stability of the reduced dihydrogen species decreases with an increase of charge, temperature, and/or the DMF content of the toluene/DMF mixture. Singly-reduced C₆₀H₂^{•-} is the most stable of the reduced compounds, and its EPR spectrum was measured and compared to

the spectrum of $C_{60}^{\bullet-}$ in neat toluene. The spectrum of $C_{60}H_2^{\bullet-}$ is centered at $g = 2.000$ and has a spectral line width of 3 G at 160 K, as compared to a $g = 1.997$ and a line width of 5.8 G for $C_{60}^{\bullet-}$.

"Study of the Reorientational Motion of $C_{60}H_2$ in Toluene- d_8 by Proton NMR"
A. D. Irwin, R. A. Assink, C. C. Henderson, P. A. Cahill
J. Phys. Chem. **1994**, *98*, 11832-4.

The proton spin-lattice relaxation time (T_1) of $C_{60}H_2$ in toluene- d_8 was measured between 281 and 338 K. Correlation times calculated from these T_1 measurements are compared with those calculated from viscosity-temperature data via the Stokes-Einstein-Debye and Gierer-Wirtz microviscosity equations, and with values reported for C_{60} by ^{13}C NMR. At room temperature, $C_{60}H_2$ in toluene rotates at about the same rate as solid state C_{60} . The Stokes-Einstein-Debye theory predicts reorientational correlation times (τ_c) that are a factor of 6-8 higher than observed, while the Gierer-Wirtz modification gives τ_c values that are 1.3-1.7 times those observed. The ^{13}C spin-lattice relaxation of C_{60} in toluene- d_8 has significant contributions from both the chemical shift anisotropy and spin-rotation mechanisms.

"Photoinduced charge transfer and charge carrier generation in polysilane films containing C_{60} molecules"
R. G. Kepler and P. A. Cahill
Appl. Phys. Lett. **1994**, *63*, 1552.

We have studied charge carrier generation and transport in poly(methylphenylsilane) films containing C_{60} molecules, and have found that the quantum efficiency for carrier generation is increased by more than an order of magnitude over poly(methylphenylsilane) films not containing C_{60} and that hole transport is unaffected. We also measured the electroabsorption spectrum of the composite films and found no evidence for charge transfer transitions. We conclude that electrons are transferred from poly(methylphenylsilane) to C_{60} molecules that have been excited to their lowest energy absorption band at about 2 eV.

"Synthesis, Isolation, and Equilibration of 1,9- and 7,8- $C_{70}H_2$ "
C. C. Henderson, C. M. Rohlfing, K. T. Gillen, and P. A. Cahill
Science **1994**, *264*, 397-9.

Equilibration of 1,9- and 7,8- $C_{70}H_2$ has allowed the relative free energy of these isomers to be measured. These "simplest hydrocarbon derivatives of C_{70} " are formed by hydroboration of C_{70} at room temperature. Analysis of the platinum-catalyzed equilibration of these isomers yielded a relative free energy at 295 Kelvin of 1.4 ± 0.2 kilocalories per mole, with the 1,9 isomer being more stable. This value is in excellent agreement with the ab initio HF/6-31G* calculated energy difference of 1.3 kilocalories per mole, whereas semiempirical calculations gave poor agreement.

"C₆₀H₄: Kinetics and Thermodynamics of Multiple Addition to C₆₀"
C. C. Henderson, C. M. Rohlffing, R. A. Assink, P. A. Cahill
Angew. Chem. Int. Ed. Eng. **1994**, *33*, 786-8

Reaction of C₆₀H₂ with 1 equivalent of BH₃:THF gave a mixture of 6 C₆₀H₄ isomers, three of which were isolated. Ab initio Hartree-Fock relative energies for 8 isomers are reported.

"Theoretical and Experimental Investigations of Fullerene Derivatives: C₆₀H₂, C₆₀H₄, C₇₀H₂, and C₆₀(CH₂)₂"
S. J. Jacobs, K. T. Gillen, P. A. Cahill, C. C. Henderson, C. M. Rohlffing
Mat. Res. Soc. Symp. Proc. **1994**, *349*, 145-150.

Hydroboration of C₇₀ in toluene yields a 2:1 mixture of 1,9-C₇₀H₂ and 7,8-C₇₀H₂. Equilibration of these two isomers in the presence of a Pt catalyst reveals a free energy difference of 1.4 ± 0.2 kcal/mol. Whereas semiempirical calculations have been found to predict the energy ordering of many fullerene derivatives incorrectly, ab initio Hartree-Fock (HF) calculations have been found to yield quantitative predictions of experiment. The HF/6-31G* level energy separation of 1,9-C₇₀H₂ and 7,8-C₇₀H₂ of 1.3 kcal/mol is in excellent agreement with experiment. Relative stabilities of isomers of bis(methano)fullerenes were found to parallel those of analogous C₆₀H₄ isomers. Density functional theory (DFT) methods have been tested and are equivalent in accuracy to HF methods if similar basis sets are used. C₆₀H₂ and C₆₀H₄ can be efficiently produced on larger (250 mg) scales with diimide generated from potassium azodicarboxylate and acetic acid in o-dichlorobenzene.

Abstract of Unpublished Works

"Characterization of Polyxylylenes with Solid State ¹³C Nuclear Magnetic Resonance Spectroscopy"

D. A. Loy, R. A. Assink, G. M. Jamison, W. F. McNamara, S. Prabakar, D. A. Schneider
Submitted to *Macromolecules*, 12/94.

Polyxylylenes are an important class of thermoplastics that are readily prepared by thermolysis of [2.2]paracyclophane and xylene precursors to afford xylylene monomers that condense and polymerize on solid surfaces to give polymer films. As most polyxylylenes are insoluble due to a high degree of crystallinity, characterization by solid state nuclear magnetic resonance spectroscopic techniques is necessary. In this paper we describe the preparation of polyxylylene **P1**, poly-2-ethylxylylene **P2**, poly-2-chloroxylylene **P3**, poly-2, 3-dichloroxylylene **P4**, and poly(α, α, α', α'-tetrafluoroxxylylene) **P5** and their characterization using solid state ¹³C Cross Polarization Magic Angle Spinning Nuclear Magnetic Resonance (CP MAS NMR) spectroscopy.

"Tribology of C₆₀ Fullerenes on Steel and Silicon Surfaces"
M. T. Dugger

The chemical and mechanical stability of C₆₀ molecules suggest that this new form of carbon may act as a friction-reducing or wear-mitigating surface film. The objective of this work was to examine the tribological properties of C₆₀ films on steel and silicon surfaces, and determine active wear mechanisms for solvent deposited and evaporated C₆₀. Examination of the CKW

Auger line shape at various primary electron beam power levels demonstrated that fullerene films are not damaged by a 10 kV, 50 nA electron beam of 50 nm diameter for exposure times of five minutes. Pin-on-disk friction tests of 440C steel pins in contact with C₆₀-coated 304 steel disks indicate that C₆₀ deposited from solution in toluene acts as an abrasive in dry air, and increases the adhesive transfer of material between the pin and the disk. A similar effect was found for silicon surfaces coated with vacuum-evaporated C₆₀. The C₆₀ film was displaced within the first two revolutions of the disk. Functionalization of the fullerene or other methods of improving the bond between C₆₀ and the substrate surface may enable this material to be used as a tribologically-protective coating.

"Disilene Addition to C₇₀"

S. J. Jacobs, C. M. Rohlfing, P. A. Cahill

Manuscript for the Fall Materials Research Society Meeting, Boston, Mass., 12/94

Semiempirical and ab initio Hartree Fock computational results indicate that the highly reactive dienophile tetramethyldisilene, Me₂Si=SiMe₂, is an excellent candidate for a novel functionalization of the equator of C₇₀ via a [2+4] cycloaddition to the 21, 22, 23, 42 carbons. Thermal or photochemical generation of tetramethyldisilene in the presence of C₇₀ results in similar complex mixtures in which the major product appears to be that of [2+2] cycloaddition to the 7,8 carbons of C₇₀. A minor product clearly results from [2+2] cycloaddition to the 1,9 carbons. Both of these products are hydrolytically unstable and are converted nonspecifically to mixtures of 1,9- and 7,8-C₇₀H₂ which are also present in HPLC traces of the reaction mixtures.

"Hydrogenated Fullerenes"

P. A. Cahill

Book chapter to The Chemistry of Fullerenes, Edited by Roger Taylor, World Scientific Publishing, 1995

A critical review of published work on C₆₀H_n and C₇₀H_n.

"Study of Acid-Base and Redox Equilibria for the C₆₀/C₆₀H₂ System in Dimethyl Sulfoxide Solvent"

M. E. Niyazymbetov, D. H. Evans, S. A. Lerke, P. A. Cahill, C. C. Henderson
J. Phys. Chem. 1995, in press.

Voltammetric techniques have been used to monitor the acid-base reactions of reduced forms of C₆₀ in dimethyl sulfoxide (DMSO) solution. In agreement with earlier work, the dihydrofullerene, C₆₀H₂, was found to show three reversible reduction processes with potentials about 0.1 negative of the corresponding C₆₀ potentials in toluene/DMSO (67/33, v/v). For C₆₀H₂, the first and second acid dissociation constants are 4.7 and 16 respectively. Also, the reversible potentials for the C₆₀H[•]/C₆₀H⁻ and C₆₀H⁻/C₆₀H^{•-} couples were found to be identical to the first two reduction potentials for C₆₀, within experimental error. The reversible potentials and pK_a-values were combined to compute the pK_a of related species. For example, pK_a for C₆₀H[•] was computed to be 9. The titration of electrogenerated C₆₀^{•-} with 4-nitrobenzoic acid (pK_a = 9) was consistent with this calculation.

Conclusion

Fullerenes C₆₀ and C₇₀ react as electron deficient alkenes. They show strong preference toward 1,2 addition to 6,6 ring fusions ("double" bonds). Kinetic effects lead to the formation of mixtures of the thermodynamically most stable isomers in multiply addended fullerenes. Semiempirical calculations are unreliable in predictions of relative isomer energies; however, ab initio Hartree-Fock calculations are in quantitative agreement with experiment. This suggests that computations can be used to guide complex materials preparation based on the fullerene building blocks. Such studies are underway under non-LDRD funding.

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