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14. ABSTRACT The principle investigator and three undergraduate student researchers utilized a previously developed and more expedient synthetic route to construct a novel tetracationic iodonium macrocycles. These parent rings are the starting material to generate carbon nanohoops, which is the long-term goal of this project. Previous studies in this research group indicated that the transformation into cycloparaphenylene-type rings via one electron reduction reactions was feasible. Therefore, the synthesis and spectroscopic investigations of these ring systems by reducing metals was undertaken. This transformation has been the continued focus of this research program. Spectroscopic					
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Report Title

Final Report: Design, Synthesis, and Applications of Carbon Nanohoops

ABSTRACT

The principle investigator and three undergraduate student researchers utilized a previously developed and more expedient synthetic route to construct a novel tetracationic iodonium macrocycles. These parent rings are the starting material to generate carbon nanohoops, which is the long-term goal of this project. Previous studies in this research group indicated that the transformation into cycloparaphenylene-type rings via one electron reduction reactions was feasible. Therefore, the synthesis and spectroscopic investigations of these ring systems by reducing metals was undertaken. This transformation has been the continued focus of this research program. Spectroscopic evidence indicates that n-cycloparaphenylenes have been successfully synthesized by palladium catalysts under reducing conditions. The development of a robust synthetic transformation would ultimately allow for facile preparation of many carbon nanohoop structures.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received

Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
William Collins	0.30	
FTE Equivalent:	0.30	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Melanie Walker	1.00	
Chloe Boehlke	1.00	
Gracie Askeland	1.00	
FTE Equivalent:	3.00	
Total Number:	3	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 3.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 3.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 2.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 2.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 2.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Scientific Progress Report:

This initial scientific progress report details the research performed by the principle investigator and three undergraduate researchers during the 10 week summer period from May 2015 through July 2015. All of the students involved in this research are continuing with this research project through the next academic year and possibly the next summer period.

Project Abstract:

This project detailed the attempts toward the development of a rapid and diversifiable synthetic route to the carbon nanohoop ([n]cycloparaphenylene) or carbon nanotube scaffold through the reductive transformation of a strained macrocyclic molecular precursor. These shape-persistent, conjugated structures are proposed to serve as soluble models of, and synthetic precursors to semi-conducting carbon nanotubes. Moreover, these nanosized rings have the long-term potential to interstitially encapsulate analytes of interest, and to form a variety of new electronic polymer architectures.

The accomplishments of this summer research period can be summarized as follows:

- 1) Previous efforts have been primarily focused on methods to generate the target cycloparaphenylene molecules from small-sized, tetracationic iodonium macrocycles. Despite the successful synthesis of several of the iodonium macrocycles (in the previous reporting periods of this grant), trying to affect the desired one-electron reduction to generate the carbon nanohoop has resulted in failure. Many different one-electron sources (e.g., sodium metal, potassium naphthalenide, zinc metal with palladium sources, photochemical methods) were tried under a variety of conditions. Careful analysis of the products generated in the one-electron reduction reactions (during this reporting period) has produced a greater understanding of the inherent failure of this transformation. The primary products of these transformations (as determined by multi-dimensional NMR and MALDI-MS) were terphenyl molecules without iodine (derived from two sides of the iodonium ring undergoing reductive coupling). Mechanistically, this implies that the iodonium reduction was occurring, but that due to the build-up of strain within the macrocycle fragmentation was occurring.
- 2) Once the characterization of the fragmentation products had been completed, our group decided to approach our overarching objective using a different strategy. Realizing that the strain energy from the small-dimension iodonium rings might be producing the decomposed products, we opted to try and generate much larger-dimension iodonium rings that possess less inherent strain energy. These ring systems had not been produced in the literature and there were some initial solubility difficulties. Nevertheless, after careful screening of solvents and reaction conditions, we were able to apply our previous, optimized, four-step procedure to generate two novel large, tetracationic iodonium macrocycles. The first ring that was generated had three phenyl rings on each side of the macrocycle (12 in total). The second ring was produced in conjunction with starting material from a previous macrocycle synthesis. This ring had two phenyl rings on one side and three on the other side (10 total phenyl rings).
- 3) All of the generated intermediates, and each of the two rings were completely characterized spectroscopically (FTIR, ¹H-¹³C-NMR, MALDI-MS, UV-VIS). Proton and carbon NMR proved to be difficult to get "clean" spectra due to the solubility problems of the large ring structures. Nevertheless, both ring structures could be generated in sufficient quantity to begin crystallization studies in hope of producing X-ray quality crystals.
- 4) With the larger tetracationic iodonium macrocycles in hand, we attempted a series of 1-electron chemical reductions to affect the reductive de-iodinization. Interestingly, the 12-macrocycle proved to undergo a relatively clean reaction with a palladium acetate catalyst and zinc metal reductant to produce a new-insoluble product. Initial investigations indicate that the material is highly conjugated due to the fluorescence properties. ¹H NMR is not yet conclusive, as chromatographic purification of the product from several by-products has proven difficult. We are establishing collaborations with another research group at the University of New Mexico who possess a preparative LC to further purify the product. We are currently in the process of expanding this methodology to the other, larger, tetracationic iodonium macrocycles.

Technology Transfer