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<p>This project investigated, as its primary objective, the influence of carbon-boron bonding in unsaturated, cyclic boranes on the energy content of this system. Such insights should aid the choice of the best carbon-boron clusters to be incorporated into high-energy fuels. To this end, the synthesis and structural characterization of the following boron-containing carbocycles were undertaken: 1) the borirene or boracyclopropene system, as exemplified by trimesitylborirene; 2) the borole or boracyclopentadiene ring, as represented by pentaarylboroles; 3) the borepin or boracycloheptatriene nucleus, as seen in heptaphenylborepin; 4) the 7-borabicyclo[2.2.1]heptadiene system, again typified by its heptaaryl derivative; and 5) the 1-boratetrahydronaphthalene derivative, which was the thermal rearrangement product of the borepin. As estimated by chemical reactivity towards heat, oxidants and protolyzing agents, the borirene and borole nuclei display unusual stability and thus can be termed aromatic. By contrast, towards the same reaction conditions the boroles are very reactive and therefore can be said to possess destabilization</p>					
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or be antiaromatic. A rich variety of both thermal and photochemical skeletal rearrangements was discovered with these boracyclopolyenes, a convincing indication that tricoordinate boron has a pronounced tendency to interact either intermolecularly or intramolecularly, with  $\pi$ -electrons. Such interactions play an important role in influencing the energy content of carbon-boron clusters.

As a secondary objective, bimetallic oxides of the type,  $R_2M-O-M'R_2$ , were synthesized and evaluated as hydrocarbon-soluble precursors to specialized ceramics. In the cases where M and M' = boron or aluminum, our preliminary results encourage us to continue these studies when funding permits.

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COMPLETED PROJECT SUMMARY

AFOSR-TR-89-0234

TITLE: "Novel Organoboranes as Intermediates for Ceramic Precursors and High-Energy Fuels"

PRINCIPAL INVESTIGATOR: Professor John J. Eisch  
Department of Chemistry  
State University of New York at Binghamton  
Binghamton, New York 13901

INCLUSIVE DATES: 1 February 1985 - 31 August 1988

CONTRACT/GRANT NUMBER: AFOSR 85-0108

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SENIOR RESEARCH PERSONNEL: Dr. Marek P. Boleslawski

JUNIOR RESEARCH PERSONNEL: Babak Shafii

PUBLICATIONS:

"The Physical and Chemical Consequences of Cyclic Conjugation in Boracyclopolyenes. The Antiaromatic Character of Pentaarylboroles," John J. Eisch, James E. Galle and Sinpei Kozima, J. Am. Chem. Soc., 108, 379-385 (1986).

"The Di- $\pi$ -Methane-like Photorearrangement of Dimesityl(mesityl-ethynyl)borane," John J. Eisch, Babak Shafii and Arnold L. Rheingold, J. Am. Chem. Soc., 109, 2526-2528 (1987).

"Fluoro(dimesityl)borane," John J. Eisch and Babak Shafii, Organomet. Syn., 4, 465-468 (1988).

"Trimesitylborane," John J. Eisch and Babak Shafii, Organomet. Syn., 4, 469-471 (1988).

"The Photochemical Generation of the Diphenylborate(I) Anion from Metal Tetraphenylborates(III) in Aprotic Media: Repudiation of a Contravening Claim," John J. Eisch, Marek P. Boleslawski and Kohei Tamao, J. Org. Chem., 1989, in press.

"The Thermal Generation and Transformation of the Borepin Ring System: A Paradigm of Pericyclic Processes," John J. Eisch, James E. Galle, Babak Shafii and Arnold L. Rheingold, in preparation for Organometallics, 1989.

"Homoaromaticity and Bond Fluxionality in the 7-Borabicyclo[2.2.1]-heptadiene Ring System: Degenerate Sigmatropic and Irreversible Ring-Opening Rearrangements," John J. Eisch, James E. Galle, Marek P. Boleslawski and Arnold L. Rheingold, in preparation for J. Am. Chem. Soc., 1989.

"Aromatic Stabilization of the Triarylborirene Ring System by Tricoordinate Boron and Facile Ring-Opening with Tetracoordinate Boron", John J. Eisch, Babak Shafii and Arnold L. Rheingold, in preparation for Organometallics, 1989.

"The Photochemical Synthesis of the Sodium Diphenylborate(I)-Tris(1,2-dimethoxyethane) Complex," John J. Eisch, Marek P. Boleslawski and Arnold L. Rheingold, in preparation for J. Am. Chem. Soc., 1989.

Synthesis of Borirenes via the Photochemical Rearrangement of Ethynylboranes, Babak Shafii, Doctoral Dissertation, State University of New York at Binghamton, 1988, pp. 170.

#### ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research project pursued, as its primary goal, the synthesis and structural characterization of cyclic arrays of  $sp^2$ -hybridized carbon and boron atoms that are of interest in the design of novel high-energy fuels. A secondary objective, to which only limited effort could be committed, has been the preparation of monometallic or bimetallic oxide precursors to novel ceramic materials, especially those involving boron or aluminum.

The following summarizes our accomplishments with cyclic, unsaturated organoboranes as potential high-energy fuels:

1) Through studies of cyclic boranes of the boracyclopropene, boracyclopentadiene and boracycloheptatriene types, it has been shown that cyclic  $\pi$ -electron delocalization between carbon and boron can profoundly influence the stabilization or energy content of the molecule;

2) Crystalline triarylboracyclopropenes (borirenes) have been synthesized for the first time by a novel photorearrangement of alkynylboranes;

3) X-ray crystallographic analysis of such borirenes has demonstrated, unequivocally, the aromatic stabilization of the ring by  $\pi$ -electron delocalization;

4) Tricoordinate boron is essential for the aromaticity of borirene, for when the boron is made tetracoordinate, the ring is immediately ruptured;

5) Pentaarylboracyclopentadienes (boroles) have been synthesized for the first time and their high chemical reactivity reveal that delocalization in this system leads not to aromatic stabilization, but to antiaromatic reactivity;

6) The 7-borabicyclo[2.2.1]heptadiene system has been synthesized and structurally characterized for the first time; its chemical and spectral properties reveal the operation of homoaromatic stabilization;

7) A rich array of facile, skeletal rearrangements, commencing with boroles and proceeding via borepins ultimately to 1-boratetrahydronaphthalenes, has been discovered; these rearrangements point to the high energy content of such boron compounds;

8) The borepin nucleus or the heptaarylboracycloheptatriene system has been synthesized and been shown to possess aromatic stabilization, even though it is eventually transformed by skeletal rearrangement into another boracarbocycle;

9) Subvalent boron compounds in the form of sodium diphenylborate(I) systems have been generated as potential carbene precursors from the photochemical rearrangement of sodium tetraphenylborate, and an erroneous report by Wilkey and Schuster has been repudiated;

10) Promising results on the coupling of  $R_2BX$  to  $R_2B-BR_2$  (diboranes(4)) have been obtained recently; this augurs well for our efforts to prepare subvalent boron intermediates, either boron(II) or borate(I) anions, by thermal processes.

AFOSR Program Manager: Dr. Anthony J. Matuszko

Final Technical Report

to

The Air Force Office of Scientific Research  
Air Force Systems Command, USAF  
Bolling AFB, D.C. 20332

on

Grant AFOSR-85-0108

"Novel Organoboranes as Intermediates for  
Ceramic Precursors and High-Energy Fuels"

for the period

February 1, 1985 to August 31, 1988

submitted by

John J. Eisch, Ph.D.

Principal Investigator and  
Distinguished Professor of Chemistry  
Department of Chemistry  
State University of New York at Binghamton  
Binghamton, New York 13901

January 1, 1989

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## Summary

This project investigated, as its primary objective, the influence of carbon-boron bonding in unsaturated, cyclic boranes on the energy content of this system. Such insights should aid the choice of the best carbon-boron clusters to be incorporated into high-energy fuels. To this end, the synthesis and structural characterization of the following boron-containing carbocycles were undertaken: 1) the borirene or boracyclopropene system, as exemplified by trimesitylborirene; 2) the borole or boracyclopentadiene ring, as represented by pentaarylboroles; 3) the borepin or boracycloheptatriene nucleus, as seen in heptaphenylborepin; 4) the 7-borabicyclo[2.2.1]heptadiene system, again typified by its heptaaryl derivative; and 5) the 1-boratetrahydronaphthalene derivative, which was the thermal rearrangement product of the borepin. As estimated by chemical reactivity towards heat, oxidants and protolyzing agents, the borirene and borepin nuclei display unusual stability and thus can be termed aromatic. By contrast, towards the same reaction conditions the boroles are very reactive and therefore can be said to possess destabilization or be antiaromatic. A rich variety of both thermal and photochemical skeletal rearrangements was uncovered with these boracyclopolyenes, a convincing indication that tricoordinate boron has a pronounced tendency to interact either intermolecularly or intramolecularly, with pi-electrons. Such interactions play an important role in influencing the energy content of carbon-boron clusters.

As a secondary objective, bimetallic oxides of the type,  $R_2M-O-M'R_2$ , were synthesized and evaluated as hydrocarbon-soluble precursors to specialized ceramics. In the cases where M and M' = boron or aluminum, our preliminary results encourage us to continue these studies when funding permits.

## I Objectives of this Research

There is an essential connection between the type of molecular bonding in organoboranes and organoaluminoxanes, precursors to high-energy fuels and to ceramics, and the macroscopic properties of these important materials. The specific arrangement of boron atoms and their bonding to carbon centers, for example, determine the internal strain and energy content of organoboranes and hence the heat released during the combustion of such fuels. Analogously, the type of aluminum-oxygen bonding in organoaluminoxanes should greatly influence the final bonding arrangement in the alumina ceramic generated thermally from the aluminoxane. Therefore, the overall objective of this AFOSR-sponsored research has been to investigate the kinds and strength of carbon-boron, nitrogen-boron, oxygen-aluminum and nitrogen-aluminum bonds in specially synthesized model compounds. From such insights into bonding, we hope to be in a position to design potential precursors to high energy fuels and to novel ceramics.

From this goal have emerged the following specific objectives:

A. The synthesis and complete structural characterization of pi-bonded boracyclopolyenes and borazacyclopolyenes of the formula,  $RB_n(CR)_m$  and  $RB_n(CR)_mN_p$ , as precursors for high-energy fuels or for boron carbides and boron carbides nitrides with graphite-like structures;

B. Developing controlled syntheses of sigma-bonded dialuminoxanes of the type,  $R_2Al-O-AlR_2$ , and studying their thermal and/or hydrolytic transformation stepwise into aluminoxanes,  $(R-Al-O)_n$ ,

and ultimately into alumina,  $Al_2O_3$ , as ceramics, coatings or thin films;

C. Developing routes to bimetallic sulfides, nitrides or oxides of the type,  $R_mM-E-M'R_p$  ( $M, M' =$  metals such as B, Al, Ti, Zr, Li,  $R =$  organo groups and  $E = S, N, O$ ), which could be converted into ceramic materials by thermal or chemical treatment. The underlying rationale here, as well as in Objective A, is that the controlled formation of the bonding,  $M-E-M'$ , will then permit this bonding to serve as a template for the build-up of the bonding in the ultimate ceramic,  $M_mE_nM_p'$ ;

D. Preparing mixed organoboranes-organoalanes of the type,  $R_2B-BR_2$ ,  $R_2Al-AlR_2$  and  $R_2B-AlR_2$ , and employing these as precursors of novel aluminum borides, which have important applications in electronics.

## II Status of this Research

### A. General

This research program was funded originally by the AFOSR for two years, during which period the emphasis of the work was placed upon the synthesis of organoboranes as potential high-energy fuels. With the granting of a third year of support, the AFOSR suggested that research effort be equally apportioned between organoboranes as fuels and boron or aluminum precursors to novel ceramics. Toward the middle of the third year, this principal investigator submitted a renewal proposal for three years of research on exclusively the ceramic aspects of this program. However, due to

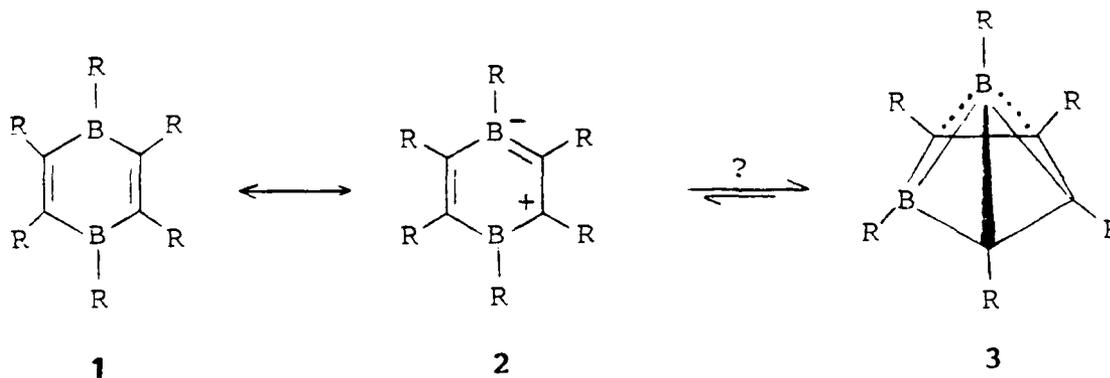
limitations of available funds, the AFOSR was unable to support our continuing efforts. Since termination of support, August 31, 1988, research on this project has been suspended.

In view of the varying emphases during this three-year period, much more has been accomplished in attaining Objectives A and D. Work directed toward Objectives B and C has, of necessity, been very preliminary and limited. Progress in these latter areas must await further external funding.

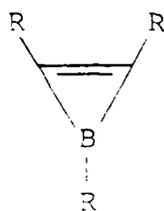
## B. Organoborane Results

### 1. Overview

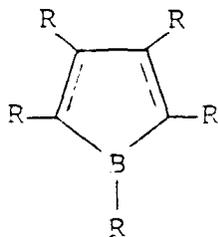
In order to probe the strength of carbon-boron bonds, be such bonding of the sigma-, pi- or multicenter-type, we have set out to synthesize a series of boron-containing, unsaturated carbocyclic rings (e.g., 1). By then assessing the strength of the sigma- and pi- bonding (2) or by observing any tendency of the system to rearrange into a multicenter-bonded carborane (3), the impact of such bonding on the energy content or thermal stability of the compound would be revealed. Exactly such information is required in designing precursors for high-energy fuels.



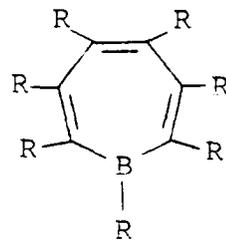
To this end, therefore, the synthesis of a series of boracyclopolyenes was undertaken; the principal targets for this effort were the borirene (4), borole (5) and borepin (6) nuclei:



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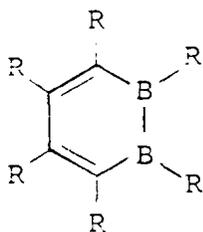


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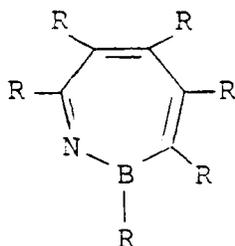


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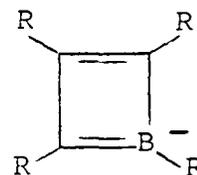
Further ring systems of interest included the aforementioned 1,4-diboracyclohexadiene (1), 1,2-diboracyclohexadiene (7), 2-azaborepin (8) and borete (9) anion:



7



8



9

Because our research in this area had already been launched some years ago under ARO sponsorship, a good number of promising observations had been gathered. Recommencing this research with AFOSR support permitted us, therefore, a head start in bringing several aspects of this project to a successful conclusion, namely the synthesis and structure determination of the borirene (4), borole (5) and borepin (6). In addition, a startling number of unforeseen skeletal rearrangements involving such nuclei points to a remarkable lability of the carbon-boron bond.

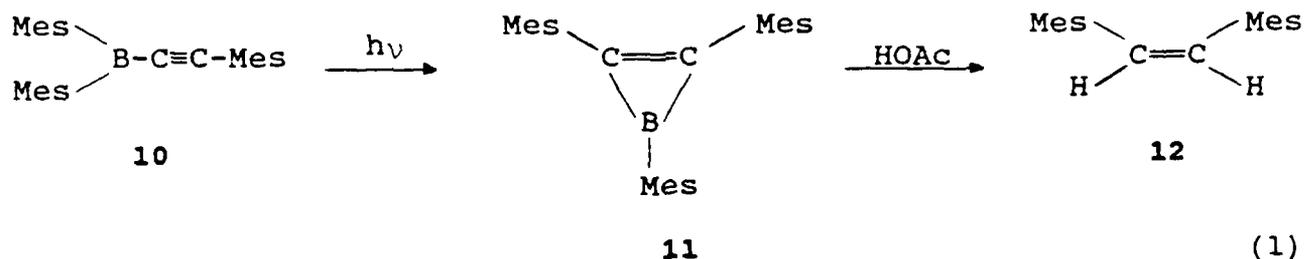
## 2. Borirenes

Since the borirene nucleus (4) consists of an array of one boron and two carbon atoms of  $sp^2$ -hybridization and two pi-electrons, it is isoelectronic with the cyclopropenyl cation and is expected to display aromatic stabilization.<sup>1</sup> The molecular orbital theory of Erich Hückel predicts that a monocyclic array of  $sp^2$ -hybridized atoms will possess unusual stabilization when the total number of pi-electrons is  $4n+2$  where  $n = 0, 1, 2, \dots$ .<sup>2</sup> With the cyclopropenyl cation<sup>3</sup> and borirene,  $n = 0$ .

Although in previous work our group<sup>3,4</sup> and other researchers<sup>5-8</sup> have either trapped borirenes chemically or made them with unusual substituents, we have set out to prepare borirenes with only organic groups as substituents (R). As our substituent R, we initially chose the 2,4,6-trimethylphenyl or mesityl group. Our rationale has been that the mesityl group should so shield the borirene that it should be more resistant to both oxidative and hydrolytic cleavage. The basis for this assumption is that while triphenylborane is sensitive to C-B bond cleavage by alcohols or by  $O_2$ , trimesitylborane is relatively inert to both reagents.

Our route to 1 is a novel di-pi-methane-like rearrangement discovered by us in 1982:<sup>4</sup> the photorearrangement of an alkynyl-(diaryl)borane (eq. 1). For this purpose, we successfully synthesized the previously unknown dimesityl(mesitylethynyl)borane (10) and found that addition of HOAc, after irradiation, yielded cis-1,2-dimesitylethene (12). The formation of this olefin

indicates that borirene **11** must have been formed in the photoreaction:

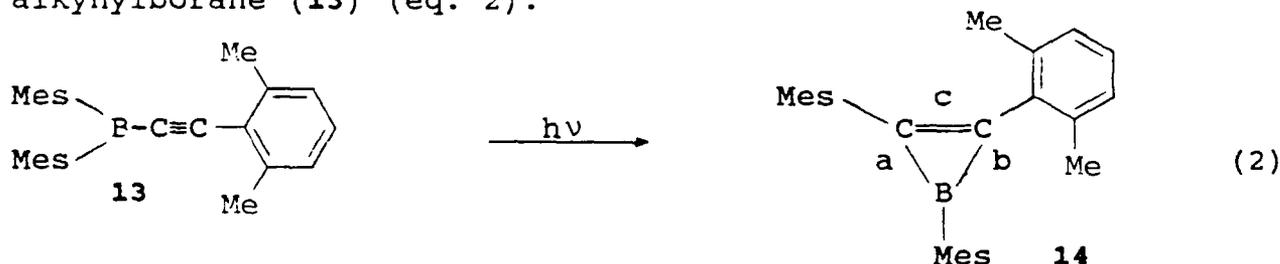


With this encouragement, we set about isolating pure **11**. By careful exclusion of moisture and oxygen, we were able to isolate colorless, monoclinic crystals of trimesitylborirene (**11**). With crystals in hand, we hoped to determine the carbon-boron and carbo-carbon bond lengths of the borirene ring. Professor Arnold L. Rheingold of the University of Delaware found by X-ray crystallography that within experimental error the borirene ring forms an equilateral triangle, *i.e.*, the C-C and C-B bond lengths were were both apparently 1.42Å. Since the C=C bond in cyclopropene is 1.304Å and the C-B bond in trivinylborane is 1.588Å, the C=C bond in **11** had been lengthened and the C-B bond shortened. Both effects are consistent with extensive pi-electron delocalization in **11**, as would be expected for a Hückel aromatic ring. These results were published as a communication in 1987.<sup>9</sup>

Yet all was not satisfactory in the X-ray analysis of **11**. The dimensions of the carbon and boron atoms were so similar, that whether a boron or a carbon occupied a given ring site could not be discerned. Since there was a three-fold disorder in the

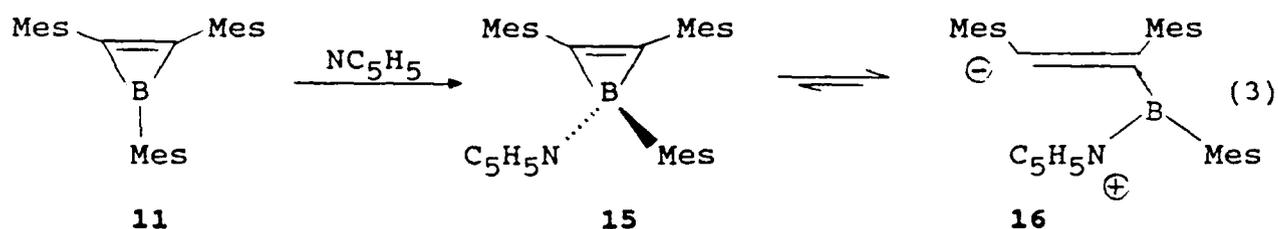
positions of the ring carbons and boron, there was concern that the observed apparent equality of the C-C and C-B bond lengths might be an average value arising from the statistical disorder and that the actual bond lengths would differ from each other.

To address this concern, we had to synthesize a borirene having dissimilar groups on the ring carbons, so as to disrupt the symmetry of **11** and thus remove any possible statistical averaging arising from random occupancy of ring sites. Therefore, we prepared 2-(2,6-dimethylphenyl)-1,3-dimesitylborirene (**14**) by an analogous photorearrangement of the appropriate alkynylborane (**13**) (eq. 2).



With such an unsymmetrically substituted borirene, no boron (carbon) site disorder arose and the X-ray analysis revealed three distinct bond lengths in the ring:  $a = 1.464$ ;  $b = 1.450$ ;  $c = 1.380$ . From these data it follows that there was some bond-length averaging due to disorder in **11**. Nevertheless, the C=C bond is still lengthened over that in cyclopropene and the C-B bond shortened over that in trivinylborane. Hence, the conclusion that the borirene ring displays extensive  $\pi$ -electron delocalization is corroborated. The findings will be communicated shortly.<sup>10</sup>

These results show that the stabilization of the otherwise highly-strained three-membered ring in borirene is due to the  $sp^2$ -hybridized boron. As a corollary to this conclusion is the expectation that changing the hybridization of boron from  $sp^2$  to  $sp^3$  should remove such aromatic stabilization and cause disruption of the borirene ring. Indeed, we have experimental evidence for this prediction: when borirene **11** is treated with pyridine, colorless **11** turns a vivid yellow and the relatively simple carbon-13 NMR spectrum of **11** becomes greatly enriched in signals. These spectral and additional chemical trapping experiments are consistent with the ring-opening of **11** by coordination with pyridine (**15**) (eq. 3):

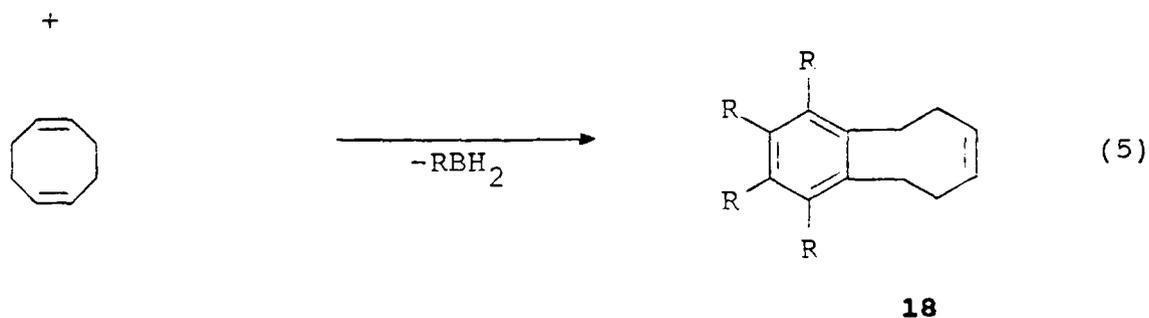
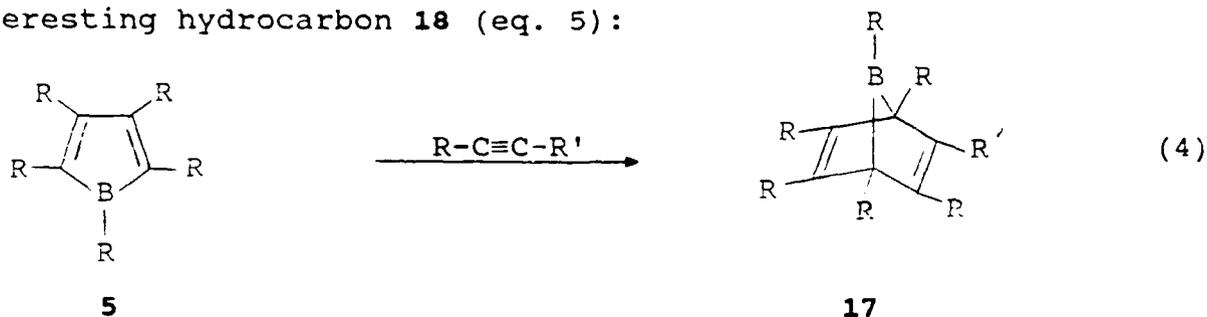


Only the generation of zwitterion **16** would account for the development of color (conjugation) and the multiple-line carbon-13 NMR spectrum (dissimilarity of mesityl groups in **16** compared with those in **11** and **15**). These results will be submitted for publication in the near future.<sup>10</sup>

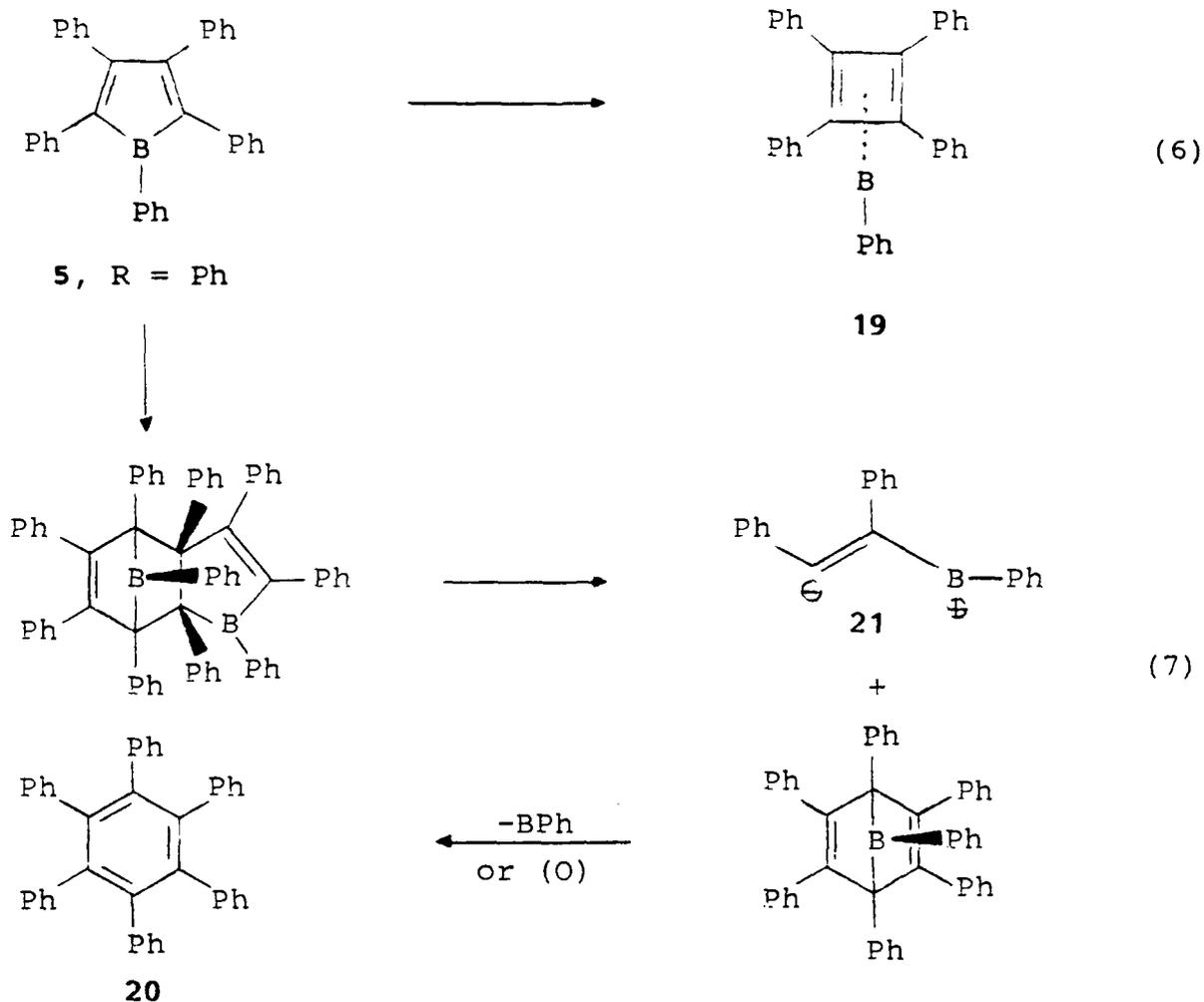
### 3. Boroles

Because of this AFOSR grant, we were able to complete a definitive manuscript on the synthesis and spectral properties of pentaarylboreles (**5**, R = Ar), which has now been published.<sup>11</sup> We then continued research on the cycloaddition reactions of

boroles, both thermal and photochemical, as exemplified by the formation of the 7-borabicyclo[2.2.1]heptadiene system **17** (eq. 4), and the reaction with 1,5-cyclooctadiene to yield, ultimately, the interesting hydrocarbon **18** (eq. 5):



In connection with these cycloaddition studies, we were also interested to learn whether boroles could undergo electrocyclic isomerization to the carborane structure **19** (eq. 6), since conjugation in boroles is actually destabilizing.<sup>11</sup> Thus, we observe that the deep blue color of boroles becomes dark green upon irradiation at 254 nm. In attempting to learn whether **19** is formed or what other photoreaction might have taken place, we found that the photolysate contained hexaphenylbenzene (**20**). This may indicate that a photodimerization of **5** has taken place, followed by the aromatization to **20** with the elimination of zwitterion **21** (cf. eq. 3) (eq. 7).



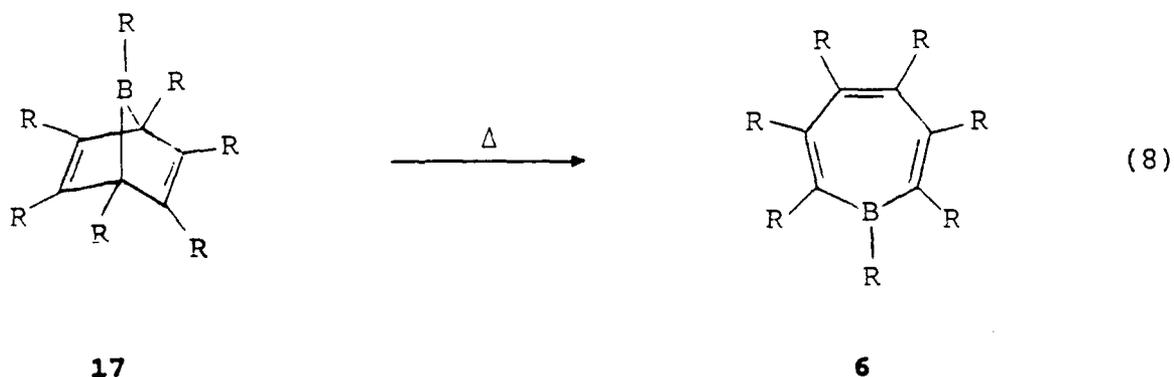
The electronic transition necessary to convert **5** into **19** should involve a  $\pi\text{-}\pi^*$  transition of relatively low energy. This viewpoint is supported by Extended Hückel Molecular Orbital calculations, which the principal investigator carried out on boroles while on sabbatical leave at Cornell University during the Fall Semester of 1985. In collaboration with Professor Roald Hoffmann, he estimated that the HOMO-LUMO energy separation is about 2 eV and hence boroles might be raised rather easily to their triplet state by irradiation.<sup>12</sup> Hence, intermediate **19** may play a role in the photoreactions depicted in eq. 7.

When these studies on the electrocyclic and cycloadditive reactivity of boroles have been completed, a full manuscript will be prepared for the Journal of the American Chemical Society.<sup>13</sup>

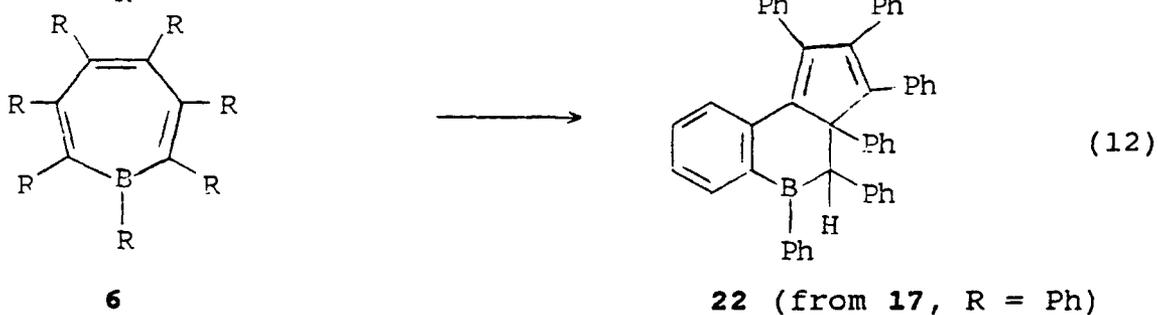
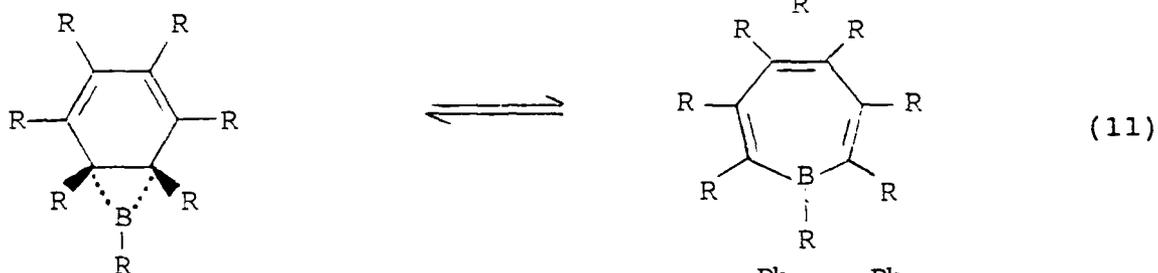
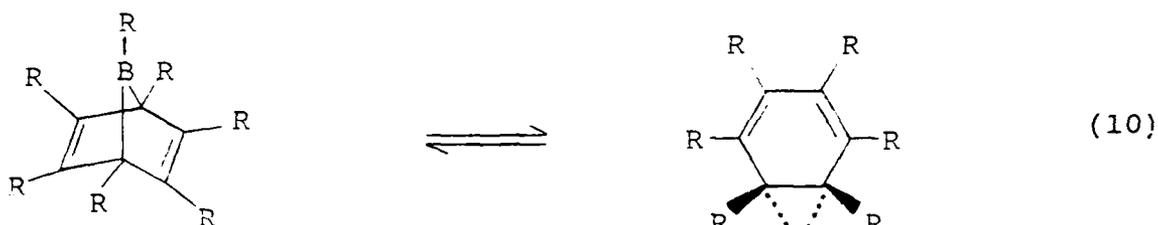
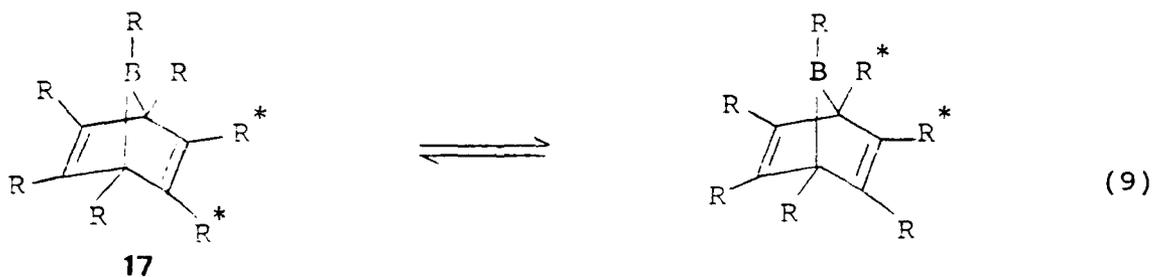
Finally, because of the extraordinary electronic properties of boroles, we are convinced that its bond angles and bond distances should also be unusual. Hence, in collaboration with Professor Arnold Rheingold, we are preparing suitably crystalline samples of pentaphenylborole and its pyridine adduct for X-ray crystal structure determination.<sup>14</sup>

#### 4. Borepins

Our work on the synthesis of borepins (6) by the thermal isomerization of 7-borabicyclo[2.2.1]heptadienes (17) is moving toward completion (eq. 8):



In the course of this work, we have uncovered an astonishing variety of skeletal rearrangements, which are summarized in the following set of equations (eq. 9 - 12):

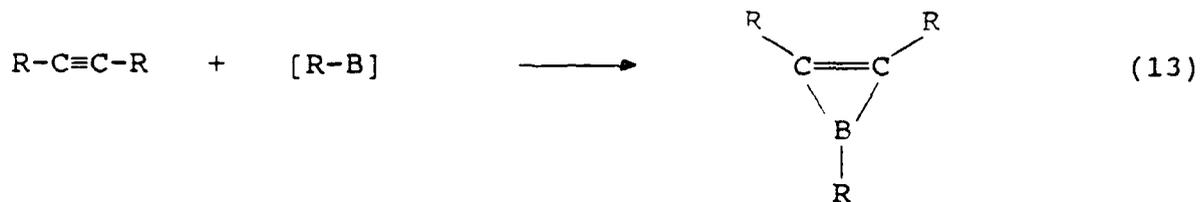


The structure **22**, formed from the irreversible isomerization of **6**, was determined by X-ray crystallography. The transformation of **6** into **22** is remarkable; it appears to involve a series of thermally allowed pericyclic reactions. Details of this unusual rearrangement will be published shortly.<sup>15</sup>

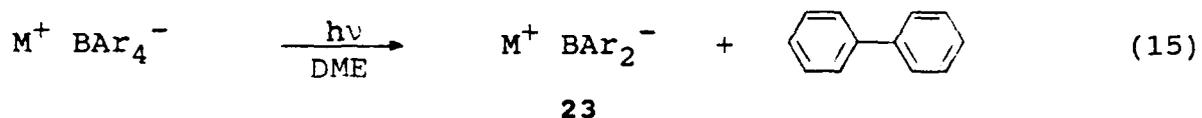
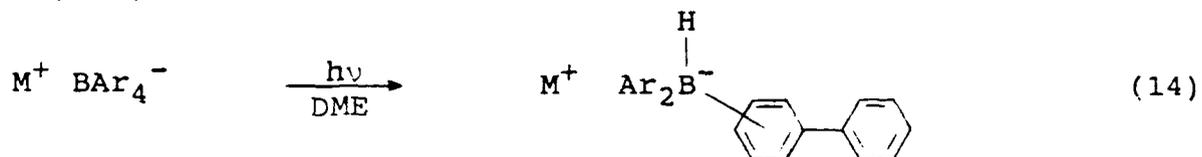
## 5. Boron(I) Precursors

As part of our search for synthetic methods leading to borirenes, we became interested in the generation of subvalent

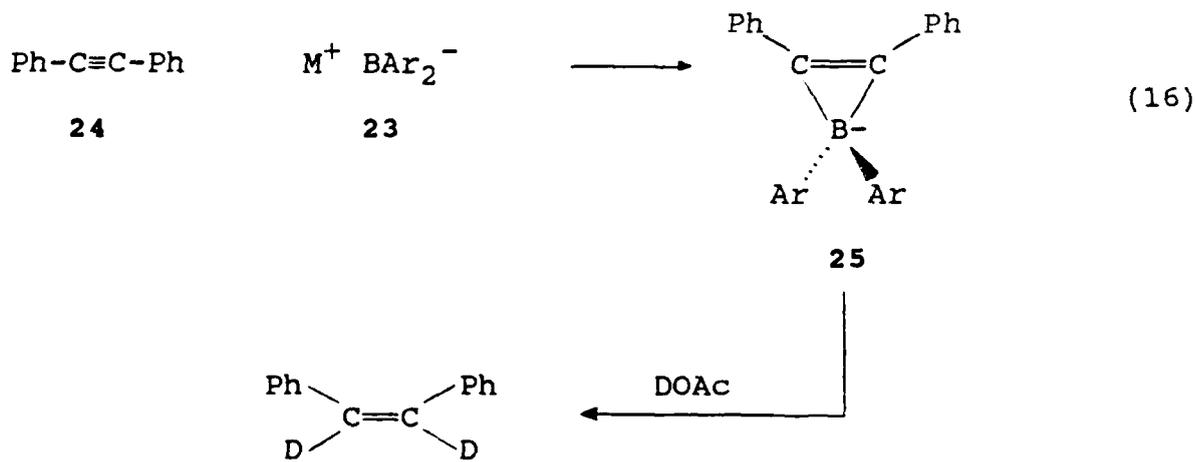
boron precursors for additions to alkynes (eq. 13):<sup>16</sup>



Accordingly, an extensive photochemical study in our group reinvestigated the photorearrangements of tetraarylborates in aprotic media and uncovered evidence for two interesting reactions (eq. 14, 15):<sup>17</sup>



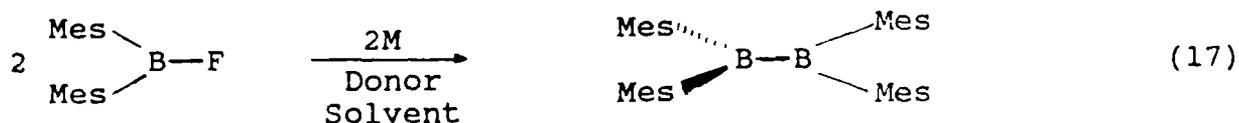
The metal diarylborate(I) (23) generated in the latter reaction was intercepted by diphenylacetylene (24) and the resulting intermediate (25) verified by deuteriolytic work-up (eq. 16):



Very recently, Schuster and co-workers have challenged the correctness of our observations and claimed that we had no experimental support for the reactions depicted in eqs. 15 and 16.<sup>18</sup> However, most recently we have carefully re-examined these reactions and have demonstrated both the reliability and reproducibility of our previous results, and at the same time have shown the carelessness and hasty nature of Schuster's investigation. A full article repudiating Schuster's rejection of our work and pointing out the experimental mistakes of his study has been accepted for publication in the Journal of Organic Chemistry and will appear in spring of 1989.<sup>19</sup>

#### 6. Tetraaryldiborane(4)

As part of our goal of preparing novel, unsaturated organoboranes, we have also attempted to generate neutral subvalent organoboranes or compounds with boron-boron bonds. To this end, we have undertaken the reaction of dimesitylboron fluoride with alkali metals. Here again, the assumption is that the ortho methyls of the mesityl groups may shield the boron-boron bond, once it is formed, from chemical disruption (eq. 17):



26

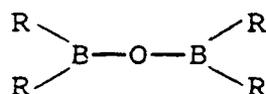
With lithium in diethyl ether we have been unable to obtain reaction and with potassium in 1,2-dimethoxyethane we find that trimesitylborane is formed. At the conclusion of our AFOSR

support we had just had encouraging signs that lithium in THF may well have generated **26** in solution.<sup>20</sup>

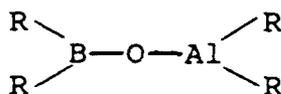
#### 7. Controlled Formation of Boron-Oxygen-Metal Bonds

As part of a modification agreed to by this project's AFOSR program manager, this investigator spent about 20% of the research effort during the last year in examining new approaches to preceramic materials.

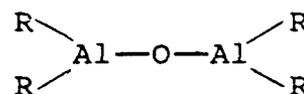
Specifically, the method to be evaluated was the controlled coupling of the same or different metals through an oxygen bridge (for example, systems like **27** and **28**):



**27**



**28**



**29**

By establishing M-O-M' bonds in such systems, one is dealing with intermediates readily soluble in hydrocarbons. Such solutions are very convenient for the spreading of films for the formation of filaments. The resulting films and filaments can then be coupled with other metal alkoxides to form layers of different M-O-M'-O-M'' bonds, or they can be pyrolyzed directly to remove the organic groups R and leave a defined metal oxide residue.

Our initial studies resulted in promising evidence that such systems can be prepared. However, time did not permit definitive studies to be made and additional work must await further support from AFOSR.

### III Written Publications

- A. John J. Eisch, James E. Galle and Sinpei Kozima, "The Physical and Chemical Consequences of Cyclic Conjugation in Boracyclopolyenes. The Antiaromatic Character of Pentaarylboroles," J. Am. Chem. Soc., **1986**, 108, 379-385.
- B. John J. Eisch, Babak Shafii and Arnold L. Rheingold, "The Di- $\pi$ -Methane-like Photorearrangement of Dimesityl(mesityl-ethynyl)borane," J. Am. Chem. Soc., **1987**, 109, 2526-2528.
- C. John J. Eisch and Babak Shafii, "Fluoro(dimesityl)borane," Organomet. Syn., **1988**, 4, 465-468.
- D. John J. Eisch and Babak Shafii, "Trimesitylborane," Organomet. Syn., **1988**, 4, 469-471.
- E. John J. Eisch, Marek P. Boleslawski and Kohei Tamao, "The Photochemical Generation of the Diphenylborate(I) Anion from Metal Tetraphenylborates(III) in Aprotic Media: Repudiation of a Contravening Claim," J. Org. Chem., **1989**, in press.
- F. John J. Eisch, James E. Galle, Babak Shafii and Arnold L. Rheingold, "The Thermal Generation and Transformation of the Borepin Ring System: A Paradigm of Pericyclic Processes," in preparation for Organometallics, **1989**.
- G. John J. Eisch, James E. Galle, Marek P. Boleslawski and Arnold L. Rheingold, "Homoaromaticity and Bond Fluxionality in the 7-Borabicyclo[2.2.1]heptadiene Ring System: Degenerate Sigmatropic

and Irreversible Ring-Opening Rearrangements," in preparation for J. Am. Chem. Soc., 1989.

H. John J. Eisch, Babak Shafii and Arnold L. Rheingold, "Aromatic Stabilization of the Triarylborirene Ring System by Tricoordinate Boron and Facile Ring-Opening with Tetracoordinate Boron", in preparation for Organometallics, 1989.

I. John J. Eisch, Marek P. Boleslawski and Arnold L. Rheingold, "The Photochemical Synthesis of the Sodium Diphenylborate(I)-Tris(1,2-dimethoxyethane) Complex," in preparation for J. Am. Chem. Soc., 1989.

J. Babak Shafii, Synthesis of Borirenes via the Photochemical Rearrangement of Ethynylboranes, Doctoral Dissertation, State University of New York at Binghamton, 1988, pp. 170.

#### IV Professional Personnel Involved

A.	John J. Eisch, Ph.D.	Principal Investigator	part-time
B.	Marek P. Boleslawski, Ph.D.	Postdoctoral Research Associate	full-time
C.	Babak Shafii, M.S.*	Graduate Research Assistant	full-time

\*This student completed his doctoral dissertation in Fall, 1988, with AFOSR support during most of his graduate studies. The title of the dissertation is "Synthesis of Borirenes via the Photochemical Rearrangement of Ethynylboranes."

V Oral Presentations

- A. John J. Eisch, "Physical and Chemical Consequences of Antiaromaticity in the Boracyclopentadiene System," invited lecture, U.S. Air Force Rocket Propulsion Meeting, Lancaster, CA, March 18-20, 1985.
- B. John J. Eisch, Babak Shafii and Marek P. Boleslawski, "Di- $\pi$ -Methane-like-Photorearrangements of  $\alpha,\beta$ -Unsaturated Organoboranes in the Synthesis of Borireres and Boracarbenoid Intermediates," invited lecture, Euchem Conference on Phosphorus, Silicon, Boron and Related Elements in Low Coordinated States, Paris-Palaiseau, France, August 22-26, 1988.
- C. John J. Eisch and Babak Shafii, "Boron-Carbon  $\pi$ -Bonding in the Formation and Reactions of Boracyclopropenes and Boracyclopentadienes," lecture, Thirteenth International Conference on Organometallic Chemistry, Turin, Italy, September 4-9, 1988.
- D. John J. Eisch, "Aromaticity and Facile Rearrangements in Unsaturated Organoboranes," invited ACS lecturer, ACS Pensacola Meeting, Pensacola, FL, November 17, 1986.
- E. John J. Eisch, same topic as entry D, invited ACS lecturer, ACS Muscle Shoals Meeting, Muscle Shoals, AL, November 20, 1986.

- F. John J. Eisch, "Aromatischer Charakter in Ungesättigten Boracyclopolyenen," invited lecture, University of Bremen, Bremen, West Germany, September 29, 1987.
- G. John J. Eisch, "Aromaticity in Unsaturated Boracyclopolyenes," Temple University, Philadelphia, PA, October 16, 1987.

#### VI Invention Disclosures or Patents

There was no invention disclosure made nor was any patent applied for on any of the results of this project.

#### VII Outlook for this Field of Research

In our investigations of carbon-boron bonding in unsaturated organoboranes, we have both deep satisfaction and gratifying corroboration in our finding that  $\pi$ -electron delocalization can markedly increase or decrease the energy content of these potential high-energy fuels. Furthermore, the rich variety of thermal rearrangements displayed by these cyclic compounds testify to their high-energy content. Our results should have great value for future research in high-energy fuels for two reasons: 1) our structure-energy correlations should guide the choice of appropriate carbon-boron atom arrays to be introduced into high-energy fuels; and 2) the many skeletal rearrangements we have uncovered may prove of great value for the synthesis of desired carbon-boron clusters for novel fuels based on boron.

The synthesis and evaluation of carbon-metal and oxygen-metal organometallic precursors to ceramics were minor efforts during our three-year AFOSR grant. However, our preliminary results have strengthened our confidence in the experimental approach. We intend to make every effort, therefore, to continue this research under future sponsorship from the AFOSR or another Government agency.

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