

DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

AD-A222 546

DTIC
LECTE
10 4 1990

1b. RESTRICTIVE MARKINGS

3. DISTRIBUTION / AVAILABILITY OF REPORT

Approved for Public Release

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

B

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

Report No. 2

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION

University of South Carolina

6b. OFFICE SYMBOL
(if applicable)

7a. NAME OF MONITORING ORGANIZATION

ONR

6c. ADDRESS (City, State, and ZIP Code)

Department of Chemistry
Columbia, SC 29208

7b. ADDRESS (City, State, and ZIP Code)

Department of Navy
Arlington, VA 22217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION

ONR

8b. OFFICE SYMBOL
(if applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

6c. ADDRESS (City, State, and ZIP Code)

800 N. Quincy Street
Arlington, VA 22217

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
N00014-89	J-3062		

1. TITLE (Include Security Classification)

Approaches to Orthogonally Fused Conducting Polymers for Molecular Electronics

2. PERSONAL AUTHOR(S)

James M. Tour, Ruilian Wu, and Jeffrey L. Schumm

13a. TYPE OF REPORT

Preprint

13b. TIME COVERED

FROM _____ TO _____

14. DATE OF REPORT (Year, Month, Day)

May 28, 1990

15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

Journal of the American Chemical Society

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

Molecular electronics, conducting polymers, poly(thiophene), poly(phenylene), Computing Instruments, Doping, Oxidized Systems
Physics (JG)

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Described is the synthesis of two spiro core segments of orthogonally arranged conducting systems. The final systems are to have a potentially conducting chain fused perpendicularly to a second potentially conducting chain via a sigma bonded network. These systems may be suitable for incorporation into future molecular electronic devices. One of the core segments synthesized is based on a thiophene conducting group and it is formed by a zirconium-promoted bis(bicyclization) of bis(diyne) systems. The second is a phenylene-based system which is derived from fluorene. Terminal bromide groups provide the linkage points for further extensions of the chains via palladium-catalyzed cross coupling methods.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT

UNCLASSIFIED/UNLIMITED SAME AS RPT. DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL

James M. Tour

22b. TELEPHONE (Include Area Code)

(803) 777-9517

22c. OFFICE SYMBOL

DISTRIBUTION STATEMENT A

Approved for public release
Distribution Unlimited

90 06 01 108

OFFICE OF NAVAL RESEARCH

GRANT : N00014 - j-3062

R&T Code 400x056yip01&02

Technical Report No. 2

Approaches to Orthogonally Fused Conducting Polymers for Molecular Electronics

by

James M. Tour, Ruilian Wu, and Jeffrey S. Schumm

Accepted for Publication in the

Journal of the American Chemical Society

**Department of Chemistry
University of South Carolina
Columbia, SC 29208**

May 28, 1990

**Reproduction in whole, or in part, is permitted for any purpose of the United States
Government**

**This document has been approved for public release and sale; its distribution is
unlimited.**

Approaches to Orthogonally Fused Conducting Polymers for Molecular Electronics¹

James M. Tour,*² Ruilian Wu, and Jeffrey S. Schumm
Department of Chemistry
University of South Carolina
Columbia, SC 29208

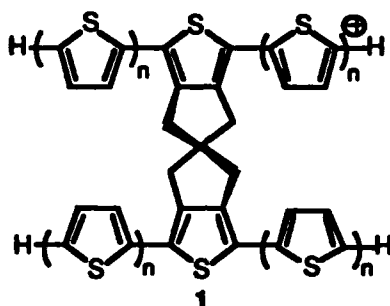
Abstract

Described is the synthesis of two spiro core segments of orthogonally arranged conducting systems. The final systems are to have a potentially conducting chain fused perpendicularly to a second potentially conducting chain via a sigma bonded network. These systems may be suitable for incorporation into future molecular electronic devices. One of the core segments synthesized is based on a thiophene conducting group and it is formed by a zirconium-promoted bis(bicyclization) of bis(diyne) systems. The second is a phenylene-based system which is derived from fluorene. Terminal bromide groups provide the linkage points for further extensions of the chains via palladium-catalyzed cross coupling methods.



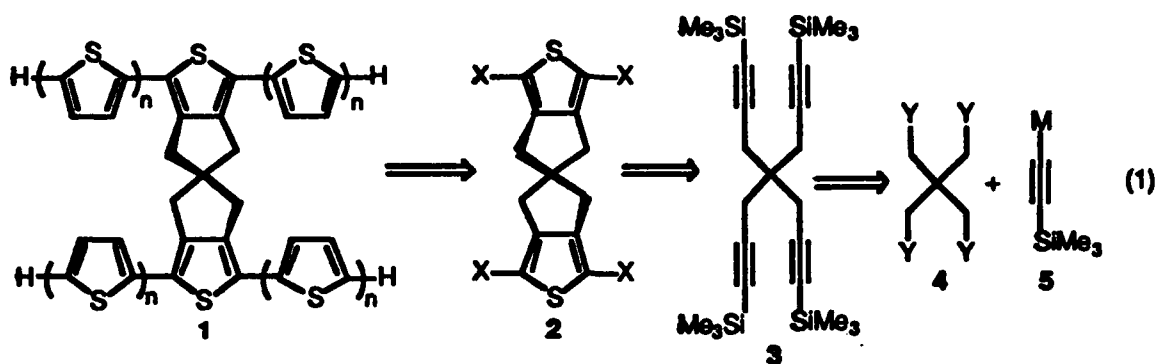
Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

Molecular electronics-based computing instruments possess tremendous technological potential. There is the hope of developing single molecules that could each function as a self-contained electronic device. Thus, one can envision computing systems with molecular-sized electronic elements and operational efficiencies far exceeding that of present systems.³ Recently, Aviram of the IBM Corporation has suggested that molecules which contain a pro-conducting (non-doped or non-oxidized system, hence insulating) polymer which is fixed at a 90° angle via a non-conjugated sigma bonded network to a conducting (doped or oxidized system) should exhibit properties which would make it suitable for interconnection into future molecular electronic devices.⁴ These devices may be useful for the memory, logic, and amplification computing systems. The molecule 1 (in doped form) is an example of this pro-conducting/sigma/conducting type of molecule.

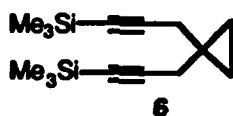


We have undertaken the synthesis of several molecules which fit the structural requirements of this electronic model. From the synthetic standpoint, several aspects are challenging. First, there must be a one spiro-fused junction separating two potentially conducting chains with a tetrahedral bonding atom at the center to maintain the 90° angle via a sigma bonded network. Secondly, all four conducting chains originating from the central segment must be *identical* in length. These requirements prohibit the use of any random polymerization methods. Initial reports suggested conducting chains ~50 Å long (from end to end rather than from end to core) would fulfill the model.⁴

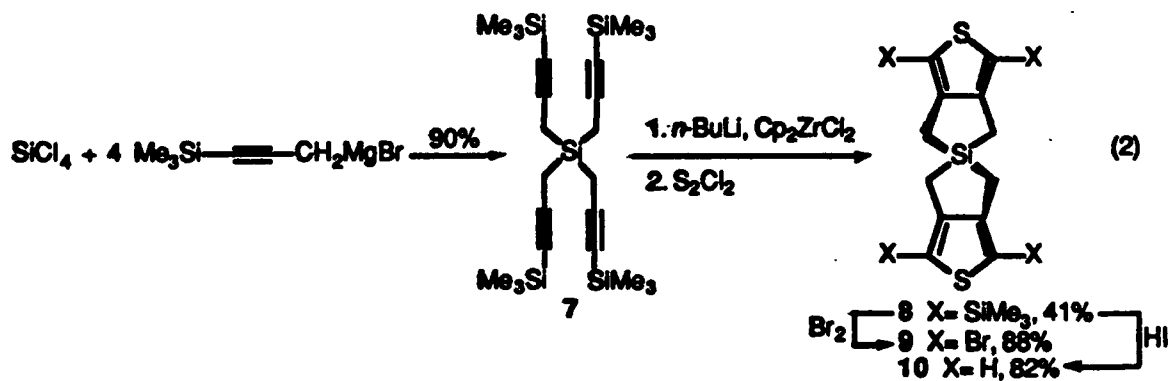
Our initial approach to these systems involved the synthesis of the key spiro core 2 from which we envisioned selective oligomerization to the target molecule 1. A retrosynthetic analysis is shown in eq 1.



Though substitutions on pentaerythritol tetrahalides involves reactions on a neopentyl system, exhaustive substitution has been accomplished using oxygen, nitrogen, and sulfur nucleophiles.⁵ Attempted formation of 3 using 1-metallo-2-(trimethylsilyl)acetylenes 5 and pentaerythritol tetrahalides and tosylates 4 proved to be very difficult even though we tried numerous coupling procedures (M= MgBr, Li, ZnCl, Cu, AlR₂ with and without Pd and Ni catalysis). In several cases, we obtained the cyclopropyl system 6.⁶ In an effort to overcome these difficulties while

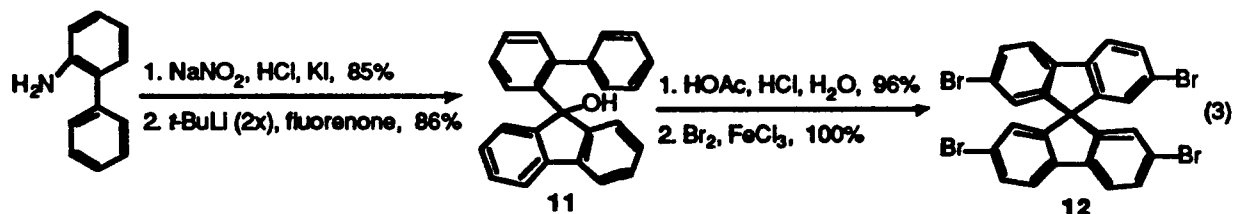


maintaining the required sigma bonded tetrahedral spiro junction, we turned our attention to the use of silicon as the central atom. Accordingly, treatment of SiCl₄ with the silyl protected propargyl Grignard reagent cleanly afforded the tetra(alkyne) 7.⁶ Treatment of 7 with a zirconocene equivalent, generated *in situ* from zirconocene dichloride and butyllithium, and quenching with sulfur monochloride afforded the trimethylsilyl-spiro core 8 (eq 2).^{6,7} To our knowledge,



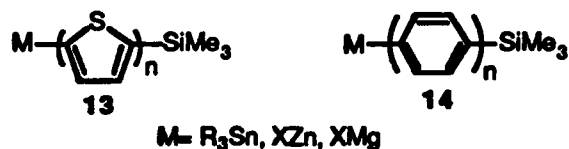
use of this group IVA coupling procedure for a *bis*(bicyclization) has never before been demonstrated. The trimethylsilyl core (8) was converted to the tetrabromide (9) and parent core (10) under electrophilic substitution conditions.^{6,8} Remarkably, no attack on the pseudo allylic central silicon atom was observed.

Likewise, we have synthesized another key core segment based on a *p*-polyphenylene⁹ conducting unit which fits the general electronic architectural requirements. Conversion of 2-aminobiphenyl to the corresponding iodide under Sandmeyer¹⁰ conditions followed by lithium halogen exchange and quenching with fluorenone afforded the alcohol 11. Acid treatment to close the spiro system¹¹ followed by reaction with bromine and FeCl₃ gave the tetrabromide 12 in excellent yields (eq 3).⁶ Bromination occurred only at the positions para to the second ring in

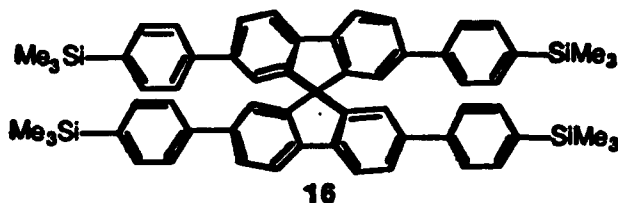
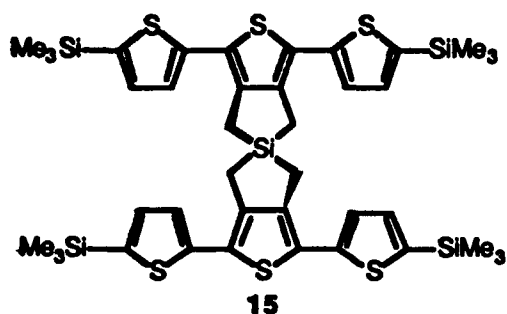


the chain as one would expect by resonance stabilization arguments of the ionic intermediate. It is imperative that the bromination take place at the para position since a 4-substituted moiety is essential to afford a highly conducting system.⁹

With two key core units in hand, we then addressed methods to selectively and equally extend the chains in all four directions. Coupling 9 and 12 with 13 and 14, respectively, using transition metal catalysis¹² would allow for the selective introduction of a known number of units.¹³ Additionally, the terminal trimethylsilyl



group in 13 and 14 would allow for selective bromination at those sites and, hence, a position for further coupling if necessary.^{8a} Accordingly, treatment of 9 with 13 (M = Bu₃Sn, n = 1) in the presence of catalytic Pd(PPh₃)₄ afforded 15 in 41% yield. Likewise, treatment of 12 with 14 (M = ClZn, n = 1) under similar catalytic conditions afforded 16 in 40% yield.⁶



Use of 3-substituted thiophenes for connection to both 9 and 12 is also being investigated to help in solublizing these systems.^{13,14}

Clearly, the efficiency of these coupling reactions must be optimized and the chain lengths further extended. However, these synthetic approaches demonstrate the power of modern synthetic methods to allow for the construction of macromolecules with the extremely specific architectural requirements necessary for the construction of the future molecular-electronics-based computing machine.

Acknowledgements

This research was funded by the Department of the Navy, Office of the Chief of Naval Research, Young Investigator Program (N00014-89-J-3062), the National Science Foundation EPSCoR program (RII-8922165), and the University of South Carolina Venture Fund.

References and Notes

1. Presented at the 199th ACS National Meeting, Polymer Division, April 1990.
2. Recipient of the Office of Naval Research, Young Investigator Award (1989-92).
3. a. Bowden, M. J. in *Electronic and Photonic Applications of Polymers*; Bowden, M. J.; Turner, S. R., Eds; (Advances in Chemistry, 218) American Chemical Society: Washington DC, 1988. b. *Molecular Electronic Devices*; Carter, F. L., Ed.; Marcel Dekker: New York, 1982. c. *Molecular Electronic Devices II*; Carter, F. L., Ed.; Marcel Dekker: New York, 1984. d. Third International Symposium on Molecular Electronic Devices, Washington DC, October, 1986; Roland Etvos Physical Society, Satellite Symposium on Molecular Electronics, Budapest Hungary, August 1987.

4. Aviram, A. *J. Am. Chem. Soc.* 1988, 110, 5687 and references therein.
5. a. Padias, A. B.; Hall, H. K., Jr.; Tomalia, D. A.; McConnell, J. R. *J. Org. Chem.* 1987, 52, 5305. b. Fujihara, H.; Imaoka, K.; Furukawa, N. *J. Chem. Soc. Perkin Trans. 1* 1986, 465.
6. All new compounds were fully characterized spectroscopically and the elemental composition was established by high resolution mass spectrometry and/or combustion analysis. All reported yields pertain to isolated homogeneous materials which were purified by recrystallization or chromatography.
7. a. Negishi, E. Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* 1989, 111, 3336. b. Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* 1988, 110, 2310.
8. a. Chan, T. H.; Fleming, I. *Synthesis*, 1979, 761. b. Utimoto, K.; Kitai, M.; Nozaki, H. *Tetrahedron Lett.* 1975, 33, 2825.
9. For a discussion of polyphenylene, see: a. Elsenbaumer, R. L.; Shacklette, L. W. in *Handbook of Conducting Polymers*, Skotheim, T. A., Ed.; Dekker: New York, 1986. For related syntheses, see b. Yamamoto, T.; Hayashi, Y.; Tamamoto, A. *Bull. Chem. Soc. Jpn.* 1978, 51, 2091. c. Kovacic, P.; Oziomek, J. *J. Org. Chem.* 1964, 29, 100.
10. Heaney, H.; Millar, I. T. *Org. Synth.* 1960, 40, 105.
11. Clarkson, R. G.; Gomberg, M. *J. Am. Chem. Soc.* 1930, 52, 2881.
12. a. Negishi, E.; Baba, S. *J. Chem. Soc. Chem. Commun.* 1976, 596. b. Negishi, E.; Takahashi, T.; Baba, S.; Van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.* 1987, 109, 2393. c. Stille, J. K. *Angew. Chem., Int. Ed. Engl.* 1986, 25, 508. d. Stille, J. K. *Pure Appl. Chem.* 1985, 57, 1771.
13. For a discussion of polythiophene and its derivatives, see: Tourillon, G. in ref. 9a.
14. For a discussion of mixed thiophene/phenylene semiconductors, see, for example: Pelter, A.; Maud, J. M.; Jenkins, I.; Sadeka, C.; Coles, G. *Tetrahedron Lett.* 1989, 30, 3461.