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Synthesis of ladder polyaromatics as new molecular device candidates☆

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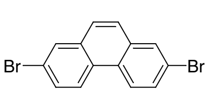
Abstract—In order to investigate one of the proposed molecular electronics switching mechanisms, we synthesized several molecules whose cores are unable to undergo conformational rotation. Preparation of these molecules, all of which are terminated with the thioacetyl moiety, takes advantage of an improved synthesis of 2,7-dibromophenanthrene, use of the reduced form of phenanthrenequinone as a protecting group, and various Sonogashira and halogen to Li to S conversions.

Ever since the establishment of single molecule conductance,[1,2] large on–off ratios, and negative differential resistance (NDR),[3] numerous molecules with these characteristics have been synthesized and tested. During this time a variety of hypotheses have been offered concerning the switching mechanism.[3–6] One hypothesis involves the conformational changes within the central core of the molecular structures.[4] Therefore we have prepared three molecular systems that have ladder-like cores that cannot undergo internal rotational motion. Once assembled and tested in the scanning tunneling microscopy (STM) testbed, they should provide the requisite data needed to clarify the conformational rotation hypothesis.



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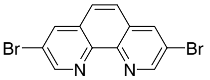

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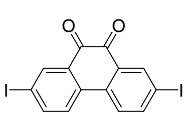

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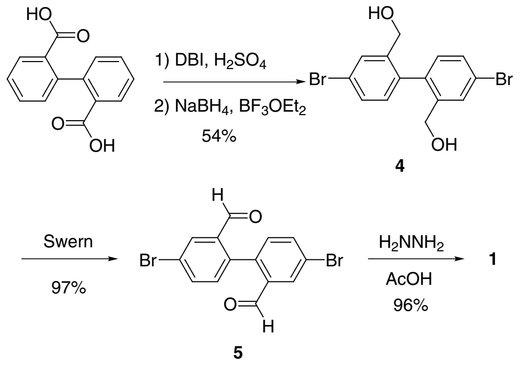
The potential molecular devices synthesized here originate from three different halogenated polyaromatics: 2,7-dibromophenanthrene (**1**), 3,8-dibromo-1,10-phenanthroline (**2**), and 2,7-diiodophenanthrenequinone (**3**). While **2** could be synthesized in one step using previously disclosed procedures,[7] and **3** could be easily prepared by iodinating the parent quinone with NIS in 85% yield, previous methods for synthesizing **1** were inefficient.[8–10] The new path to afford **1** (Scheme 1) begins with diphenic acid, which is brominated with dibromoisocyanuric acid (DBI) to afford a mixture of bromination isomers that are subsequently reduced to the diol. Swern oxidation of the isolated diol gave the dialdehyde followed by cyclization[11] to afford **1**. Hence **1** can now be synthesized in large quantities with an overall yield of 50% over three steps. The best previous methodology produced this simple material in only 16% overall using the more expensive dihydrophenanthrene and the now difficult to obtain solvent CCl_4.



Scheme 1. Synthesis of 2,7-dibromophenanthrene.

Keywords: Molecular electronics; Ladder polyaromatics; Phenanthrene.

☆ Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2004.02.028

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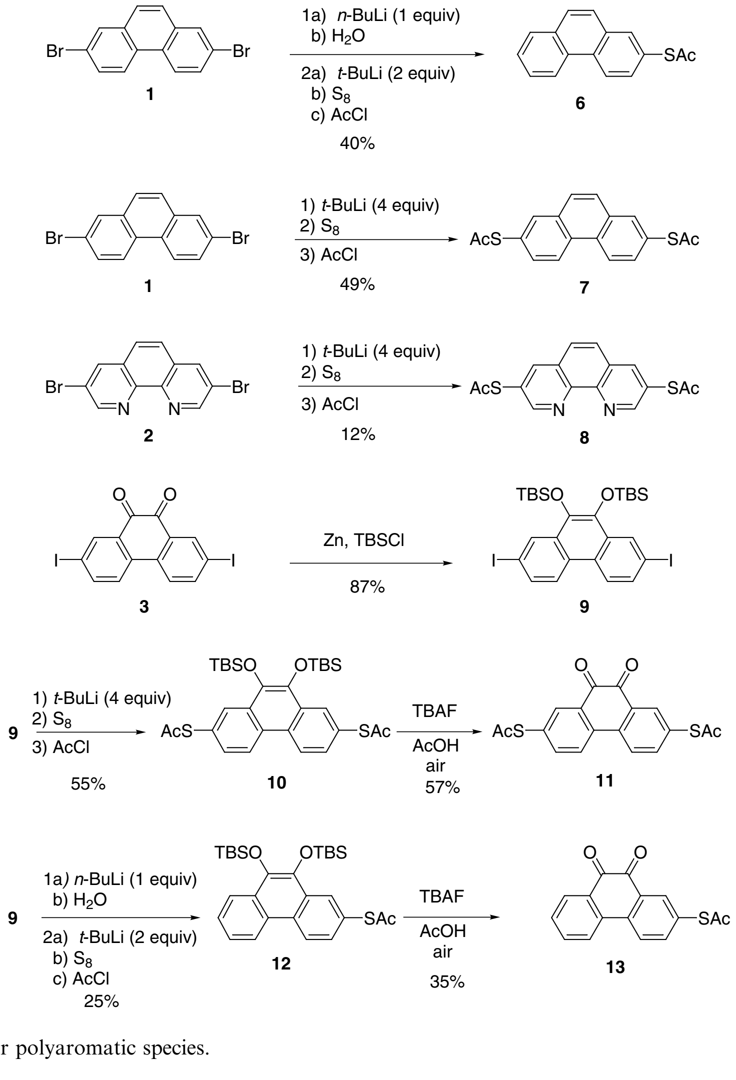
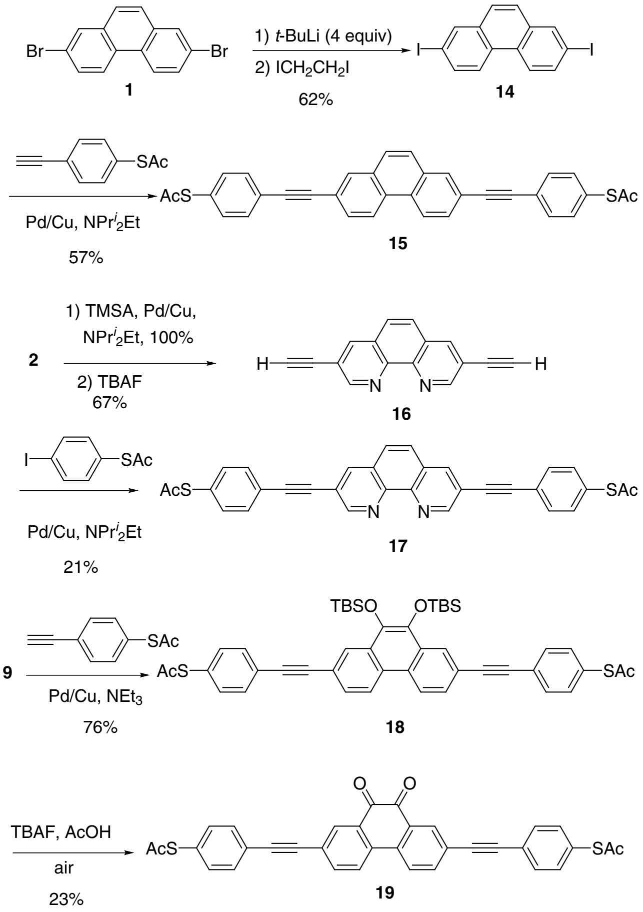
With the halogenated precursors in hand, all three compounds were converted to a form conducive to ordered assembly in a molecular testbed. Since a terminal thiol group is compatible with all commonly used molecular electronic testbeds,[12] the dihalogenated species were converted to five different compounds terminated in the thioacetyl moiety (Scheme 2). The acetyl-protected form of the thiol is used since it is far easier to handle (it is not prone to oxidative dimerization as the thiol is) and can be deprotected in situ.[13] As shown in Scheme 2, in the cases where the polyaromatic species are terminated with only a single thioacetyl group, the compound was synthesized by monolithiation of the dihalide using *n*-butyllithium followed by quenching with water to give a mixture primarily containing the monohalogenated compound. This mixture was then treated with *tert*-butyllithium, followed by sulfur and acetyl chloride to give the monothioacetate as in **6**. Formation of the thioacetates in this manner proved to be simpler than selective monohalogenation of the dihalides. In the cases of the dithioacetyl compounds such as **7** and **8**, bis-lithiation followed by treatment with sulfur and acetyl chloride afforded the desired products.

The synthesis of the thioacetyl-terminated phenanthrenequinones required the use of a carbonyl-protecting group. Though the acetal-protecting group was tried, their later chemoselective removal was not possible. However, we have found that the quinone could be transformed to a bis-TBS ether of the dihydroxyquinone and then reoxidized in air.[14] Hence, **3** was reduced with zinc in the presence of TBSCl to afford **9**.[15] Thioacetyl attachment could then be effected as done on **1** and **2**. Reoxidation of the dihydroxyquinone back to the quinone was carried out with TBAF for silyl removal and the addition of air. AcOH is added to buffer the TBAF or else removal of the acetyl moiety ensues.[16] Addition of DDQ in a later test reaction increased the yield slightly although it had not been routinely used.

Though the shorter molecules, **6**, **7**, **8**, **11**, and **13**, are compatible with the STM testbed, most other testbeds[12] for molecular devices require a longer distance between the termini so as to retard metal leakage across the self-assembled monolayer. Hence, phenylene ethynylene spacers were added to **1**–**3** (Scheme 3). In all cases the basic carbon framework was assembled through single or multiple Sonogashira couplings. Compound **1** was



Scheme 2. Synthesis of the planar polyaromatic species.



Scheme 3. Synthesis of elongated polyaromatics.

found to be too unreactive to couple with the 4-ethynyl(thioacetyl)benzene[16] in acceptable yields. Thus **1** was converted to the diiodo species, **14**, before undergoing coupling. Compound **2** would not couple with 4-ethynyl(thioacetyl)benzene under moderate conditions. However, coupling first to the more reactive trimethylsilylacetylene, deprotecting and then coupling to the aryl thioacetyl group was effective.

The final compound of interest was the phenanthrenequinone compound **19**. Extensive work with this compound (both by the authors and co-workers[17]) has shown that although **3** can undergo Sonogashira couplings, the yields are irreproducible, often giving no product. A more reproducible route to **19** involves using **9**. When the quinone functionality was protected, coupling was reliably achieved. Deprotection and oxidation afforded the desired compound **19**.

In summary, we provide detailed syntheses of several potential molecular devices. All of the target molecules contain rigid polyaromatic cores that are being used to discern the mechanism for switching in molecular devices. In progression toward these devices a new method for synthesizing 2,7-dibromophenanthrene was developed and various Sonogashira, and halogen to Li to S conversion sequences were utilized.

Supporting information available: The experimental details as well as spectroscopic data are available. This material is available free of charge via the Internet.

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References and notes

1. Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L., II; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705.
2. Reed, M. A.; Zhou, C.; Muller, C. J.; Burgin, T. P.; Tour, J. M. *Science* **1997**, *278*, 252.
3. Chen, J.; Reed, M. A.; Rawlett, A. M.; Tour, J. M. *Science* **1999**, *286*, 1550.
4. Donhauser, Z. J.; Mantooth, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. D.; Stapleton, J. J.; Price, D. W.; Rawlett, A. M.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **2001**, *292*, 2303.
5. Seminario, J. M.; Zacarias, A. G.; Tour, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 3015.
6. Ramachandran, G. K.; Hopson, T. J.; Rawlett, A. M.; Nagahara, L. A.; Primak, A.; Lindsay, S. M. *Science* **2003**, *300*, 1413.
7. Saitoh, Y.; Koizumi, T.; Osakada, K.; Tamamoro, T. *Can. J. Chem.* **1997**, *75*, 1336.
8. Miller, J. C.; Meek, J. S.; Strickler, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 8175.
9. Bochenkov, V. N. *J. Org. Chem. USSR (Engl. Transl.)* **1977**, *12*, 2355.
10. Brown, W. G.; Bluestein, B. A. *J. Am. Chem. Soc.* **1943**, *65*, 1235.
11. Bacon, R. G. R.; Lindsay, W. S. *J. Chem. Soc.* **1958**, 1375.
12. Tour, J. M. *Molecular Electronic: Commercial Insights, Chemistry, Devices, Architecture and Programming*; World Scientific: New Jersey, 2003.
13. Tour, J. M.; Jones, L., II; Pearson, D. L.; Lamba, J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh, A. N.; Atre, S. V. *J. Am. Chem. Soc.* **1995**, *117*, 9529.
14. Yamato, T.; Fujimoto, M.; Miyazawa, A.; Motsuo, K. *J. Chem. Soc., Perkin Trans. 1* **1997**, *8*, 1201.
15. Fox, J. M.; Goldberg, N. R.; Katz, T. J. *J. Org. Chem.* **1998**, *63*, 7456.
16. Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376.
17. Zhao, Y.; Shirai, Y.; Chiu, Y.-H.; Yao, Y.; Yang, H.; Tour, J. M. Unpublished data.