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Rational Synthesis of Graphene Nanoribbons

Student: Sam Beavin

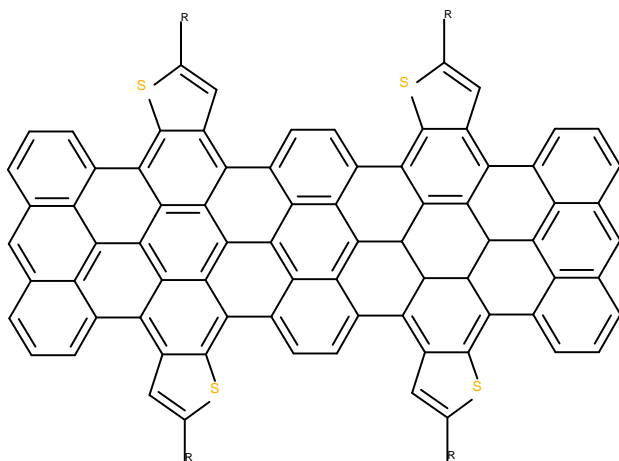
Faculty Mentor: John Anthony

The study and isolation of graphene is a relatively new development in the field of materials science. Graphene is a single layer of carbon atoms bonded together in a two-dimensional, honeycomb-like crystal lattice, essentially a single layer of the more familiar three-dimensional structure of graphite. (Theoretically, graphene can be thought of as an indefinitely large aromatic molecule, though only relatively small samples have been isolated.) In an academic sense, graphene, referring to a single layer of bonded carbon atoms, has been known to exist as long as the structure of graphite itself has been known; however, for many years it was considered unfeasible if not thermodynamically impossible to isolate such a two-dimensional crystal lattice from a three-dimensional material. Only in 2004 did a team from the University of Manchester isolate a single-plane graphene crystal, opening up new possibilities for electronic applications and the study of low-dimensional physics (Geim, 2007).

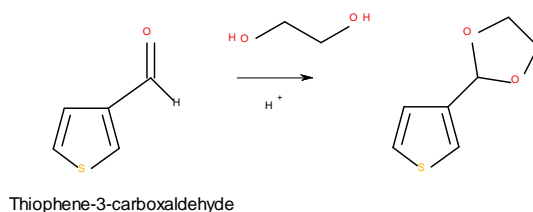
The electronic properties in particular have made graphene the object of significant research interest since the crystals were first described several years ago. Potential applications include as components in gas detection systems, transistors, integrated circuits, and solar cells. Many of these potential applications stem from the development of graphene nanoribbons, thin strips of graphene that are structurally similar to unrolled carbon nanotubes. Research with these molecules has shown semiconductive properties that suggest they could potentially replace silicon semiconductors as well as the copper used in integrated circuits (Geim, 2007).

Graphene was first isolated using what is known as the Scotch tape or drawing method. Using an adhesive, graphene layers were peeled off from a graphite source, the adhesive was dissolved in acetone, and the graphite flakes then deposited on an SiO₂ wafer, where single-layer graphene could be detected under an optic microscope. This method (without the liquid step) is still used to produce the majority of graphene used for research purposes today. Other efforts have been made to isolate graphene by epitaxial growth on SiC and metal substrates, exfoliation methods, and several others, but have met with only limited success (Choi, 2010).

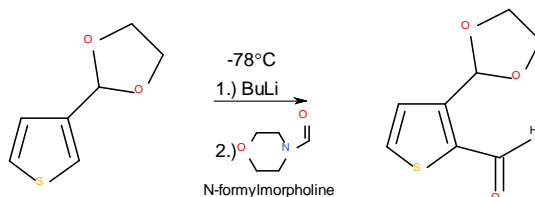
Previous efforts to synthesize graphene have focused on mechanical means of cleaving the existing 'graphene layers' from a much larger graphite source. Graphene nanoribbons, though, are simply large organic molecules that may be accessible by traditional means of organic synthesis, building the graphene from smaller component molecules. Ideally a synthesis would yield a target molecule that is a large, conjugated structure containing both thiophene and aromatic rings:



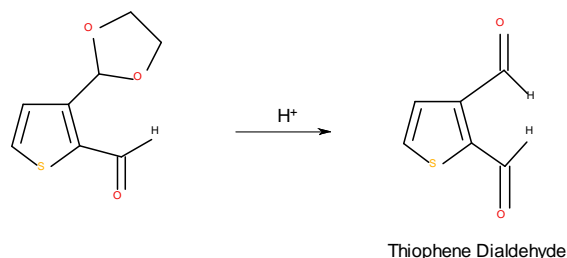
The first steps of such a synthesis have been demonstrated as successful reactions with good yields. The synthesis begins with a commercially available reagent, thiophene-3-carboxaldehyde. The aldehyde substituent is first protected by taking up the starting material in benzene and heating under a Dean-Stark trap in the presence of excess ethylene glycol and an acidic catalyst such as p-TsOH. By allowing the reaction to heat overnight, yields in excess of 90% can be consistently achieved:



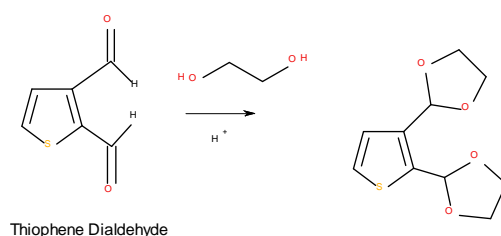
Once the existing aldehyde group has been protected, addition chemistry can be carried out using a strong base such as butyl lithium and a formylating agent. The protected starting material is taken up in THF in a dry flask under a nitrogen atmosphere, and the reagents are chilled to -78°C in an ice bath of isopropyl-alcohol and dry ice. First, an excess of butyl lithium is dripped into the reaction flask, followed approximately 15 minutes later by a formylating agent such as N-formylmorpholine:



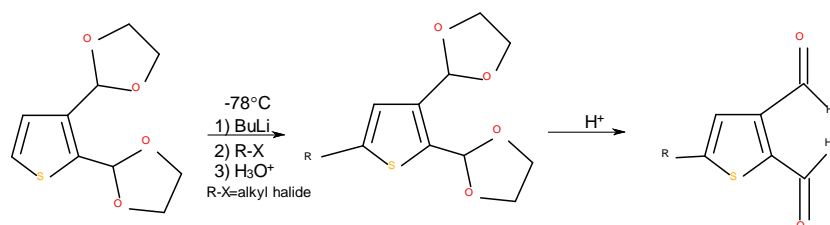
Following a workup, the product of the preceding reaction can be added without purification to an aqueous solution of 80% acetic acid and stirred at room temperature for several days to deprotect the 3-position aldehyde group. Following workup, purification, and recrystallization, yields of 55% thiophene dialdehyde can be achieved for the preceding two steps:



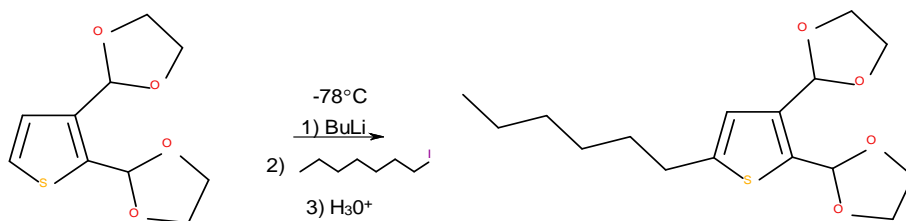
The reaction continues with a series of similar steps in order to add an alkyl group in the 4 position on the thiophene ring. Once again, the thiophene dialdehyde is taken up in benzene and heated in the presence of excess ethylene glycol and an acidic catalyst to protect the two aldehyde groups. Yields of 85% have been achieved for this protection:



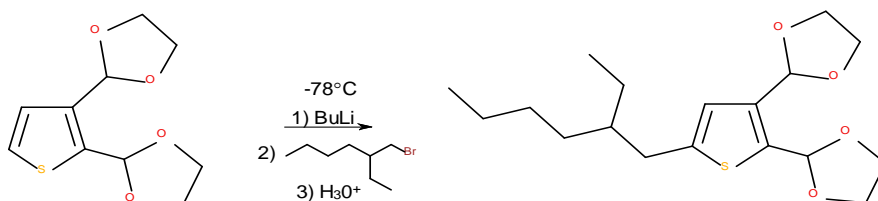
Also similar to the previous reaction steps, the protected thiophene compound is once again taken up in THF in a dry flask under nitrogen atmosphere, and the reaction solution is cooled to -78°C in an ice bath of isopropyl alcohol and dry ice. Butyl lithium is slowly dripped in, followed approximately 15 minutes later by an alkyl halide such hexyl iodide. After isolating the product, the aldehyde groups can once again be deprotected by introducing an aqueous solution of 80% acetic acid:



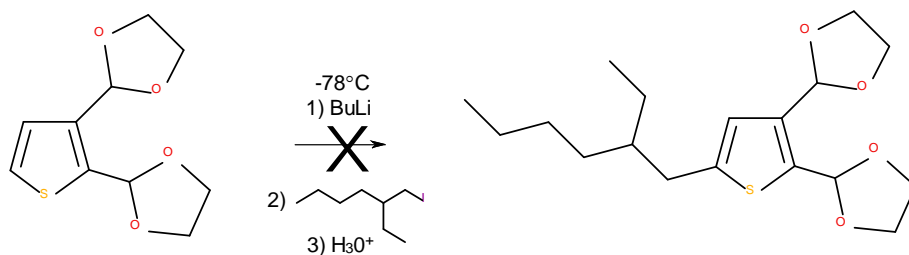
Initially, the alkyl halide used was hexyl iodide, which gave a yield of 42% for the previous two steps. However, in subsequent steps, the hexyl thiophene dialdehyde proved to be insufficiently soluble for the reaction to be carried out in the necessary solvents. Therefore, the synthesis was repeated with 2-ethylhexyl bromide, in the hope that an additional side ethyl chain would increase the molecule's solubility in organic solvents. With 2-ethylhexyl bromide, the reaction proceeded to some degree but gave very poor yields. Attempts to improve the yield by using 2-ethylhexyl iodide, which has a better leaving group, proved unsuccessful:



Yield: 42%



Yield: 9%



Ideally, the second reaction sequence will be optimized to yield a more soluble tri-substituted thiophene product in better yield. The reaction of these thiophenes with 1,4-cyclohexanedione should yield a quinone consisting of 5 rings, which, with two further reaction steps, will yield the target compound, a hetero-graphene nanoribbon structure.

References

Choi, Wonbong, Lahiri, Indranil, Seelaboyina, Raghunandan, & Kang, Yong Soo. Synthesis of Graphene and Its Applications: A Review. *Critical Reviews in Solid State and Materials Sciences* 35:1, 52-71 (2010).

Geim, A.K., & Novoselov, K.S. The Rise of Graphene. *Nature Materials* 6, 183 - 191 (2007)