Synthesis, Structure and Properties of [7]Heterohelicenes Possessing Phenolic Hydroxy Functions

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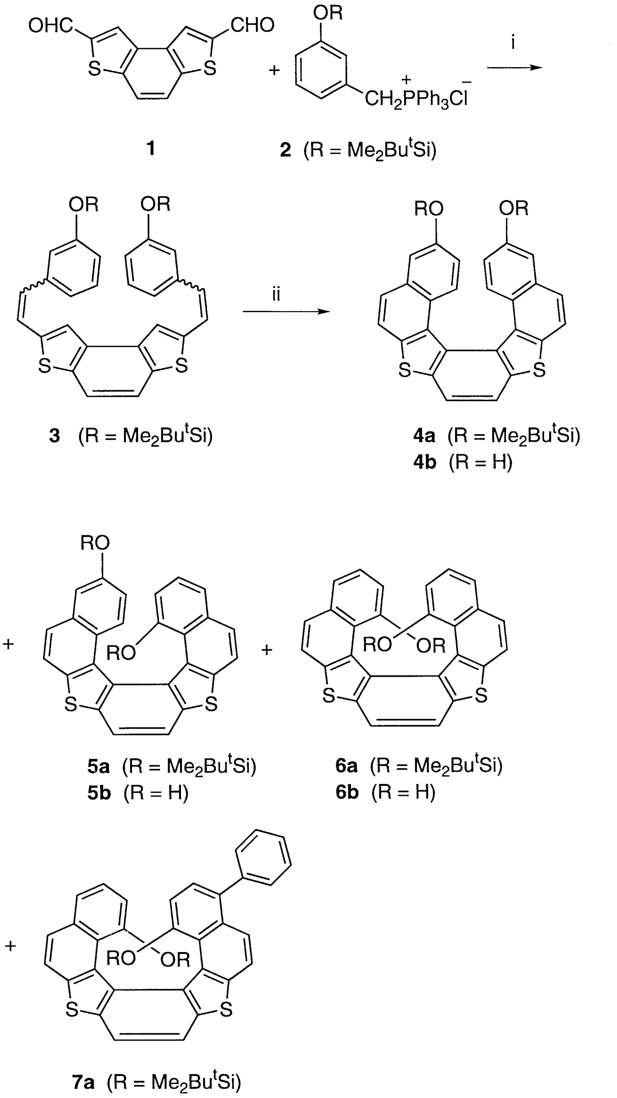
Photocyclization of 2,7-bis[3-(*t*-butyldimethylsilyloxy)-phenylvinylene]benzo[1,2-b:4,3-b']dithiophene affords three regioisomers of the bis(silyloxy)[7]thiaheterohelicenes together with the unexpected 4-phenyl-substituted [7]thiaheterohelicene. Cleavage of the silyl ethers gave the helical quinone, which includes ethanol as guest molecules to form a 1:1 inclusion complex.

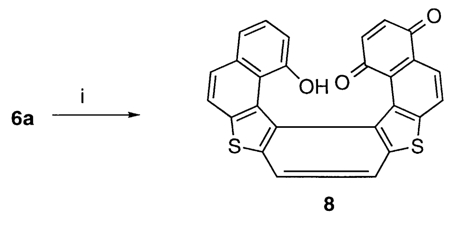
Atropisomeric 1,1'-bi-2-naphthol has been used in a wide range of asymmetric synthesis[1] as well as in optical resolution,[2,3] where the phenol functions are essential for high stereo-differentiating reactions. In contrast, the asymmetric synthesis based on helicity is relatively unexplored,[4-8] probably due to the difficulty in the preparation of optically active functionalized helical molecules with high stability. Among helices such as helicenes,[9-11] helicates[12,13] and helixanes,[14] helicene skeletons have a rigid framework and possess high optical stability. The synthesis and properties of functionalized carbohelicenes such as helical bis(quinones) have been extensively studied by Katz and co-workers, who utilize a Diels-Alder reaction for the construction of the quinones.[15] However, the chemistry of helical phenol derivatives has not been fully investigated. We report here the photocyclization of 2,7-bis[3-(*t*-butyldimethylsilyloxy)phenylvinylene]benzo[1,2-b:4,3-b']dithiophene (**3**), and the structure and properties of the resulting [7]thiaheterohelicenes containing phenolic hydroxy functions.

The olefin **3** was obtained in 80% yield from 2,7-diformylbenzodithiophene (**1**) and phosphonium salt (**2**) derived from 3-hydroxybenzaldehyde (Scheme 1). Irradiation of **3** with a high-pressure mercury lamp under Katz's conditions[16] gave a mixture of three possible regioisomers, the *para,para*-coupled product (**4a**), the *ortho,para*-coupled product (**5a**) and the *ortho,ortho*-coupled product (**6a**) in 63% yield with a ratio of 1:3:2. The structures of **4a**, **5a** and **6a** were determined by ^{1}H-NMR and MS,[17] and in the case of **6a** by X-ray crystallographic analysis (Figure 1). The stereoview of **6a** clearly indicates that the two *t*-butyldimethylsilyl groups located on opposite sides of the helicene framework are directed *anti* in order to minimize the steric interaction and the whole molecule conforms to the idealized C_2 symmetry. We were surprised to isolate a minor, additional product (3% yield) in this photocyclization reaction because the crystal structure analysis shows that the compound **7a**[17] possesses both helical and biphenyl frameworks (Figure 2). The dihedral angle between the terminal benzene units of the helicene part is 15.9°, and the phenyl ring of the biphenyl part is tilted relative to the terminal benzene by 49.7°, which is very close to that of 2,2'-biphenylcarboxamide (49.6°).[18]

Treatment of **4a** with $(n\text{-Bu})_4$NF at 0 °C in THF gave 3,14-(dihydroxy)dinaphtho[1,2-d:1',2'-d']benzo[1,2-b:4,3-b']dithiophene (**4b**) as a yellow solid in 90% yield. In contrast, the reaction of **6a** with $(n\text{-Bu})_4$NF produced a dark-red solution. Stirring the solution overnight under aerobic conditions afforded a black



Scheme 1. *Reagents and conditions*: i, *t*-BuOK, THF; ii, hν, I_2, benzene.



Scheme 2. *Reagent and conditions*: i, $(n\text{-Bu})_4$NF, THF.

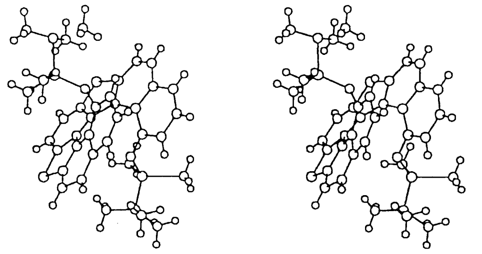


Figure 1. Stereoview of **6a**.

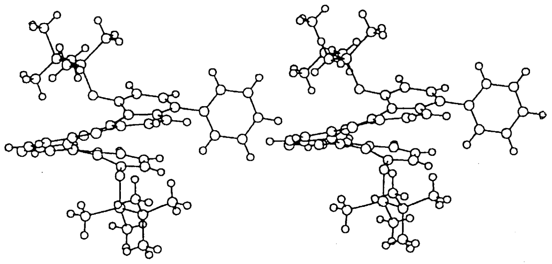


Figure 2. Stereoview of **7a**.

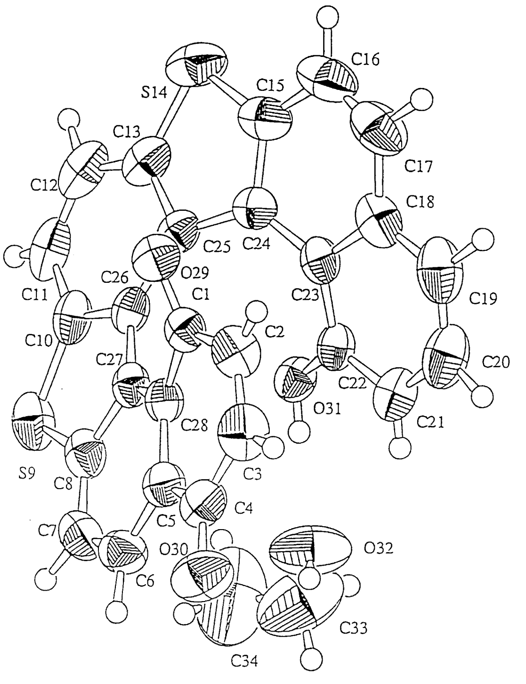


Figure 3. Molecular structure of [**8**][EtOH].

solid after chromatography on silica gel. X-ray analysis indicates that the molecule possesses a helical quinone structure **8** and contains both ethanol and a disordered guest in its cavity, although it was not possible to determine unambiguously the identity of the second guest[17] (Figure 3). The oxygen atom of the guest molecule is hydrogen-bonded to the hydroxy group of one enantiomer of **8** with O$\cdots$H = 1.86 Å and O$\cdots$H-O = 170 °, while the hydrogen atom interacts with the C=O group of its antipode through a hydrogen bond with H$\cdots$O = 1.86 Å and O-H$\cdots$O = 164°. The dihedral angle between the quinone plane and the phenol plane of **8** is 26.2°. This is the first example of isolation of the supramolecular helical inclusion complex where the guest molecules are embedded between (*M*)- and (*P*)-quinones.

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