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Tetrahedron Letters 48 (2007) 5821–5824
Tetrahedron Letters

Synthesis of a dipolar nanocar

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Received 23 April 2007; revised 6 June 2007; accepted 15 June 2007
Available online 21 June 2007

Abstract—The synthesis of a nanocar with a built-in strong net dipole is disclosed. The synthesis was executed to explore a more effective handle on electric-field-induced rolling of nanocars.

The emerging field of molecular machinery has afforded various intriguing designs including motors, switches, scissors, gyroscopes, elevators, walkers, and transporters.[1] We have sought to observe and manipulate single-molecule-sized machines on surfaces with the initial demonstration of a nanocar and its fullerene-wheel-based rolling motion.[2] Now we direct our research efforts toward designing and synthesizing new nanocars that are more sensitive to different types of external stimuli.[3] The original nanocar showed thermal- and electric-field-induced specific motion.[2] Here, the dipolar nanocar **1** is designed to enhance the electric-field-induced motion by incorporating a strong net dipole along its chassis structure. The carborane wheels are a complementary design element to the original fullerene-wheel system; tryptycene wheels have been used to facilitate single molecular rolling.[1i] The carborane wheels greatly facilitate the synthesis since they need not be incorporated at the final step; unlike fullerenes, carboranes do not inhibit transition metal-catalyzed cross-coupling reactions (see Fig. 1).[3]

A molecule with an incorporated dipolar unit has been shown to exhibit intramolecular rotary motion with AC fields.[4] Changes in the dipolar orientation from external stimuli can be detected in solution because of the conformational changes accompanying the rotation.[5,6] Surface-bound molecular rotors with an inherent dipolar moment have also been observed and tested using scanning tunneling microscopy (STM).[7,8] Our goal is similar, namely, to incorporate a strong dipolar unit to observe an enhancement in the electric-field-induced motion of the nanocar.

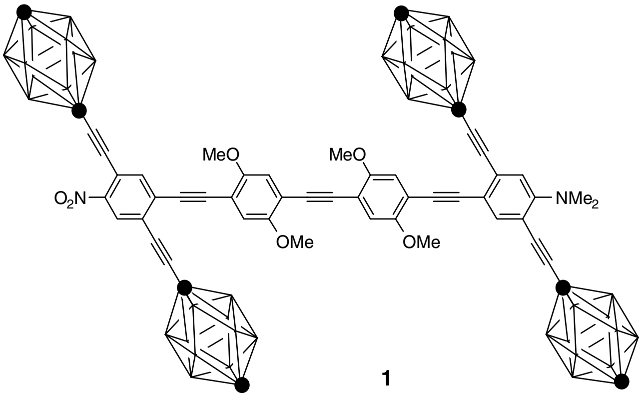

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Figure 1. Dipolar nanocar **1** with carborane wheels. The *p*-carboranes have BH at every intersection except at the points denoted by (●) which represents C and CH positions, *ipso* and *para*, respectively.

In the new design here, we concentrated our efforts on incorporating a dimethylamino moiety as the potent electron-donating end and a nitro group as the efficient electron-withdrawing end in the nanocar. AM-1 calculations suggested that the oligo(phenylene ethynylene) (OPE) tetramer, convenient for spacing the front and rear carborane-wheel-bearing axles, would permit a significant dipole moment with the chosen donor and acceptor moieties (Table 1). Also the differences in length versus width of the molecule is enough to determine the orientation of the molecules using STM.[2]

The methoxy groups in nanocar **1** provide two features. First, they act as polarity inducing groups to facilitate

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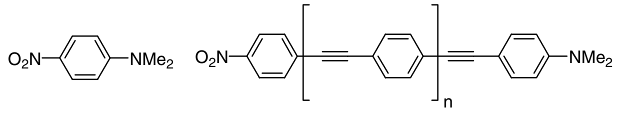
doi:10.1016/j.tetlet.2007.06.080

Table 1. PC Spartan AM-1 calculation of dipole moments of the planarized molecules



A **B-D:** n = 0, 1, 2, 3

Compound	Dipole moment (μ)
A	7.0
B	7.8
C	8.0
D	8.1

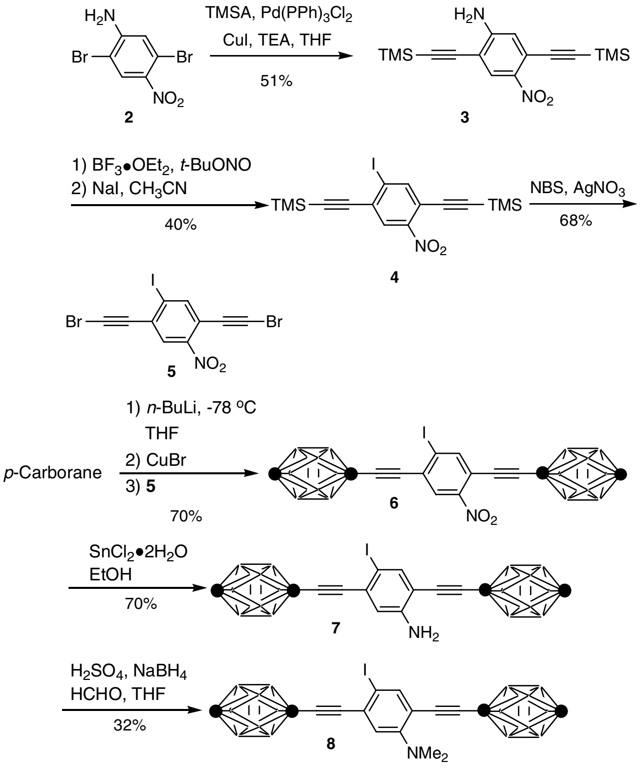
purifications during synthesis. Second, they would slow OPE-backbone molecular rotation via steric interactions with the surface. Electronic communication through an OPE would be reduced if the *p*-orbitals of the phenyl rings were orthogonal to each other. The methoxy groups will retard such rotation on the surface and enhance its dipole moment for electric-field induced motion, much like the planar molecules **B**–**D** in Table 1.

The dipolar components of the nanocar were prepared (Scheme 1) by first coupling trimethylsilylacetylene (TMSA) with **2**[9] by means of Sonogashira coupling to afford **3**. Diazotization of the amine followed by replacement with the iodide afforded **4**. The TMS-protected alkynes were converted to the corresponding alkynyl bromides in **5** with NBS and $AgNO_3$ in acetone.[10]

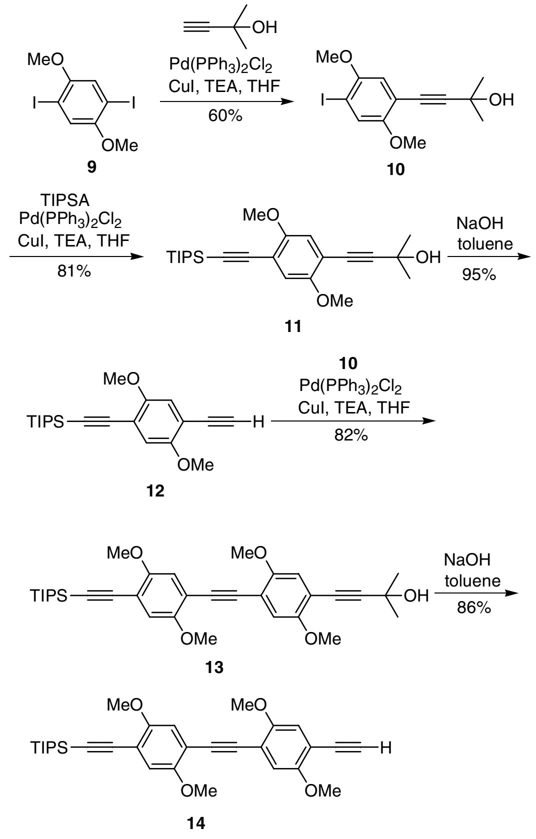
The *p*-carborane wheels were attached to **5** by first lithiating the *p*-carborane with *n*-BuLi followed by transmetalation with CuBr,[11] then adding **5** to afford **6** as the electron-deficient portion of the dipolar nanocar. The nitro group was then reduced[12] to afford **7**, and dimethylated[13] to afford **8** as the electron-rich portion of the dipolar nanocar.

The chassis **14** was prepared (Scheme 2) through multiple Sonogashira couplings and selective deprotections starting with mono-iodo coupling of **9**[14] with 2-methyl-3-butyn-2-ol[15] to afford **10**. The remaining iodide was coupled with triisopropylsilyacetylene (TIPSA) to afford **11**. Selective removal[16] of the dimethyl carboanol (as acetone) with NaOH in toluene at 100 °C for 5 h gave the corresponding terminal alkyne **12**. This was then coupled with the previously made iodide **10** to give the dimeric OPE species **13**. Again the selective removal of the carbanol afforded the terminal alkyne dimer **14**.

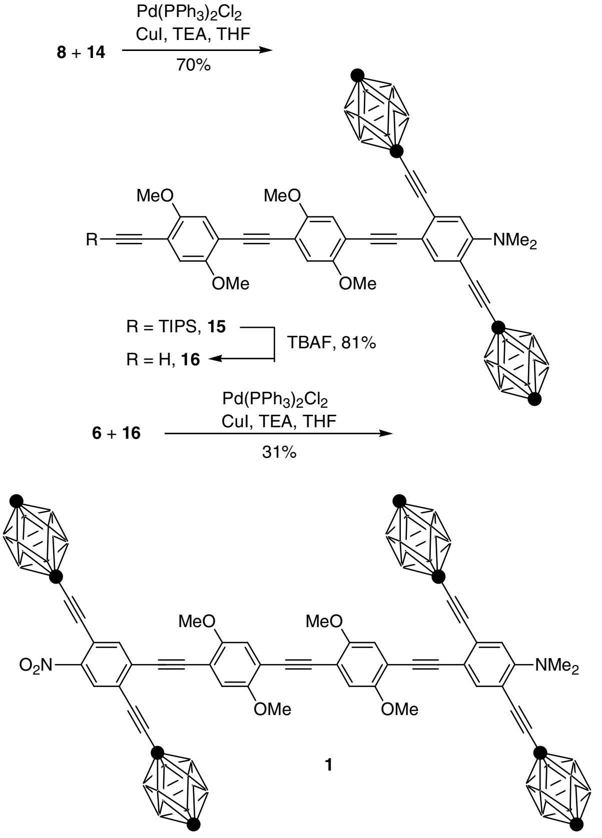
The assembly of the dipolar nanocar was completed (Scheme 3) by first coupling the electron-rich **8** and the dimer chassis **14** again using Sonogashira conditions to afford **15**. Removal of the TIPS group with tetrabutylammonium fluoride (TBAF) afforded the corresponding terminal alkyne **16** followed by coupling with the electron-deficient axle **6** as the final step to generate the dipolar nanocar **1**. Note that the stepwise Sonogashira coupling proceeded with the electron-rich portion first because a fluoride source is known to cause the forma-



Scheme 1. Syntheses of the carbonane axle **8**.



Scheme 2. Synthesis of the chassis **14**.



Scheme 3. Synthesis of the dipolar nanocar **1**.

tion of isatogen byproducts when an aromatic nitro group is *ortho* to an alkyne.[17]

In summary, we have designed and successfully synthesized a new dipolar nanocar **1**. The dipolar nanocar **1** bears a donor–acceptor functionality that should allow for the enhanced electric-field-induced rolling of the molecule by an oriented electric field. The STM-based electron-field-induce rolling experiment and the synthesis of dipolar nanocars with other wheel systems such as C_{60} are currently underway.

Acknowledgments

We thank the Welch Foundation, Zyvex Corporation, American Honda Motor Co., and the NSF Penn State MRSEC for financial support. The NSF, CHEM 0075728, provided partial funding for the 400 MHz NMR. We thank Drs. I. Chester of FAR Research, Inc. and R. Awartari of Petra Research, Inc. for providing trimethylsilyacetylene.

Supplementary data

The supplementary data include experimental details as well as spectroscopic data (melting point, FTIR, ^1H NMR, ^{13}C NMR, mass spectrometry) for compounds **1**, **3–8**, **10–16**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.06.080.

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