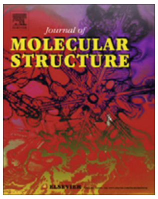
Journal of Molecular Structure 1015 (2012) 41–45

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc



Synthesis, characterization and DFT study of 1-bromo-4-(3,7-dimethyloctyl)benzene

Siddappa A. Patil [a,b], Chananate Uthaisar [a,c], Veronica Barone [a,c,*], Bradley D. Fahlman [a,b,*]

[a] Science of Advanced Materials Program, Central Michigan University, Mount Pleasant, MI 48859, United States
[b] Department of Chemistry, Central Michigan University, Mount Pleasant, MI 48859, United States
[c] Department of Physics, Central Michigan University, Mount Pleasant, MI 48859, United States

ARTICLE INFO

Article history:
Received 30 November 2011
Received in revised form 10 February 2012
Accepted 10 February 2012
Available online 20 February 2012

Keywords:
Garphene nanoribbons
1-Bromo-4-(3,7-dimethyloctyl)benzene
1-Trimethylsilyl-4-(3,7-dimethyloctyl)benzene
NMR
DFT
GIAO

ABSTRACT

In this paper, we present the synthesis, characterization, and *ab initio* calculations of 1-bromo-4-(3,7-dimethyloctyl)benzene. This compound is a precursor for the bottom-up synthesis of planar one-dimensional graphene nanoribbons with controlled edge morphology and narrow widths. We discuss the synthetic procedures and characterization using ^{1}H NMR, ^{13}C NMR, IR spectroscopy, and elemental analysis. These results are complemented by density functional theory (DFT) calculations of the optimized structure, as well as calculated IR and NMR spectra for this compound.

1. Introduction

A discrete layer of graphite, known as graphene, has attracted a lot of interest in the scientific community due to its peculiar physical properties [1]. These properties extend the possibility for a broad range of applications, provided that one is able to control its electronic behavior. One way of achieving this control is by forcing electronic confinement as we reduce the dimensionality of the system to form graphene nanoribbons (GNRs) [2].

Several methods for synthesizing GNRs have been reported [3–8]. These methods, however, rely on top-down synthetic approaches that operate under harsh environmental conditions, resulting in defective GNRs with irregular edge morphologies. Synthetic organic methodology provides the bottom-up approach required for the controlled synthesis of narrow GNRs [9,10]. These synthetic routes are extremely involved, yet efficient in controlling the size and edge morphology of GNRs. As reported by Yang et al. [9] one such bottom-up synthesis requires 1-bromo-4-(3,7-dimethyloctyl)benzene, as a starting material for 1,4-diiodo-2,3,5,6-tetraphenylbenzene. However, the synthetic route for this compound has not yet appeared in the literature. Accordingly, in this paper, we detail the optimized synthesis, characterization (^{1}H NMR, ^{13}C NMR, IR, elemental analysis), and *ab initio* calculations of 1-bromo-4-(3,7-dimethyloctyl)benzene. As this compound is colorless oil, X-ray diffraction is not possible; hence, density functional theory (DFT) calculations were carried out to elucidate its relevant structural parameters.

2. Experimental

All the reagents used were of AR grade and the solvents were dried, distilled and purified by the standard methods. Manipulations of air- and moisture-sensitive compounds were performed under nitrogen or argon using standard Schlenk techniques. 1 M solution of 3,7-dimethyloctanyl-1-magnesiumbromide, 1-bromo-4-trimethylsilylbenzene, [PdCl$_2$(dppf)], sodium acetate, bromine, sodium sulfite and MgSO$_4$ were procured commercially from Sigma–Aldrich and were used without further purification. Nuclear magnetic resonance (NMR) spectra were obtained using a 1.0–2.5% solution in deuterochloroform (CDCl$_3$). ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer. Proton and carbon chemical shifts are reported in parts-per-million (δ) with respect to tetramethylsilane (TMS) as internal reference (δ = 0.0 ppm). IR spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR Spectrometer employing acetone as the solvent. Mass spectra were obtained on a GC–MS instrument (Waters Micromass GCT Premier Mass Spectrometer) operating in TOF-MI^{+} mode. CHN

---

* Corresponding authors. Address: Science of Advanced Materials Program, Central Michigan University, Mount Pleasant, Michigan 48859, United States.

E-mail addresses: v.barone@cmich.edu (V. Barone), fahlm1b@cmich.edu (B.D. Fahlman).

doi:10.1016/j.molstruc.2012.02.025

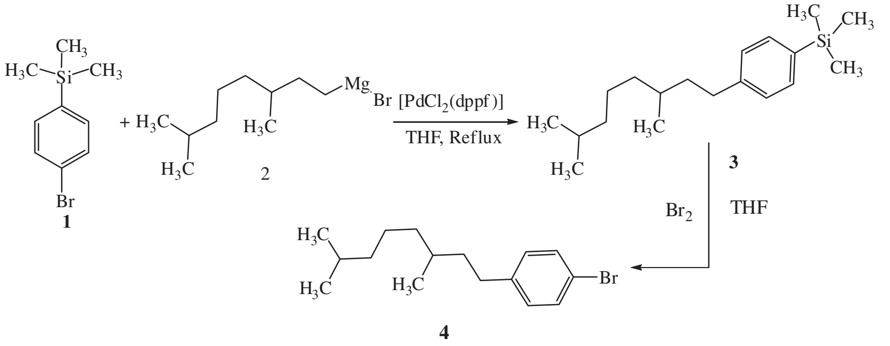


Fig. 1. Synthesis of 1-bromo-4-(3,7-dimethyloctyl)benzene.

analysis was done with an Exeter Analytical CE-440 Elemental Analyzer and was within ±0.4% of the theoretical values.

2.1. Synthesis (see Fig. 1)

The synthetic pathway for the 1-bromo-4-(3,7-dimethyloctyl)-benzene GNR precursor, **4**, described in this work is outlined in Fig. 1. The synthesis of **4** starts with commercially-available 4-bromo-trimethylsilyl benzene. After a palladium catalyzed Kumada cross-coupling reaction with 3,7-dimethyloctyl bromide, the compound was transformed into 1-trimethylsilyl-4-(3,7-dimethyloctyl) benzene, **3**. The TMS group was further converted into a bromo moiety through bromination as detailed below.

2.1.1. Synthesis of 1-trimethylsilyl-4-(3,7-dimethyloctyl)benzene (3)

In a 300-mL round bottom flask, 22 mL of a 1 M solution of 3,7-dimethyloctanyl-1-magnesiumbromide was added dropwise to a solution of 2.5 g (10.9 mmol) 1-bromo-4-trimethylsilylbenzene dissolved in 150 mL of dry THF and 250 mg [PdCl$_2$(dppf)] catalyst. The resulting mixture was stirred under reflux in an inert atmosphere overnight. The reaction was quenched with methanol and the solvent removed under reduced pressure. Purification using column chromatography on silica gel with petroleum ether as the eluent afforded 2.8 g 1-trimethylsilyl-4-(3,7-dimethyloctyl)benzene as a colorless oil. Yield: 90%. ^{1}H NMR (CDCl$_3$) δ (ppm) 7.46 (d, J = 8.4 Hz, 2H, ArH), 7.20 (d, J = 7.5 Hz, 2H, ArH), 2.71–2.52 (m, 2H, -CH$_2$), 1.70–1.04 (m, 10H, -CH$_2$, CH, CH$_2$, CH$_2$, CH$_2$, CH), 0.95 (d, J = 6.0 Hz, 3H, CH$_3$), 0.89 (d, J = 6.0 Hz, 6H, CH$_3$), 0.28 (s, 9H, CH$_3$). ^{13}C NMR (CDCl$_3$) δ (ppm) 143.9, 137.0, 133.3, 127.8, 39.3, 38.8, 37.1, 33.5, 32.6, 27.9, 24.6, 22.7, 22.6, 19.6, −1.0. Mass data (TOF MS EI$^+$): calculated for C$_{19}$H$_{34}$Si [M$^+$] 290.24, found: 290.24. Compound was analyzed for C$_{19}$H$_{34}$Si (calculated C 78.54, H 11.79, Si 9.67%; found C 78.42, H 11.67, Si 9.65%). IR absorptions (KBr, cm^{-1}): 2953 (s), 2925 (m), 2868 (w), 1716 (m), 1601 (w), 1462 (m), 1396 (w), 1364 (m), 1247 (s), 1218 (m), 1108 (s), 850 (s), 836 (s), 804 (m), 754 (m), 720 (w), 691 (w).

2.1.2. Synthesis of 1-bromo-4-(3,7-dimethyloctyl)benzene (4)

To obtain 1-bromo-4-(3,7-dimethyloctyl)benzene, 1-trimethylsilyl-4-(3,7-dimethyloctyl) benzene (2.9 g, 10.0 mmol) and sodium acetate (2.72 g, 20.0 mmol) were dissolved in THF (60 mL) at 0 °C. Bromine (1.59 g, 20.0 mmol) was then added dropwise via a dropping funnel, and the mixture was stirred for 20 min. The reaction was quenched with saturated sodium sulfite aqueous solution (40 mL). The organic layer was then extracted with CH$_2$Cl$_2$ (65 mL × 3) and dried over MgSO$_4$. After being filtered, the solvent was removed *in vacuo* and the crude product was purified by column chromatography (eluent petroleum ether), affording 2.5 g of 1-bromo-4-(3,7-dimethyloctyl)benzene as transparent oil in a yield of 85%. ^{1}H NMR (CDCl$_3$) δ (ppm) 7.37 (d, J = 8.7 Hz, 2H, ArH), 7.04 (d, J = 8.1 Hz, 2H, ArH), 2.64–2.45 (m, 2H, -CH$_2$), 1.62–1.04 (m, 10H, -CH$_2$, CH, CH$_2$, CH$_2$, CH$_2$, CH), 0.91 (d, J = 6.3 Hz, 3H, CH$_3$), 0.86 (d, J = 6.3 Hz, 6H, CH$_3$). ^{13}C NMR (CDCl$_3$) δ (ppm) 142.1, 131.2, 130.1, 119.1, 39.3, 39.2, 38.7, 37.0, 32.8, 32.3, 27.9, 24.6, 22.6, 19.5. Mass data (TOF MS EI$^+$): calculated for C$_{16}$H$_{25}$Br [M$^+$] 296.11, found: 296.01. Compound was analyzed for C$_{16}$H$_{25}$Br (calculated C 64.64, H 8.48, Br 26.88%; found C 64.59, H 8.45, Br 26.72%). IR absorptions (KBr, cm^{-1}): 2953 (s), 2867 (m), 1716 (m), 1488 (s), 1463 (m), 1403 (m), 1377 (w), 1364 (m), 1259 (w), 1218 (m), 1072 (s), 1011 (s), 801 (s).

3. Computational details

DFT calculations of 1-bromo-4-(3,7-dimethyloctyl)benzene and 1-trimethylsilyl-4-(3,7-dimethyloctyl)benzene have been carried out using the Gaussian 09 program [11]. We have employed the widely used [12] B3LYP/6-311+G(2d,2p) level of theory for geometry optimizations as well as IR frequencies and chemical shifts (additional functionals can be found in Supporting information). NMR parameters were evaluated using the gauge-including atomic orbitals (GIAOs) formalism [13]. Values of δ are presented with respect to TMS, obtained at the same level of theory.

4. Result and discussion

Fig. 2 shows the basis set effect on selected ^{13}C chemical shifts with the deshielding trend of the larger basis sets and the opposite behavior for smaller basis sets (for complete chemical shifts of ^{13}C and ^{1}H see Supporting Figs. S-9 and S-10). We have evaluated the effect of chloroform as a solvent on the NMR chemical shifts using a PCM model [14]. The solvent effect was found to be negligible in both the geometrical parameters as well as the NMR chemical shifts (shown in Fig. 2) and will therefore not be discussed further. IR frequencies have been obtained at the B3LYP/6-311+G(2d,2p) level of theory and scaled as reported previously (with a scaling factor of 0.96) [15].

Selected bond lengths and bond angles of the DFT optimized structure of these compounds are shown in Fig. 3. The optimized bond lengths [C3–Si = 1.89, C6–C24 = 1.51, C3–Br = 1.92 and C6–C11 = 1.51 Å] and angles [C2–C3–Si = 120.55, C4–C3–Si = 122.69, C2–C3–Br = 119.54 and C4–C3–Br = 119.53°] are in good agreement with the bond lengths and bond angles found in the similar compounds 4-(trimethylsilyl)benzoic acid and 2-(4-bromobenzyl)-1,3-diphenylpropane-1,3-dione reported in literature [16,17].

Calculated values of δ^{1H} and δ^{13C} agree well with their experimental values, within the accuracy of the theoretical framework employed. These results are shown in Fig. 4, wherein we observe a good correlation between fist-principles calculations and