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

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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 bottomup 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

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 onedimensional graphene nanoribbons with controlled edge morphology and narrow widths. We discuss the synthetic procedures and characterization using ¹H NMR, ¹³C 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.

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synthesis, characterization (¹H NMR, ¹³C 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, [PdCl₂(dppf)], sodium acetate, bromine, sodium sulfite and MgSO4 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 (CDCl₃). ¹H and ¹³C 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



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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 4bromo-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 3,7dimethyloctanyl-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 [PdCl₂(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%. ¹H NMR (CDCl₃) 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, -CH₂), 1.70-1.04 (m, 10H, -CH₂, CH, CH₂, CH₂, CH₂, CH), 0.95 (d, J = 6.0 Hz, 3H, CH₃), 0.89 (d, J = 6.0 Hz, 6H, CH₃), 0.28 (s, 9H, CH₃). ¹³C NMR (CDCl₃) 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 C₁₉H₃₄Si [M⁺] 290.24, found: 290.24. Compound was analyzed for C₁₉H₃₄Si (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_2Cl_2 (65 mL \times 3) and dried over MgSO₄. 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%. ¹H NMR (CDCl₃) 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, -CH₂), 1.62–1.04 (m, 10H, -CH₂, CH, CH₂, CH₂, CH₂, CH), 0.91 (d, J = 6.3 Hz, 3H, CH₃), 0.86 (d, J = 6.3 Hz, 6H, CH₃). ¹³C NMR (CDCl₃) 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 C₁₆H₂₅Br [M⁺] 296.11, found: 296.01. Compound was analyzed for C₁₆H₂₅Br (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 ¹³C chemical shifts with the deshielding trend of the larger basis sets and the opposite behavior for smaller basis sets (for complete chemical shifts of ¹³C and ¹H 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



Fig. 2. Basis set and solvent effects on selected ¹³C chemical shifts using the B3LYP functional. Experimental values are shown in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. Structural parameters for the DFT optimized structures at B3LYP/ 6-311+G(2d,2p) level of theory: (a) 1-trimethylsilyl-4-(3,7-dimethyloctyl)benzene and (b) 1-bromo-4-(3,7-dimethyloctyl)benzene.



Fig. 4. Calculated vs. experimental ¹³C and ¹H NMR chemical shifts obtained at the B3LYP/6-311+G (2d,2p) level of theory.



Fig. 5. Experimental (upper panel) and calculated (lower panel) IR spectra for 1-trimethylsilyl-4-(3,7-dimethyloctyl)benzene.

experiments, with two main exceptions. The first exception is the over-estimation of the ¹³C NMR chemical shift of C atom directly bonded to Br in the brominated compound, whereas the chemical shift obtained experimentally at about 120 ppm. The calculated value, however, was obtained without considering heavy atom and

vibrational effects, which have been shown to have an impact of about -11 ppm and +1.5 ppm, respectively, on the chemical shift of the C atom neighboring Br [18]. The second exception is simply due to the flexible nature of the aliphatic chain, not accounted for in our calculations.



Fig. 6. Experimental (upper panel) and calculated (lower panel) IR spectra for 1-bromo-4-(3,7-dimethyloctyl)benzene.

Experimental and calculated IR spectra for the Si- and Brsubstituted compounds are shown in Figs. 5 and 6, respectively. Experimental peaks corresponding to the acetone solvent are not present in the calculated spectrum (1712, 1360 and 1220 cm^{-1}). Neglecting the solvent peaks, we find a very good agreement between the two, additionally supporting the structure of the synthesized compounds. Calculations also allow us to elucidate the nature of the vibrational modes responsible for the broader regions of the experimental spectrum. Medium to strong absorptions around 2953–2867 cm⁻¹ observed corresponding to the aliphatic $(v_{CH}, v_{CH2} \text{ and } v_{CH3})$ and aromatic (v_{CH}) CH stretch. The strong bands at 1109 and 1011 cm⁻¹ may be assigned to C-Si and C-Br stretching modes, respectively. In-plane bending (scissoring, δ_s , rocking, δ_r), and out-of-plane bending (wagging, δ_w , twisting, δ_t) of aliphatic and aromatic CH absorptions observed around 897- 660 cm^{-1} .

5. Conclusions

In conclusion, we present the synthesis, characterization, and ab initio calculations of 1-trimethylsilyl-4-(3.7-dimethyloctyl)benzene and 1-bromo-4-(3,7-dimethyloctyl)benzene. The latter compound is required as a critical first step towards the bottom-up synthesis of planar one-dimensional graphene nanoribbons with controlled edge morphology and narrow widths. We discuss the detailed synthetic procedures and present experimental results for ¹H NMR, ¹³C NMR shifts, IR, and elemental analysis. These results are complemented by density functional theory calculations of 1-bromo-4-(3,7-dimethyloctyl)benzene as well as 1-trimethylsilyl-4-(3,7-dimethyloctyl)benzene optimal structures and their IR and NMR spectra obtained at the B3LYP/6-311+G(2d,2p) level. Calculated NMR and IR results agree well with experimental values, providing valuable structural parameters for these compounds and providing additional support to the experimental characterization tools.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2012.02.025.

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