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COMMUNICATION

Scalable Synthesis of Tetrapodal Octaamine

Ishfaq Ahmad, Javeed Mahmood, Jong-Beom Baek**

Abstract: An effective and high-yield synthesis of an air stable tetrapodal octaamine, a rigid shape-persistent molecule with four *ortho*-phenylenediamine moieties, is reported. It can be potentially transformed into a wide range of benzimidazole, benzotriazole, and pyrazine derivatives for practical applications.

Introduction

Rigid tetrapodal molecules, containing four identical rigid groups protruding from a common center toward each corner of a tetrahedron, have appealed to researchers as versatile building blocks for the synthesis of giant three-dimensional (3D) molecules. The formation of such bulky molecules are generally investigated in both materials and supramolecular chemistry studies.[1] Tetraphenylmethane[2] and its derivatives[3] are a class of shape persistent organic units containing four rigid aromatic rings projecting from a central carbon in a tetrahedral structure.[3-4] To construct shape persistent structures,[5] including dendrimers and porous polymers,[6] cage molecules,[7] interlocked structures[8] and organic frameworks,[5,9] as well as coordination polymers[4,10] and metal organic frameworks (MOF),[11] the tetraphenylmethane moiety primarily provides the rigidity at a molecular structure level.[3-4,12]

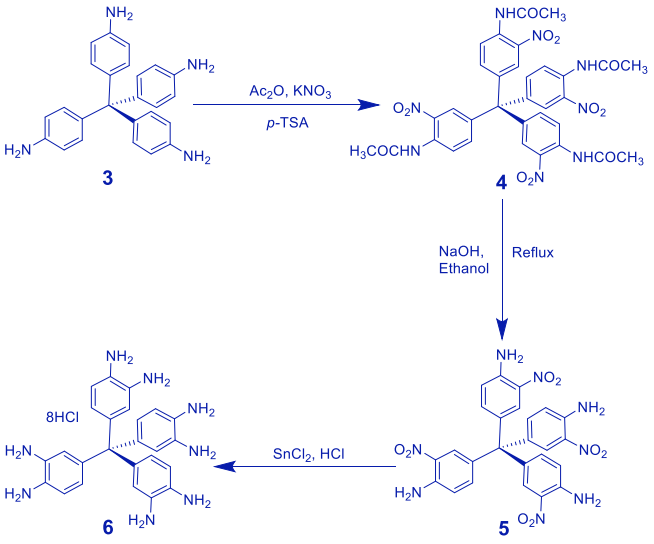
The *ortho (o)*-phenylenediamine group is an important chemical unit, which can be powerfully transformed into a variety of other aromatic rings, such as quinoxalines,[13] metal salphens,[14] benzimidazoles,[15] and etc.

Organic constituents with the tetraphenylmethane unit are of great interest due to their unique structure.[5] When each phenyl ring of the tetraphenylmethane is functionalized, its predefined geometry and rigidity allow the formation of diamond-like 3D network polymers.[5] Tetraphenylmethane decorated with an *o*-diamine group at each phenyl ring can be a crucial unit for diverse modifications. For example, the *o*-phenylenediamine constituents promptly condense with diketone containing molecules to provide diverse heterocyclic functionalities and organic frameworks.[13,17] However, one major drawback associated with molecules containing the *o*-phenylenediamine moiety is their oxidative instability. Rapid oxidation occurs after reduction of the corresponding aromatic nitro precursor.[16] Consequently, the designed tetrapodal octaamine has to be treated in inert atmosphere (air free) and then needs to be used right after reduction of the nitro precursor (no storage is possible). Although tetrakis-phenylnediamine functionalized tetraphenylmethane (4,4',4'',4'''-methanetetrayltetrakis(benzene-1,2-diamine)) can potentially be formulated into a wide range of interesting materials, including 3D porous organic polymers,[13b,13c,15b,17] metal organic frameworks,[10b,18] and 3D cage like metal complexes,[14a] to date its large-scale synthesis and purification has been extremely limited.

Results and Discussion

In order to efficiently synthesize tetrakis-phenylnediamine functionalized tetraphenylmethane, a versatile and high yield synthesis route is necessary. Here, we report a facile route for the synthesis of soluble and air stable 4,4',4'',4'''-methanetetrayltetrakis(benzene-1,2-diamine) without any purification using column chromatography.

Tetrakis(4-aminophenyl)methane (**3**) was synthesized from tetraphenylmethane according to literature reports (**SI**).[19] Tetrakis(4-nitrophenyl)methane (**2**) was obtained after nitration with fuming nitric acid at −10 °C, and then the resulting product (**Figure S1 and S2**) was subsequently reduced in the presence of palladium on activated carbon (Pd/C, **Caution**: *Pd/C can self-ignite when dry*) and hydrazine hydrate ($N_2H_4 \cdot H_2O$) to give compound (**3**) in high yield (**Figure S3 and S4**). The synthesis of octaamine (**6**) starts with the protection of the amino groups of the tetrakis(4-aminophenyl) methane with acetic anhydride.



Scheme 1. *Our New Three Step Synthesis of Air Stable Tetrapodal Octaamine 8HCl* ***(6)***

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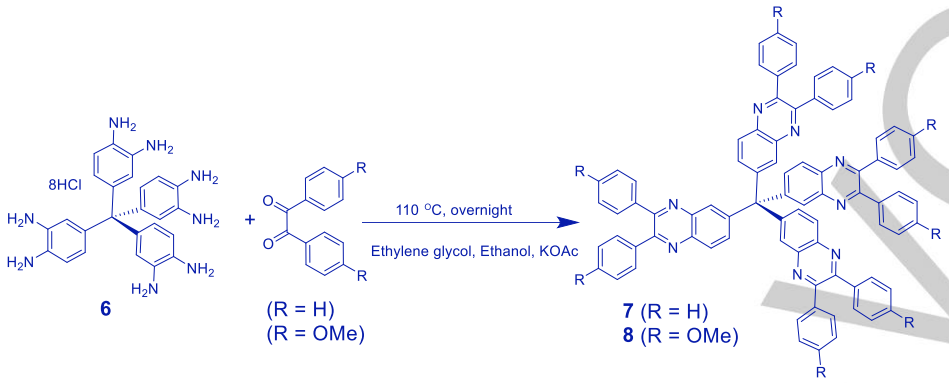
Subsequent *in-situ* nitration to the *ortho* position of *para*-aminophenyl (*p*-aminophenyl) with potassium nitrate (KNO_3) in the presence of *para*-toluene sulfonic acid (*p*-TSA) at room temperature results in the high yield of **4** (**Scheme 1**).[20] The *ortho* nitro derivative (**4**) was recrystallized from dimethylformamide (DMF) and a small amount of water to give a light-yellow powder (**Figure S5 and S6**). The purified **4** was refluxed in aqueous ethanol in the presence of sodium hydroxide (NaOH) to remove the acetyl protecting groups. The product, 4,4',4'',4'''-methanetetrayltetrakis(2-nitroaniline) (**5**), was precipitated in water after evaporation of the ethanol. The resulting yellowish solid was collected by filtration and washed with water, which was technically pure enough to proceed without further purification (**Figure S7 and S8**).

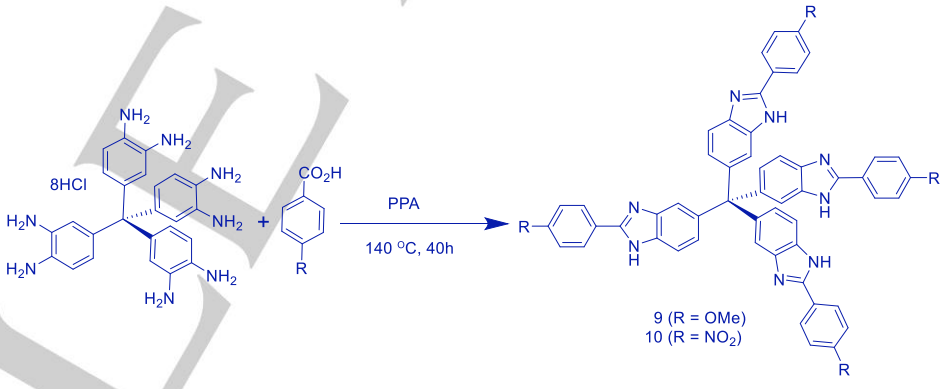


Scheme 2. *Synthesis of quinoxaline derivatives (**7**, **8**) of tetrapodal octamine*

Finally, the *ortho* nitro derivative (**5**) was reduced to tetrapodal octaamine octahydrochloride in ethanol in the presence of tin(II) chloride dihydrate ($SnCl_2{\cdot}2H_2O$) and concentrated hydrochloric acid (37% HCl). The product (**6**) was recrystallized while cooling to room temperature. The crystals were collected by filtration and washed with concentrated HCl (3×8 mL). The precipitate was also washed with ethyl acetate to remove unbound HCl from the material. After drying, the crystals were dissolved again in warm water and recrystallized by adding concentrated HCl. Creamy white powdery crystals formed were collected and dried (**Figure S9 and S10**). The crystals were stable in a sealed vial on the bench top for at least six months.

This synthesis strategy of tetrapodal octaamine is an efficient, facile and high-yield method with practical uses. The most appealing feature is the formation of an air-stable hydrochloride salt form of tetrapodal octaamine. With a convenient and high-yield synthetic route, tetrapodal octaamine octahydrochloride (**6**) is an potentially attractive building block for diverse applications, such as supramolecular superstructures, 3D covalent organic network structures,[5],[9d] dendritic macromolecules[6b] and rotaxanes[21]. Specifically, 3D porous materials can be extensively used in gas storage, opto-electronics, asymmetric catalysis,[1d] and beyond.

As a proof of concept, the compound **6** was treated with benzil and 4,4′-dimethoxybenzil to give compounds **7** and **8** in ethyl glycol/ethanol in the presence of potassium acetate (**Scheme 2**). The compounds **7** and **8** were isolated in ~60% yield after column chromatography and were characterized by NMR, HR-MS and EA (**Figure S11-S14**). The synthesis of benzimidazole derivatives of the compound **6** were also carried out. To prepare benzimidazole derivatives compound **6** was treated with 4-methoxybenzoic acid and 4-nitrobenzoic acid to obtain compounds **9** and **10** in polyphosphoric acid (PPA) at 145 °C.[15c] The resultant products were characterized by Direct Insertion Probe MS (DIP-MS). Due to poor solubility further purification and characterization was not possible. These quinoxaline and benzimidazole derivatives illustrate that a broad range of materials can be designed and synthesized using this new tetrapodal octamine building block.



Scheme 3. *Synthesis of benzimidazole derivative (**9**, **10**) of tetrapodal octamine.*

Conclusions

In summary, we report a facile and efficient route for the scalable synthesis of *othro*-diamine functionalized tetraphenylmethane (4,4',4'',4'''-methanetetrayltetrakis(benzene-1,2-diamine)), which is air-stable and thus can be stored in a vial on the benchtop at ambient conditions for several months without exceptional precaution. The extra advantage associated with this synthetic route is that it does not involve column chromatography for the purification of all three compounds (**4**, **5** and **6**). Air stable tetrapodal octaamine **6** can be a useful precursor and/or a

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building block for a variety of condensation reactions for extended tetraphenylmethane derivatives.

Experimental Section

General Methods. All the reagents and solvents were purchased from Sigma-Aldrich unless otherwise stated. Solvents were degassed with nitrogen purging prior to use. All the reactions were carried out under nitrogen atmosphere using oven dried glassware. Tetraphenylmethane was purchased from Alfa Aesar. Tetrakis(4-aminophenyl) methane was synthesized according to a procedure described in the literature.[19] Proton (^{1}H) and carbon thirteen (^{13}C) nuclear magnetic resonance (NMR) spectra were recorded on an AVANCE III HD 400 MHz FT-NMR (Bruker) spectrometer. Elemental analysis (EA) was performed with a Thermo Scientific Flash 2000 Analyzer. Melting points were measured on a KSP1N automatic melting point meter (A. Krüss Optronic GmbH, Germany). High resolution mass spectra (HRMS) measurements were conducted using JEOL/JMS-700 (2).

N,N',N'',N'''-(methanetetrayltetrakis(2-nitrobenzene-4,1-diyl))tetraacetamide (4). Tetrakis(4-aminophenyl) methane (**3**, 2 g, 5.26 mmol) and acetic anhydride (90 mL) were charged into a three-necked round-bottom flask (250 mL). The mixture was stirred for 30 min, and then *p*-toluenesulfonic acid monohydrate (4.50 g, 23.67 mmol) was added. The solution was cooled to 0 °C in an ice bath and KNO_3 (2.23 g, 22.09 mmol) was slowly added. The ice bath was removed, and the solution was stirred overnight at room temperature, resulting in a cloudy pinkish orange solution. The reaction mixture was poured into water (700 mL), giving a yellow precipitate, which was collected by suction filtration and washed with water. The product was recrystallized from DMF with the addition of a small amount of water. To the boiling DMF water was slowly to avoid any turbidity of the solution and the addition was continued until the solution maintains transparency. The light-yellow powder was precipitated out from the solution after cooling to room temperature (3.72 g, 97 %): mp 242-244°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.35 (s, 4H), 7.72 (s, 4H), 7.65-7.63 (d, *J* = 8 Hz, 4H), 7.54-7.52 (d, *J* = 8 Hz, 4H) δ 2.07 (s, 12H); ^{13}C NMR (400 MHz, DMSO) δ 169.0, 141.9, 140.8, 136.6, 130.7, 125.7, 125.5, 62.6. Anal. Calcd for $C_{33}H_{28}N_8O_{12}$: C, 54.40, H, 3.87, N, 15.38, O, 26.35. Found: C, 54.41 H, 3.92, N, 15.48, O, 26.38. HRMS calcd for $C_{33}H_{28}N_8O_{12}$ 728.1827, found 728.1804.

4,4',4'',4'''-Methanetetrayltetrakis(2-nitroaniline) (5). In a three-necked round-bottom flask (500 mL), compound **4** (2.24 g, 3.07 mmol) was dispersed in ethanol (300 mL), and sodium hydroxide (0.81 g, 20.13 mmol) in water (14 mL) was slowly added. The mixture was refluxed for 2 h with stirring and then cooled to room temperature. The solution was concentrated by the evaporation of ethanol on a rotary evaporator. Then water (100 mL) was added to isolate product, which was collected on a Buchner funnel as a yellow powder (1.70 g, 98 %): mp > 350 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.71 (s, 4H), 7.59 (s, 8H, -NH_2), 7.06-7.04 (d, *J* = 8 Hz, 4H), 7.01-6.99 (d, *J* = 8 Hz, 4H); ^{13}C NMR (400 MHz, DMSO-d_6) δ 145.60, 139.27, 131.87, 129.42, 125.02, 119.93, 60.34. Anal. Calcd for $C_{25}H_{20}N_8O_8$: C, 53.57, H, 3.60, N, 19.99, O, 22.84. Found: C, 53.57, H, 3.58, N, 19.62, O, 22.66. HRMS (EI) calcd for $C_{25}H_{20}N_8O_8$ 560.1404, found 560.1402.

4,4',4'',4'''-Methanetetrayltetrakis(benzene-1,2-diamine) (6). A suspension of compound **5** (1.50 g, 2.68 mmol) and tin(II) chloride dihydrate (24 g, 105 mmol) in ethanol (150 mL) and concentrated hydrochloric acid (90 mL) were charged into three-necked round-bottom flask (500 mL), and refluxed for 24 h with stirring. After cooling the reaction mixture down to room temperature, creamy white precipitates were collected by filtration, washed with concentrated hydrochloric acid (3 × 24 mL), and dried under reduced pressure (0.05 mmHg). Then, the product was further washed with ethyl acetate to remove unbound HCl. The product was recrystallized from diluted HCl solution. Concentrated HCl was added to the boiling water containing the compound 6 slowly until the solution remains transparent. On cooling down to room temperature creamy white powdery crystals were formed (1.87 g, 95.71 %): mp 286-288 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.15-7.13 (d, *J* = 8 Hz,4H), 7.06 (s, 4H), 7.01-6.99 (d, *J* = 8 Hz, 4H); ^{13}C NMR (400 MHz, DMSO-d_6) δ 143.93, 129.00, 127.07, 125.21, 124.58, 122.76, 62.84 Anal. Calcd for $C_{25}H_{36}N_8Cl_8$: C, 41.04, H, 4.96, N, 15.30, Cl, 38.73. Found: C, 41.54, H, 4.95, N, 15.58. HRMS (EI) calcd for $C_{25}H_{28}N_8$ 440.2437, found 440.2448.

Tetrakis(2,3-diphenylquinoxalin-6-yl) methane (7). A mixture of ethylene glycol (10 mL) and ethanol (10 mL) was added in a three-neck round bottom flask (100 mL) containing compound (**6**) (100 mg, 0.14 mmol) and benzil (143.4 mg, 0.68 mmol) under nitrogen atmosphere. Potassium acetate (105 mg, 1.07 mmol) was also added to the reaction mixture and heated to 110 °C for 12 h. After completion of the reaction, the mixture was cool to room temperature and poured into ice cold water to precipitate out the product as a light yellow solid. Then, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 4:1) to obtain pure product as a white powder (99 mg, 64 %). mp 275-278 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 4H), 8.15-8.13 (d, *J* = 8 Hz, 4H), 7.80-7.78 (d, *J* = 8 Hz, 4H), 7.52-7.46 (dd, *J* = 8 Hz 16H), 7.35-7.33 (t, *J* = 8 Hz, 12H), 7.31-7.27 (t, *J* = 8 Hz, 12H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 154.29, 154.13, 146.72, 141.28, 140.36, 139.10, 139.04, 134.19, 130.31, 129.96, 129.13, 128. 90, 128.40. 65.90; Anal. Calcd for $C_{81}H_{52}N_8$: C, 85.54, H, 4.61, N, 9.85. Found: C, 85.15, H, 5.16, N, 9.25. HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{81}H_{52}N_8Na$: 1159.4213, found 1159.4211.

Tetrakis(2,3-bis(4-methoxyphenyl)quinoxalin-6-yl)methane (8). Compound (**6**) (100 mg, 0.14 mmol) and 4,4′-dimethoxybenzil (184.3 mg, 0.68 mmol) were charged into a three-neck round bottom flask (100 mL) containing ethanol (10 mL) and ethylene glycol (10 mL). Then, potassium acetate (105 mg, 1.07 mmol) was added. The reaction mixture was under reflux for 12 h. After completion of the reaction, the mixture was allowed to cool to room temperature and poured into ice cold water to precipitate out the product. Then, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 7:3) to obtain pure product as a white powder (125 mg, 66 %). mp 246-248 °C; ^{1}H NMR (400 MHz, $(CD_3)_2CO$-d_6) δ 8.23 (s, 4H), 7.91-7.89 (d, *J* = 8 Hz, 4H), 7.68-7.66 (d, *J* = 8 Hz, 4H), 7.44-7.41(d, *J* = 8 Hz, 8H), 7.38-7.36 (d, *J* = 8 Hz, 8H), 6.79-6.77 (d, *J* = 8 Hz, 8H), 6.71-6.69 (d, *J* = 8 Hz, 8H), 3.70 (s, 12H) 3.64 (s, 12H); ^{13}C NMR (400 MHz, acetone-d_6) δ 161.07, 160.99, 154.00, 153.82, 147.11, 141.43, 140.44, 134.40, 132.50, 132.45, 132.13, 130.64, 129.19, 114.21, 114. 13, 66.26. 55.55; Anal. Calcd for $C_{89}H_{68}N_8O_8$: C, 77.60, H, 4.98, N, 8.13, O, 9.29 Found: C, 77.41 H, 4.96, N, 7.89. O, 10. 12. HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{89}H_{68}N_8O_8Na$: 1399.5058, found 1399.5052.

Bis(2-(4-methoxyphenyl)-1H-benzo[d]imidazol-5-yl)bis(2-(4-methoxyphenyl)-1H-benzo[d]imidazol-6-yl)methane (9) Compound **6** (0.20 g, 0.27 mmol), 4-methoxybenzoic acid (0.33g, 2.16 mmol) and polyphosphoric acid (5.00 g) were taken in a three-neck round bottom flask (100 mL). The temperature of the reaction was slowly increased to 145 °C and continued for 40 h. After cooling down to room temperature the mixture was poured into ice cold water and basified with sodium hydroxide to precipitate out the product. Because of poor solubility in NMR solvents, characterization by NMR was not possible. DIP-MS calcd for $C_{57}H_{44}N_8O_4$ 904.3486, Found 905.2.

Bis(2-(4-nitrophenyl)-1H-benzo[d]imidazol-5-yl)bis(2-(4-nitrophenyl)-1H-benzo[d]imidazol-6-yl)methane (10) Compound **6** (0.20 g, 0.27 mmol), 4-nitrobenzoic acid (0.36 g, 2.16 mmol) and polyphosphoric acid (7.00 g) were charged into a three-neck round bottom flask (100 mL). The temperature was slowly raised to 145 °C and continued for 40 h. After

completion of the reaction, the mixture was allowed to cool to room temperature and poured into ice cold water and basified with sodium hydroxide to precipitate out the product. As the solubility of this compound was also poor, we were unable to obtain NMR spectrum. further purification was done except mass spectrometry. DIP-MS calcd for $C_{53}H_{32}N_{12}O_8$ 964.2466, Found 965.2.

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Keywords: Synthesis design • Amine • Fused-ring systems • Tetrapodal • 3D octamine • tetraphenylmethane

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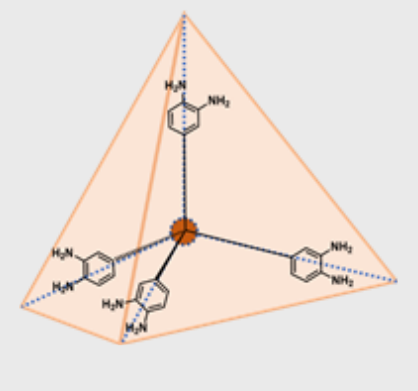
COMMUNICATION

A high yield synthesis of an air stable and a rigid shape-persistent tetrapodal octaamine, is reported. It can be potentially transformed into a wide range of functionalities, e.g., benzimidazole, benzotriazole, and pyrazine, for application-oriented 3D organic framework synthesis.



Tetrapodal Octaamine

Ishfaq Ahmad, Javeed Mahmood, Jong-Beom Baek**

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Scalable Synthesis of Tetrapodal Octaamine

*Tetrapodal octamine, 3D organic frameworks