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Synthesis and Structure of 2,6,14- and 2,7,14-Trisubstituted Triptycene Derivatives

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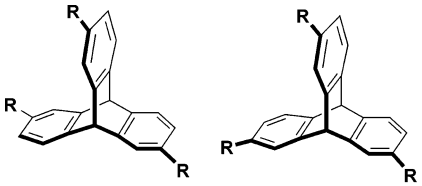

A series of 2,6,14- and 2,7,14-trisubstituted triptycene derivatives were efficiently synthesized and their structures were determined by NMR, MS spectra, and X-ray analysis. These trisubstituted triptycenes are potential building blocks for constructing novel receptors and synthetic molecular machines.

Triptycene[1] and its derivatives are a class of interesting compounds with three-dimensional rigid frameworks. They have been found to have unique electrochemical and photochemical properties,[2] interesting reactivities,[3] potential pharmaceutical properties,[4] and attractive applications in supramolecular chemistry[5] and materials science.[6] Moreover, they have also been shown to be useful building blocks in constructing molecular devices and synthetic molecular machines.[7]

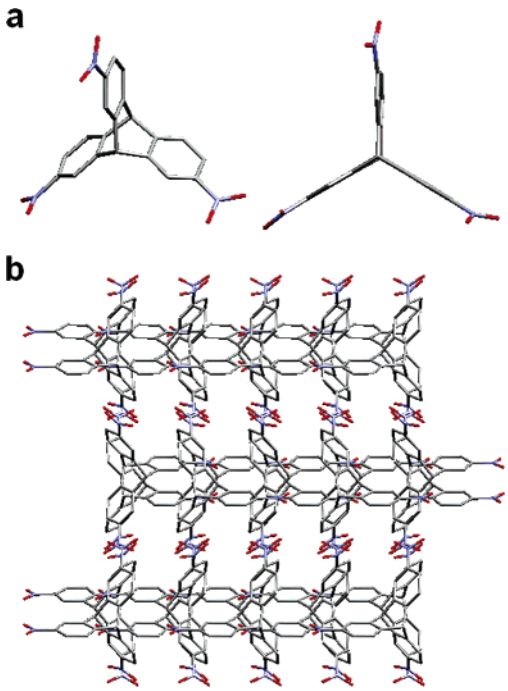

FIGURE 1. (a) Two views of the crystal structure of compound **2b**; (b) crystal packing of **2b** viewed along the *a*-axis. Hydrogen atoms are omitted for clarity.

Recently, we[8] were interested in the development of new supramolecular systems based on triptycene. Consequently, some of triptycene derivatives with unique structure and properties are needed. Herein we report the efficient synthesis of a series of 2,6,14- and 2,7,14-trisubstituted triptycene derivatives, which are potential building blocks for constructing novel receptors and synthetic molecular machines.

2,6,14-Trinitrotriptycene and 2,7,14-trinitrotriptycene were first synthesized as byproducts in 1973[9] by the reaction of triptycene and acetyl nitrate in the presence of acetic anhydride and glacial acetic acid. Recently, MacLachlan et al.[10] reported that the nitration of triptycene with concentrated HNO_3 gave

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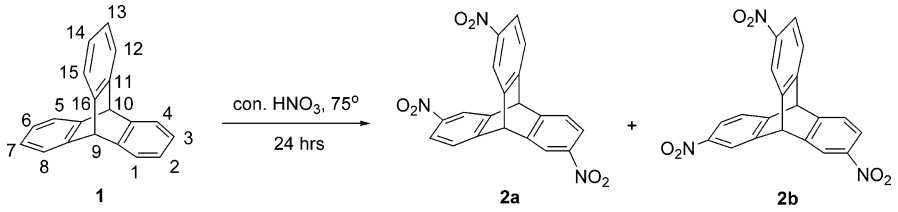
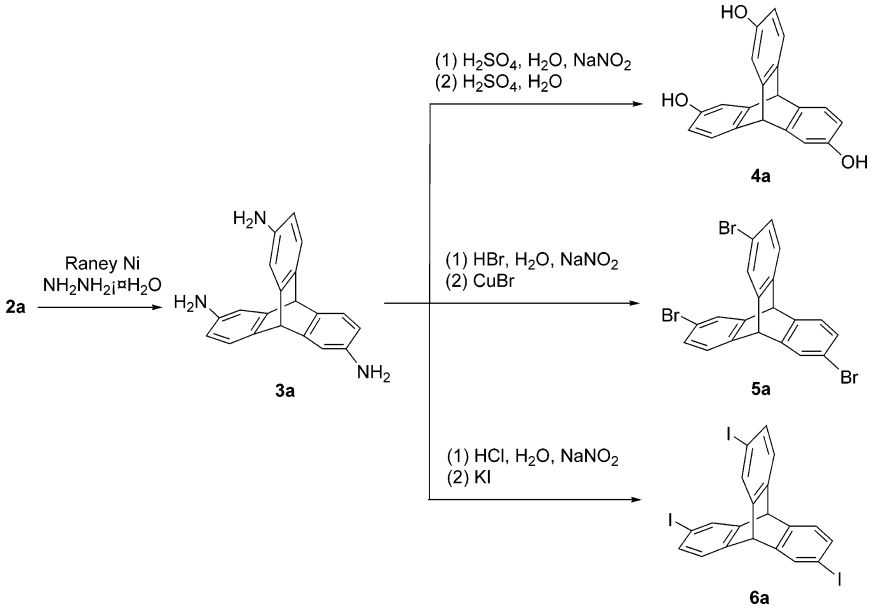
SCHEME 1



SCHEME 2



the 2,6,14-trinitrotriptycene in 33% yield as the sole isolated product. Following the same nitration condition as above, we found that by increasing the reactive temperature and prolonging the reactive time not only 2,6,14-trinitrotriptycene **2a** was obtained in 64% yield, but also 2,7,14-trinitrotriptycene **2b** could be isolated in 21% yield (Scheme 1). Compared with that of compound **2a**, ^{1}H NMR spectrum of compound **2b** shows a very simple splitted mode of aromatic protons and much different shifts for the two bridgehead protons. Moreover, 11 signals for the aromatic carbons of **2a** were observed while ^{13}C NMR spectrum of **2b** shows only 6 signals for the aromatic carbons. These observations are all consistent with the C_3 symmetric structure of **2b**.

The structure of 2,7,14-trinitrotriptycene **2b** was further determined by its X-ray single-crystal analysis. Single crystals of **2b** suitable for X-ray diffraction were obtained by slow evaporation of a CH_2Cl_2/hexane solution. As shown in Figure 1a, the three nitro groups in **2b** are positioned in the same direction, and one of the benzene rings is a little distorted. Moreover, it was found that **2b** could pack into microporous networks (Figure 1b), in which multiple N−O···H−C hydrogen bonds and $\pi-\pi$ stacking interactions played an important role (Supporting Information).

The trinitrotriptycenes could be easily reduced by Raney Ni in the presence of hydroazine to afford the corresponding triaminotriptycenes in almost quantitative yields. It was known that the aryl diazonium salts are the most broadly useful substrates for nucleophilic aromatic substitution, and aryl diazonium ions are easily prepared by the reaction of an aniline with nitrous acid generated in situ from a nitrite salt. Consequently, the triaminotriptycenes could be considered as useful precursors for the preparation of other trisubstituted triptycene derivatives.

As shown in Scheme 2, when compound **3a** was treated with the aqueous solution of sodium nitrite and concentrated sulfuric acid, the trihydroxytriptycene **4a** could be obtained in 75% yield. Treating compound **3a** with a solution of sodium nitrite in concentrated hydrobromic acid and water and then with CuBr gave tribromotriptycene **5a** in 68% yield. Similarly, triiodotriptycene **6a** was synthesized in 71% yield by the reaction of the diazonium salt derived from **3a** with KI. Compounds **4a**, **5a**, and **6a** were all characterized by the ^{1}H NMR, ^{13}C NMR, and MS spectra, respectively.

Under the same conditions as above, compounds **4b**, **5b**, and **6b** were synthesized in 81%, 62%, and 80% yields, respectively, by the aromatic substitution via diazonium ions derived from the triaminotriptycene **3b** (Scheme 3). Compounds **4b**, **5b**, and **6b** all showed six signals for the aromatic carbons and two signals for the bridgehead carbons in their ^{13}C NMR spectra. Consequently, they all have the C_3 symmetric structure, in which the three substituted groups are positioned in the same direction. We further obtained the single crystals of **6b** suitable for X-ray analysis from vapor diffusion of *n*-pentane into dichloromethane solution. As expected, its crystal structure (Figure 2) shows the same results as those in solution. Moreover, it was found that compound **6a** could also pack into a microporous structure by the multiple I···I and C−I···π interactions[11] (Supporting Information).

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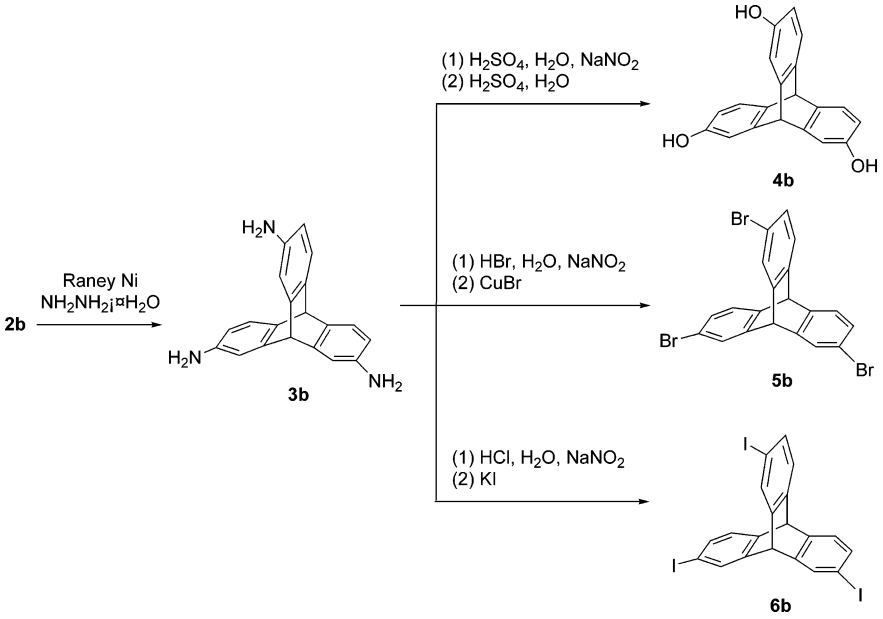
SCHEME 3



In summary, we have provided an efficient method for the synthesis of a series of both 2,6,14- and 2,7,14-trisubstituted triptycene derivatives in reasonable yields, which could be potential building blocks for constructing novel receptors and synthetic molecular machines, and studies on them are undergoing.

Experimental Section

Synthesis of Trinitrotriptycenes 2a and 2b. To triptycene **1** (2.5 g, 10 mmol) was added concentrated HNO_3 (100 mL) and the mixture was heated at 75 °C for 24 h. The brown solution was cooled to room temperature, then poured into H_2O (1000 mL) and stirred. The precipitate was collected, washed with cooled water, and then dried in air. The crude products were separated by column chromatography on silica gel with dichloromethane/petroleum ether (1:1) as eluent to afford the white solids **2a** (2.5 g) and **2b** (0.82 g).

Compound 2a: yield, 64%; mp 178−180 °C (lit. 173−176[10] or 180 °C[9]). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.82 (s, 1H), 5.84 (s, 1H), 7.62−7.67 (m, 3H), 8.03−8.07 (m, 3H), 8.32−8.34 (m, 3H).

Compound 2b: yield, 21%; mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.80 (s, 1H), 5.84 (s, 1H), 7.62 (d, J = 8.2 Hz, 3H), 8.05 (dd, J = 8.2, 2.2 Hz, 3H), 8.34 (d, J = 2.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.1, 53.6, 119.5, 122.5, 125.0, 144.7, 146.3, 148.8. EI-MS: m/z 389 (M^+). Anal. Calcd for $C_{20}H_{11}N_3O_6$: C, 61.70; H, 2.85; N, 10.79. Found: C, 61.84; H, 2.95; N, 10.53.

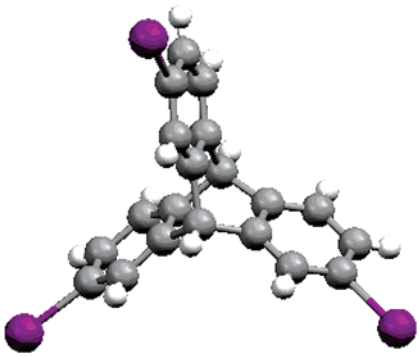


FIGURE 2. The crystal structure of compound **6b**.

General Method for Synthesis of Triaminotriptycenes 3a and 3b. To a solution of compound **3a** or **3b** (1.0 g, 2.6 mmol) in THF (20 mL) was added hydrazine monohydrate (1.5 mL) and Raney Ni (∼1.0 g). After heating at 60 °C until all hydrazine was quenched, the mixture was cooled to room temperature and then filtered. The filtrate was concentrated by rotary evaporation to remove the solvent, and the product as a white solid was obtained in quantitative yield.

Compound 3a: mp 290−292 °C (lit. 279−283 °C[10]). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.47 (s, 6H), 5.01 (s, 1H), 5.04 (s, 1H), 6.21−6.26 (m, 3H), 6.69−6.73 (m, 3H), 7.04−7.07 (m, 3H). ^{13}C NMR (75 MHz, DMSO): δ 51.3, 52.5, 108.2, 108.5, 109.8, 110.2, 122.9, 123.3, 133.2, 134.1, 145.3, 145.5, 147.0, 147.8. EI-MS: m/z 299 (M^+).

Compound 3b: mp 152−154 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.40 (s, 6H), 4.97 (s, 1H), 5.05 (s, 1H), 6.23 (dd, J = 7.7, 2.1 Hz, 3H), 6.70 (d, J = 7.7 Hz, 3H), 7.03 (d, J = 2.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 51.5, 54.5, 110.9, 111.7, 123.4, 137.3, 143.4, 146.4. HRMS calcd for $C_{20}H_{17}N_3$, $[M]^+$ 299.1422; found, 299.1418.

General Method for Synthesis of Trihydroxytriptycenes 4a and 4b. To a solution of **3a** or **3b** (0.6 g, 2.0 mmol) in concentrated sulfuric acid (2 mL) and water (10 mL) cooled in an ice-salt bath was added dropwise a solution of sodium nitrite (0.4 g, 7.0 mmol) in water (5 mL) for over 10 min. After being stirred for 20 min, the mixture was slowly added into the refluxing solution of concentrated sulfuric acid (10 mL) and water (15 mL) over 30 min. The mixture was refluxed for another 2 h, cooled, and then extracted with ether (30 mL × 3). The combined extracts were washed with water (20 mL × 2), dried over anhydrous sodium sulfate, and concentrated to remove the solvent. The residue was subjected to chromatography on silica gel with dichloromethane/petroleum ether (1:2) as eluent to give the product as a pale yellow solid.

Compound 4a: yield, 75%; mp > 300 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ 5.23 (s, 2H), 5.04 (s, 1H), 6.36−6.40 (m, 3H), 6.89−6.91 (m, 3H), 7.11−7.16 (m, 3H). ^{13}C NMR (75 MHz, acetone-d_6): 52.2, 53.2, 109.9, 110.1, 111.1, 111.3, 123.6, 123.9, 136.5, 137.3, 147.8, 148.5, 154.6, 154.8. HRMS calcd for $C_{20}H_{14}O_3$, $[M]^+$ 302.0943; found, 302.0941.

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Compound 4b: yield, 81%; mp > 300 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ 5.23 (s, 1H), 5.24 (s, 1H), 6.39 (dd, J = 7.9, 2.4 Hz, 3H), 6.93 (d, J = 7.9 Hz, 3H), 7.12 (d, J = 2.4 Hz, 3H). ^{13}C NMR (75 MHz, acetone-d_6): δ 51.2, 54.1, 110.3, 111.6, 123.3, 138.0, 147.1, 154.5. HRMS calcd for $C_{20}H_{14}O_3$, $[M]^+$ 302.0943; found, 302.0944.

General Method for Synthesis of Tribromotriptycenes 5a and 5b. To a solution of **3a** or **3b** (1.0 g, 3.6 mmol) in concentrated hydrobromic acid (3 mL) and water (10 mL) cooled in an ice-salt bath was added dropwise a solution of sodium nitrite (0.8 g, 12.6 mmol) in water (5 mL) for over 10 min. After being stirred for 20 min, the mixture was slowly added into the refluxing mixture of CuBr (2.2 g, 15.0 mmol) and concentrated hydrobromic acid (5 mL) over 30 min. The mixture was refluxed for another 2 h, cooled, and then extracted with dichloromethane (30 mL × 3). The combined extracts were washed with water (20 mL × 2), dried over anhydrous sodium sulfate, and concentrated to remove the solvent. The residue was subjected to chromatography on silica gel with dichloromethane and petroleum ether (1:10) as eluent to give the product as a white solid.

Compound 5a: yield, 68%; mp 127−129 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.26 (s, 1H), 5.29 (s, 1H), 7.12 (dd, J = 7.8, 1.8 Hz, 3H), 7.20 (d, J = 7.8 Hz, 3H), 7.49 (d, J = 1.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 52.6, 52.7, 119.1, 119.2, 125.3, 125.4, 127.1, 127.2, 128.47, 128.51, 143.0, 143.3, 146.4, 146.7. EI-MS: m/z 490 (M^+), 492 ($M^+ + 2$). Anal. Calcd for $C_{20}H_{11}Br_3$: C, 48.92; H, 2.26. Found: C, 48.61; H, 2.44.

Compound 5b: yield, 62%; mp 121−123 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.25 (s, 1H), 5.31 (s, 1H), 7.13 (dd, J = 7.8, 1.8 Hz, 3H), 7.21 (d, J = 7.8 Hz, 3H), 7.49 (d, J = 1.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.4, 52.8, 119.1, 125.2, 127.2, 128.6, 143.5, 146.1. EI-MS: m/z 490 (M^+), 492($M^+ + 2$). Anal. Calcd for $C_{20}H_{11}Br_3$: C, 48.92; H, 2.26. Found: C, 48.65; H, 2.39.

General Method for Synthesis of Triiodotriptycenes 6a and 6b. To a solution of **3a** or **3b** (0.6 g, 2.0 mmol) in concentrated hydrochloric acid (5 mL) and water (10 mL) cooled in an ice-salt bath was added dropwise a solution of sodium nitrite (0.4 g, 7.0 mmol) in water (5 mL) for over 10 min. After the mixture was stirred for another 20 min, potassium iodide (2.5 g, 15.0 mmol) in water (5 mL) was added dropwise over 30 min. The mixture was heated at 80 °C for 2 h, cooled, and then extracted with dichloromethane (30 mL × 3). The combined extracts were washed with saturated sodium bisulfate (20 mL × 2), dried over anhydrous sodium sulfate, and concentrated to remove the solvent. The residue was subjected to chromatography on silica gel with dichloromethane and petroleum ether (1:4) as eluent to give the product as a white solid.

Compound 6a: yield, 71%; mp 155−157 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.23 (s, 1H), 5.25 (s, 1H), 7.09 (d, J = 7.7 Hz, 3H), 7.34 (dd, J = 7.7, 1.5 Hz, 3H), 7.69 (d, J = 1.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 52.4, 52.5, 90.5, 125.7, 125.8, 132.8, 132.9, 134.6, 143.7, 143.9, 146.5, 146.8. EI-MS: m/z 631 (M^+). Anal. Calcd for $C_{20}H_{11}I_3$: C, 38.01; H, 1.75. Found: C, 38.10; H, 1.77.

Compound 6b: yield, 80%; mp 164−166 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.22 (s, 1H), 5.27 (s, 1H), 7.10 (d, J = 7.7 Hz, 3H), 7.34 (dd, J = 7.7, 1.5 Hz, 3H), 7.69 (d, J = 1.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.3, 52.6, 90.4, 125.6, 132.9, 134.6, 144.2, 146.3. EI-MS: m/z 631 (M^+). Anal. Calcd for $C_{20}H_{11}I_3$: C, 38.01; H, 1.75. Found: C, 38.15; H, 1.82.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **2a**,**b**, **3a**,**b**, **4a**,**b**, **5a**,**b**, **6a**,**b**; X-ray crystallographic files (CIF) for **2b** and **6b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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