

# Triptycene structure-directing agents in aluminophosphate synthesis



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## ABSTRACT

The synthesis of aluminophosphates is investigated using a number of triptycene-based organic structure-directing agents (OSDA). These OSDAs are designed to synthesize extra-large pore and/or large cavity-containing molecular sieves. Starting from the hydrophobic triptycene molecule, OSDAs are prepared by introducing three amine-based centers that can be charged either by protonation in the acidic aluminophosphate reaction media or through quaternization. VPI-5 is synthesized using these triptycene OSDAs, and the OSDAs are occluded inside the pores. This synthesis marks the first time VPI-5 has been made as a single phase with an OSDA occluded inside the framework of the as-made material that is not removed by simple washing with water or other solvents. Additionally, several other aluminophosphates with unknown structures are synthesized using these new OSDAs.

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## 1. Introduction

For both industrial and fundamental reasons, the synthesis of extra-large pore molecular sieves continues to be important [1,2]. The lack of organic structure-directing agents (OSDA) with the appropriate properties to control the synthesis of these materials is just one of the issues that hinders the creation of extra-large pore materials. Organic molecules that are the appropriate size to fit within extra-large pore materials typically suffer from being too hydrophobic for the traditional molecular sieve synthesis (exceptions include those listed in Refs. [3,4]). One solution to this problem is to introduce multiple charge centers into the OSDA. The creation of three charge centers in a single OSDA has seen limited use in the past to prepare molecular sieves [5,6]. ZSM-18 was the first molecular sieve made with a triquaternized organic structure directing agent. ZSM-18 is a three dimensional zeolite with one 12 T-atom pore and has the rare zeolite feature of containing three T-atom rings [5]. While ZSM-18 does not contain extra-large pores, it does have a large cage where the OSDA resides. In addition to the aluminosilicate ZSM-18, ECR-40 is a silicoaluminophosphate with the equivalent topology [7]. More recently, our lab has used this concept of triquaternized structure directing agents in the synthesis of germanosilicate LTA [8].

Here, we report the synthesis of five OSDAs, all based on triptycene (Fig. 1), and their use in the synthesis of aluminophosphates. Triptycene is an intriguing SDA precursor because of its  $D_{3h}$  symmetry. SDA's with this space group have previously synthesized multi-dimensional large pore molecular sieves [9]. We hypothesized that the rigid ring system of triptycene would limit distortion of the OSDA in the molecular sieve synthesis. These OSDAs were used to make a known extra-large pore aluminophosphate (VPI-5), as well as three aluminophosphates products with unknown structure.

## 2. Experimental

### 2.1. Synthesis of organic structure-directing agents

Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of argon. All reagents were purchased from commercial sources and used as received. Compounds **1** and **5** were synthesized by adapting known procedures [10,11]. Liquid NMR spectra were recorded on Varian Mercury spectrometers. High-resolution mass spectra were obtained from the California Institute of Technology mass spectrometry facility.

2,6,14-Triaminotriptycene **1**. A 500 mL flask was charged with triptycene (7.50 g, 29.50 mmols) and concentrated nitric acid (220 mL, 68.0–70.0 % by weight). The flask was fitted with a reflux condenser and heated to 80 °C for 2 h. Reaction was cooled to 25 °C and poured into D. I. water (1300 mL). The resulting mixture was stirred for 10 min and then filtered and the resulting solids are

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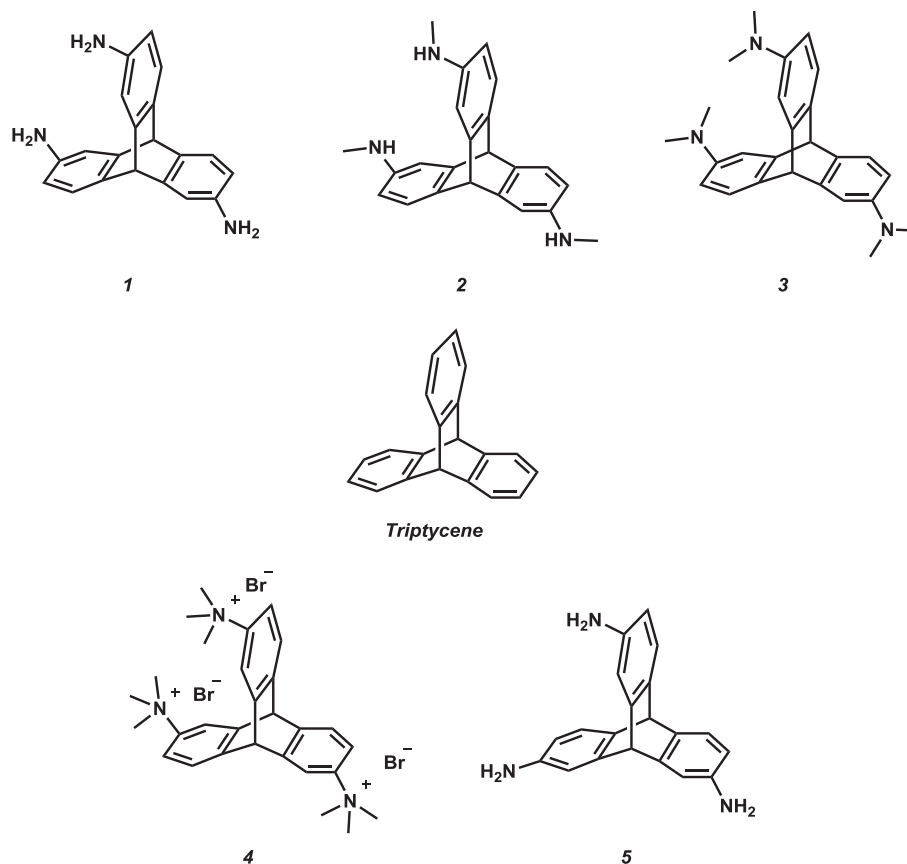


Fig. 1. Triptycene structure directing agents investigated.

collected. Solids were dissolved in  $\text{CH}_2\text{Cl}_2$  (250 mL) and dry loaded onto silica gel (150 mL) using a rotary evaporator. The crude product was then purified by column chromatography on silica gel (eluant: 27% ethyl acetate: 73% Hexanes then 50% ethyl acetate: 50% Hexanes) to give 2,6,14-trinitrotriptycene (6.70 g, 58–65% yield) as a yellow solid and 2,7,14-trinitrotriptycene (3.20 g, 20–27% yield) as a yellow solid. 2,6,14-trinitrotriptycene.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.34–8.32 (m, 3H), 8.07–8.03 (m, 3H), 7.66–7.62 (m, 3H), 5.83 (s, 1H), 5.82 (s, 1H). Spectral data match those previously reported [10,11]. 2,7,14-trinitrotriptycene.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.34 (d,  $J = 2.2$  Hz, 3H), 8.05 (dd,  $J = 8.2, 2.2$  Hz, 3H), 7.62 (d,  $J = 8.2$  Hz, 3H), 5.84 (s, 1H), 5.80 (s, 1H). Spectral data match those previously reported [10,11]. A 1 L flask was charged with 2,6,14-trinitrotriptycene (6.70 g, 17.21 mmols), THF (80 mL), and Raney nickel (1.00 g). The flask was fitted with a reflux condenser and the solution was heated to 65 °C. Hydrazine mono hydrate was added in 1 mL portions (16.00 mL, 206.51 mmols), after addition of hydrazine vigorous bubbling was observed, the next aliquot of hydrazine was added after bubbling subsided. After all of the hydrazine was consumed, the reaction was cooled to room temperature and filtered over a small pad of celite. The flask and pad were washed with ethanol ( $3 \times 30$  mL). The filtrate was evaporated under reduced pressure to afford 2,6,14-triaminotriptycene **1** (4.37 g, 85% yield) as a brown solid and was used without further purification.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.07–7.04 (m, 3H), 6.73–6.69 (m, 3H), 6.26–6.21 (m, 3H), 5.04 (s, 1H), 5.02 (s, 1H), 3.46 (s, 6H). Spectral data match those previously reported [10,11]. 2,6,14-triaminotriptycene **1** can decompose over time if left standing at room temperature for several weeks. 2,6,14-triaminotriptycene **1** was purified by column chromatography periodically (solvent system; 75%  $\text{CH}_2\text{Cl}_2$ :24%EtOAc:1%Et<sub>3</sub>N).

2,7,14-Triaminotriptycene **5**. 2,7,14-triaminotriptycene was synthesized identically to 2,6,14-triaminotriptycene **1** from 2,7,14-trinitrotriptycene. 2,7,14-triaminotriptycene **5** (2.09 g, 85% yield) was obtained as a brown solid and was used without further purification.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.05 (d, 3H), 6.74 (d, 3H), 6.25 (dd, 3H), 5.07 (s, 1H), 5.00 (s, 1H), 3.49 (s, 6H). Spectral data match those previously reported [10,11].

2,6,14-N-methyltriaminotriptycene **2**. A 250 mL flask is charged with 2,6,14-triaminotriptycene **1** (3.00 g, 10.02 mmol), THF (100 mL, dried over molecular sieves), and anhydrous pyridine (16 mL). Reaction was cooled to 0 °C and ethyl chloroformate (7.20 mL, 75.16 mmols). Reaction was allowed to gradually warm to 25 °C and stirred for an additional hour. The reaction mixture was evaporated under reduced pressure and dry loaded onto silica gel. The crude product was purified by column chromatography on silica gel (eluant: 25% ethyl acetate: 75% hexanes → 40% ethyl acetate: 60% hexanes → 60% ethyl acetate: 40% hexanes) to give 2,6,14-N-ethylcarbamoyltriaminotriptycene (4.20 g, 81% yield) as an orange solid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.60–7.52 (m, 3H), 7.27–7.22 (m, 3H), 6.87–6.79 (m, 3H), 6.46 (s, 3H), 5.07–5.05 (m, 2H), 4.18 (q,  $J = 6$  Hz, 6H) 1.28 (t,  $J = 6$  Hz, 9H). A 250 mL flask fitted with a reflux condenser was charged with 2,6,14-N-ethylcarbamoyltriaminotriptycene (4.20 g, 8.10 mmols) and THF (60 mL). This reaction was cooled to 0 °C. Lithium aluminum hydride (3.00 g, 80.02 mmols) was added, and the reaction was stirred for 1 h at 0 °C. The reaction was warmed to 25 °C and stirred for 5 min. The reaction was then refluxed at 95 °C for 3 h. The reaction was cooled back down to 0 °C and celite (50 mL) was added. D. I. water was slowly added in portions until all unreacted lithium aluminum hydride was quenched. Reaction slurry was filtered and washed with ethyl acetate ( $3 \times 40$  mL). The filtrate was dry loaded

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