



## Crystal structure of tris(binol)cyclotriphosphazene. A new clathration system



Mathias Reynes<sup>a,\*</sup>, David Virieux<sup>a,\*</sup>, Olivier Jeannin<sup>b</sup>, Marc Fourmigué<sup>b</sup>, Joël Moreau<sup>a</sup>, Olivier J. Dautel<sup>a,\*</sup>

<sup>a</sup>Architectures Moléculaires et Matériaux Nanostructurés, Institut Charles Gerhardt Montpellier, UMR CNRS 5253, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'Ecole Normale, 34296 Montpellier Cedex 05, France

<sup>b</sup>Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université Rennes1, Campus de Beaulieu, 35042 Rennes, France

### ARTICLE INFO

#### Article history:

Received 19 July 2016

Revised 26 July 2016

Accepted 28 July 2016

Available online 29 July 2016

#### Keywords:

Organic crystal

Cyclotriphosphazene

Inclusion

### ABSTRACT

The crystal structure of inclusion compound constituted by chiral tris(binol)cyclotriphosphazene ((*S,S,S*)-**TBP**) host and *o*-xylene guest has been determined. It has an orthorhombic unit cell with space group  $P2_12_12_1$  (no. 19) and unit cell dimensions  $a = 10.9265(4)$  Å,  $b = 17.8959(8)$  Å, and  $c = 30.3964(1)$  Å. Guest free (*S,S,S*)-**TBP** is an amorphous material according to the literature (*Chem. Eur. J.* **2001**, *7*, 1486–1494) and crystal structure has not been reported so far. Formation of inclusion adduct with *o*-xylene guests acting as a molecular glue allowed to determine the structural features. (*S,S,S*)-**TBP** has a propeller-like shape with binol units considered as paddles. Naphthalene units are twisted at 51° in those paddles. Effects of this twist on spirocyclic seven-membered ring and on cyclotriphosphazene ring are discussed.

© 2016 Elsevier Ltd. All rights reserved.

### Introduction

Inclusion compounds are elaborated by the association of host molecules forming network structure and guest molecules that fill the empty space between hosts.<sup>2</sup> Most members of the trisubstituted spirocyclic cyclotriphosphazene family are known to form inclusion compounds with a wide variety of guests.<sup>3,4</sup> Those compounds are interesting hosts since their molecular structure is easily tunable. Their synthesis is usually performed by reacting central cyclotriphosphazene hub substituted by chlorine atoms with aromatic di-nucleophiles.<sup>5</sup> Thus, adapting the nucleophile gives control over size, shape, and interactions of the cyclotriphosphazene hosts. So far, inclusion adduct formation of five-membered,<sup>6–8</sup> six-membered,<sup>9</sup> and seven-membered<sup>10</sup> spirocyclic cyclotriphosphazene has been investigated.

Some of those compounds could separate other molecules by selective formation of inclusion adducts, depending on the size, the shape, and the intrinsic nature of guests.<sup>6,11–13</sup> However, elaboration of clathrate from chiral cyclotriphosphazene host with the aim of enantiomeric separation has not been investigated up to date. Tris(2,2'-dioxybiphenyl)cyclotriphosphazene (**TbiPhP**) and tris(3,3'-dihydroxy-2,2'-bipyridine) (**TbiPyP**) are seven-membered ring cyclotriphosphazenes that give chiral crystals (**Chart 1**).<sup>10,14</sup>

However, those molecules are not chiral in solution due to a low energy interconversion barrier and a mixture of crystals with different enantiomeric conformation are expected in the solid state. Thus, even if one enantiomeric guest crystallizes with host in one type of enantiomeric conformation, crystal separation would be needed to resolve the racemic mixture. Synthesis of chiral tris(binol)cyclotriphosphazene (**TBP**) molecules have already been reported by Carriedo et al.<sup>15</sup> but inclusion adduct formation has not been investigated until now.

We report herein the elaboration of inclusion compounds from (*S,S,S*)-**TBP** host and achiral guests and its crystal structure. Information on host–guest packing modes and on intermolecular interactions is a preliminary result that will be useful for the future aim to use chiral TBP for racemic resolution. Moreover, molecular structure allows a better understanding on spirocyclic seven-membered ring cyclotriphosphazene and, more precisely, on the influence of locking aromatic conformational arrangement from biphenyl units in **TbiPhP** or bipyridyl units in **TbiPyP** to binaphthyl units in chiral **TBP**.

### Results and discussion

#### Synthesis of (*S,S,S*)-**TBP**

(*S,S,S*)-**TBP** was synthesized in one step from (*S*)-binol, hexachlorocyclotriphosphazene, and  $\text{C}_2\text{S}_2\text{CO}_3$  in refluxing acetone. Product was obtained as a white powder in 94% yield (**Fig. 1**).

\* Corresponding authors.

E-mail address: [olivier.dautel@enscm.fr](mailto:olivier.dautel@enscm.fr) (O.J. Dautel).

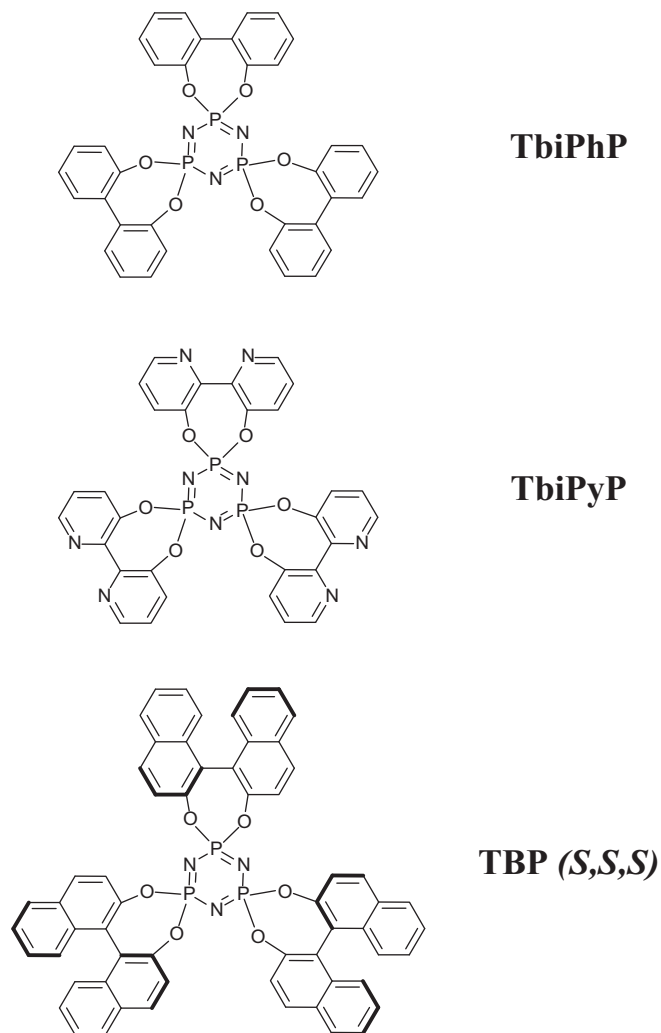


Chart 1. Structures of seven-membered ring cyclotriphosphazenes.

### Crystal structure<sup>17,18</sup>

(*S,S,S*)-**TBP** co-crystallizes with two *o*-xylene molecules in an orthorhombic unit cell with space group  $P2_12_12_1$  (Fig. 2). Each unit cell contains four (*S,S,S*)-**TBP** host and eight *o*-xylene guest molecules. The (*S,S,S*)-**TBP** molecules interact essentially through C··H van der Waals interactions characteristic of the herringbone structures of aromatics, to give a columnar arrangement along *a*-axis. Host–host interactions in the *bc* plane are almost absent.

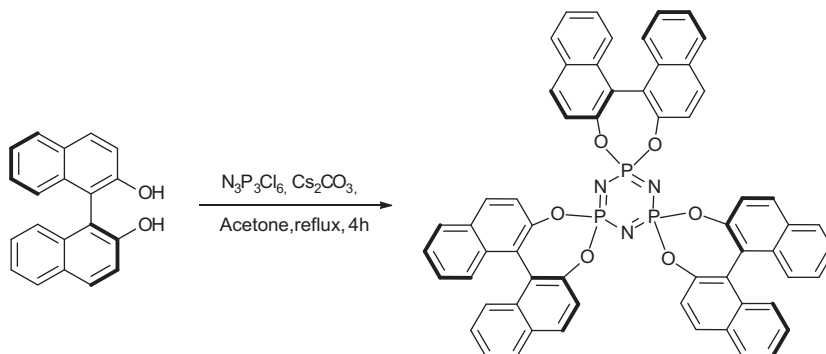


Figure 1. Synthetic path to the (*S,S,S*)-**TBP**.<sup>16</sup>

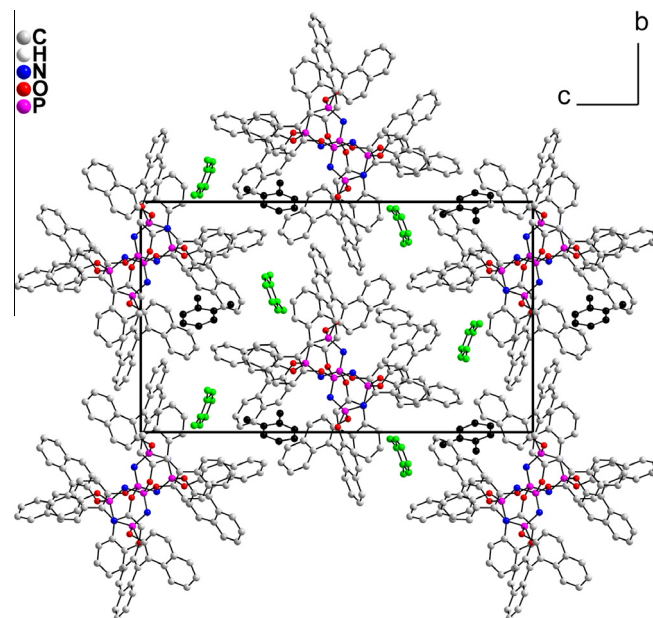


Figure 2. Unit cell of (*S,S,S*)-**TBP** inclusion adduct. *o*-Xylene molecules are represented in black and green (see text).

One of the two *o*-xylene molecules (in green in Fig. 2) lies within these cage-like cavities between host rods shaped columns running along *a*-axis, while the second one (in black in Fig. 2) is sandwiched between naphthyl moieties, interacting with hosts of the same column and between hosts of different columns. This complex set of interactions suggests that the crystal structure is highly guest dependent.

**TbiPhP** does not form inclusion compounds and crystallizes alone in a very different manner. **TbiPyP** forms inclusion adduct with a mixture of toluene and dichloromethane but crystal arrangement is also different.

### Molecular structure

#### General features

(*S,S,S*)-**TBP** has a propeller-like molecular structure with three binaphthyl units twisted in the same direction (Fig. 3). In the case of **TbiPhP** and **TbiPyP**, conformation of the two aromatic substituents of each paddle is not locked as for binol units. Thus rotation between the two aromatic units is possible. In **TbiPhP** crystal structure, molecules adopt a compact arrangement with two paddles twisted in one direction and the third one twisted in the opposite direction. By contrast, in toluene-dichloromethane-**TbiPyP**

Download English Version:

<https://daneshyari.com/en/article/5258676>

Download Persian Version:

<https://daneshyari.com/article/5258676>

[Daneshyari.com](https://daneshyari.com)