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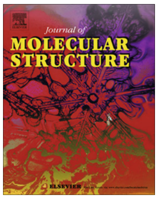

Two unprecedented aromatic guanidines supramolecular chains self-assembled by hydrogen bonding interaction

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HIGHLIGHTS

- Two aromatic guanidines were synthetized with high yields which self-assembled into supramolecules *via* H-bond interactions.
- Crystal **1** showed helix chains while crystal **2** presented ladder-like chains with alternate ring structures.
- Using POMs (polyoxometalates) to help assembly was found to be a good way to design supramolecular chains.

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ABSTRACT

Two aromatic guanidine derivatives, $C_6H_5N=C(NHCy)_2$ (**1**), (n-TBA)$C_6H_5NHC(NHCy)_2Mo_2O_7$ (**2**) (Cy = cyclohexyl), were synthetized with high yields. Both of them self-assembled into supramolecules *via* H-bond interactions. Single crystal XRD indicated that crystal **1** showed helix chains combining pseudo four-fold and pseudo six-fold symmetries, while crystal **2** presented ladder chains with alternate ring structures. In this paper, a novel way to design ladder-like supramolecular chains from helix chains was presented, using POMs (polyoxometalates) to provide protons to help assembly.

Introduction

Hydrogen bonding interaction has raised concerns in the fields of supramolecular chemistry, crystal engineering, biological chemistry and enzyme catalysis [1]. It is of great importance to investigate the self-assembly of supramolecular by hydrogen bond interaction, which plays a vital roles in the design of new crystalline materials. The charge-assisted hydrogen bonds have been widely studied and exploited to build periodical supramolecular structures since 1989 [2]. Hydrogen bonding is essential in biological structures. H-bond donor (HBD) groups in some enzyme can serve as active sites and promote the reactivity of electrophilic substrates and thus participate in conceptually parallel processes [3]. Jacobsen et al. reported efficient catalytic versions of the addition of CN^- onto ketone or imines and relevant chemistry by using a series of crescent-shaped organic structures designed with HBDs including guanidine-based small molecules [4]. Besides, strong hydrogen bonds also have been well studied by Wang's group who mainly reported the proton-transfer supramolecular salts between organic acids and bases [5].

Guanidine derivatives, RN = C(NHR′)(NHR″) (Fig. 1), are one of the strongest organic bases (pKa = 13.6) known in chemistry, which can be used as base catalysts in organic synthesis and serve as important biological chemicals [6]. It is worth mentioning that aromatic guanidines have good biological activities and significant effects on antibacterial, antiviral, diabetes, etc. Therefore, it is widely used in medicine and pesticide industries [7,8]. The investigation on guanidine derivatives, especially aromatic guanidine derivatives, is an important step to better understand the biological activities and the pharmacological effects. Furthermore, the study on the self-assemblies of many supramolecular guanidine compounds [9] may provide us a deeper insight on the

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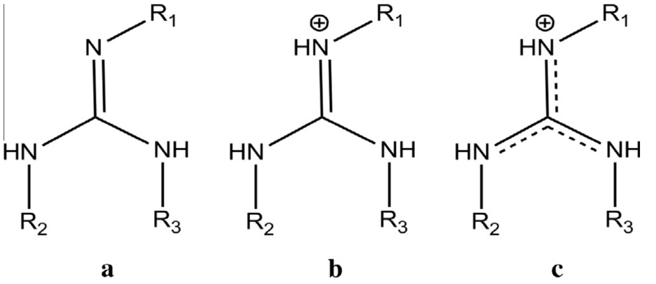


Fig. 1. The structures of guanidines.

understanding of the nature and mechanisms of guanidine compounds to participate in the physiological process *via* hydrogen bonding and the intermolecular interactions which control the supramolecular formations. We assumed that novel supramolecular guanidines or guanidinium can be obtained by controlling the protonation conditions and the self-assembly of hydrogen bond interactions. In our group, a growing number of POM-based organoimido derivatives are obtained by imidoylization [10], the well-developed DCC procedure, in which α-$[Mo_8O_{26}]^{4-}$, different amines, the corresponding amine hydrochlorides, and DCC are mixed together at different ratios has been used under anhydrous conditions. However, we found that a lot of guanidine derivatives could be obtained under anhydrous conditions by increasing the amount of aromatic amines (e.g. aniline) and DCC.

In this paper, two aromatic guanidine derivatives, $C_6H_5N = C(NHCy)_2$ (compound **1**, see Scheme 1a and Fig. 2) and (n-TBA)$C_6H_5NHC(NHCy)_2Mo_2O_7$ (compound **2**, see Scheme 1b and Fig. 3, Cy = cyclohexyl), were synthetized by a simple and efficient method. Both of them could self-assemble into supramolecular structures *via* hydrogen bonding interactions, which provided us the opportunity to study the role of strong hydrogen bonds in the self-assembly of supermolecules and weak interactions in crystal packing.

Experimental

*Syntheses, elemental analyses and FTIR spectra characterization of compounds **1**–**3***

All the chemicals, including solvents, were commercially available as reagent grade and used as received without further purification from Adamas-beta® except for anhydrous acetonitrile which was dried by refluxing in the presence of CaH_2 and was distilled prior to use. Elemental analyses were performed by Elementar Analysensysteme GmbH (vario EL). IR spectra were measured by using KBr pellets and recorded on a Perkin Elmer FT-IR spectrometer.

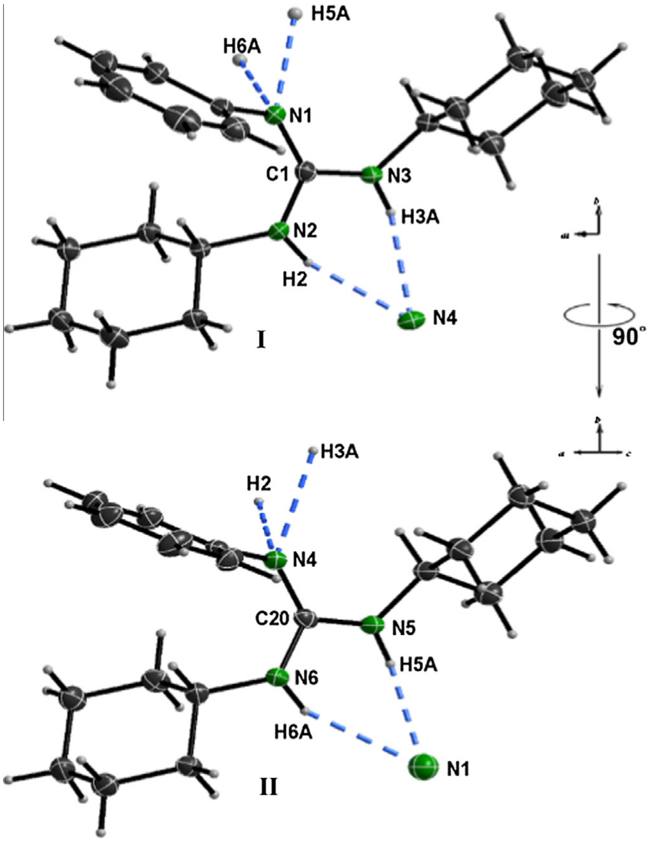
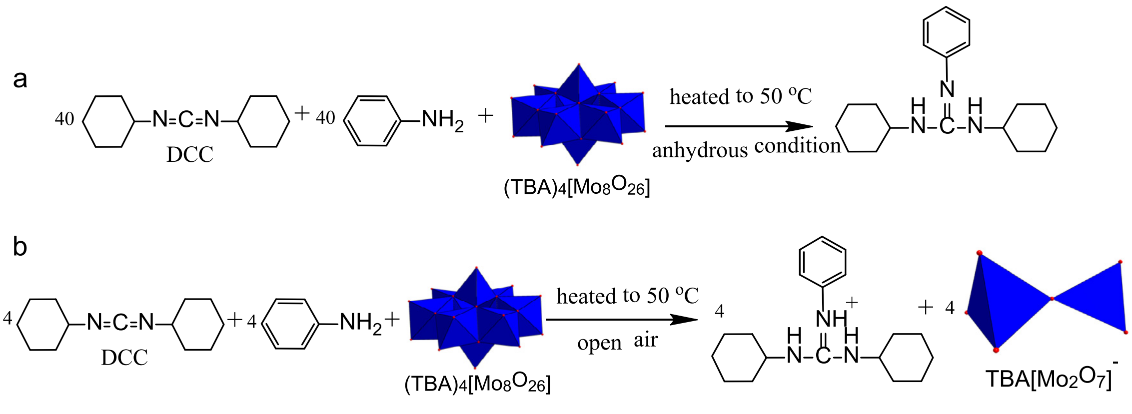


Fig. 2. ORTEP plot of compound **1**. Thermal ellipsoids are drawn at the 50% probability level. Broken lines represent hydrogen bond interactions. Part **I** and **II** almost the same after **II** turns 90° (Color code: N, green; C, black; H, gray). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

*$C_6H_5N = C(NHCy)_2$ (Cy = cyclohexyl, compound **1**)*

(n-TBA)$_4$$[Mo_8O_{26}]$ (1.077 g, 0.5 mmol) was transferred to a conical flask containing a solution of *N,N′*-dicyclohexylcarbodiimide (DCC) (4.127 g, 20 mmol) and phenylamine (1.863 g, 20 mmol) in 20 mL of anhydrous acetonitrile. The mixture was stirred for 5 min and then heated to 50 °C in anhydrous condition for 6 h. After cooling to room temperature, the brown solution (some



Scheme 1. The synthesis of compounds **1** and **2**.