

# On the structure and spectroscopic properties of free and protonated adamantanes

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## Abstract

The equilibrium structures of a selection of tetraazatricyclo-alkanes, containing a small, medium or macro-intramolecular cavity, were investigated with the density functional theory *ansatz* B3LYP/6-31G+(d,p). The four nitrogen lone pair orbitals (LPOs) are outwardly oriented in the smallest two members of the class (hexamethylenetetramine and next homologue), while they point towards the inside in the larger cages (hexaethylenetetramine and next homologues). These conformational arrangements are maintained in the monoprotinated derivatives, whose theoretical structural models are consistent with evidence obtained from IR, NMR and X-ray spectroscopic data. The case of inside-coordination is characterized by a relatively strong five-centre intramolecular hydrogen bond, which involves asymmetric protonation at one nitrogen and nearly equivalent interaction with the other three unprotonated nitrogens. The NMR chemical shifts, calculated by the continuous set of gauge transformations formalism with the B3LYP/6-311+G(2d,p) method, are fairly consistent with NMR observation, in particular for the very low-field signal of the encapsulated proton. The electronic structure of the free bases was also studied by means of ab initio outer valence Green function calculations, which give a consistent, overall description of the different manifolds of photoionization, associated with the nitrogen LPOs. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Ab initio calculations; Structures; Nuclear magnetic resonance chemical shifts; Photoelectron spectra

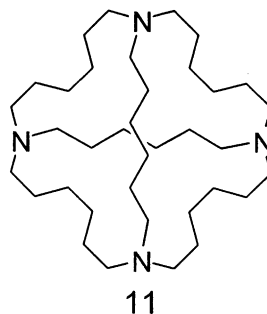
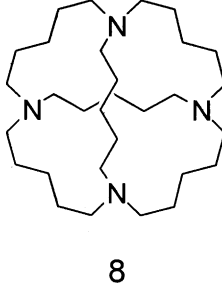
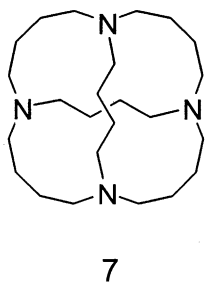
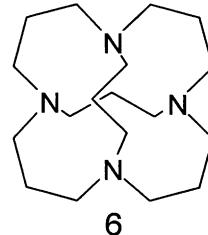
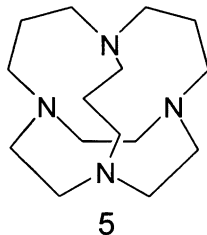
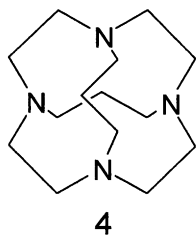
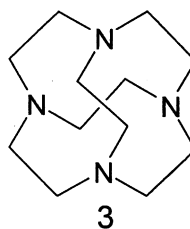
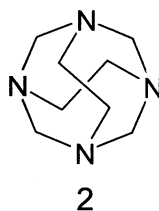
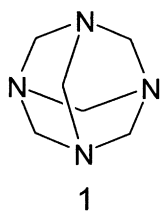
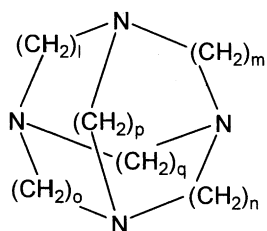
## 1. Introduction

Tricyclic alkanic tetraamines are a class of caged compounds containing four nitrogen atoms in an approximately tetrahedral arrangement which are interconnected by six different alkanic chains. Since the official IUPAC names of these com-

pounds are very impractical, the simplified nomenclature suggested by Springborg et al. [1] has been adopted throughout this paper; accordingly, they are referred to as *adamanzanes*. The compounds investigated here can be represented by the notations  $[r^s]$  and  $[r^s.t^u]$ , which indicate  $r$  chains  $-(\text{CH}_2)_s-$  and  $t$  chains  $-(\text{CH}_2)_u-$ , respectively.

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The synthetic approaches, thus far reported, to such free and protonated compounds have yielded a surprising variety of situations. Indeed, the first two members **1** [1<sup>6</sup>] ('hexamethylenetetramine') and **2** [1<sup>4</sup>.2<sup>2</sup>] have been long documented in the

literature [2,3]. Three macrotricyclic compounds have been recently obtained by Ichikawa and co-workers [4–6]: **8** [5<sup>6</sup>], **9** [5<sup>3</sup>.6<sup>3</sup>], and **10** [5<sup>2</sup>.6<sup>4</sup>]. Earlier, Schmidtchen [7] succeeded in preparing the largest analogues **11** [6<sup>6</sup>] and **12** [8<sup>6</sup>]. In con-

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