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CONFORMATION OF THE AMIDE BOND IN TOPOGRAPHICALLY RESTRICTED ENVIRONMENT

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Abstract Graph set methodology used for the group of di- and tetraza-coronands showed characteristic intra- and intermolecular hydrogen bond patterns stabillizing molecular conformation and crystal lattice.

INTRODUCTION

Prediction of relations between amide units in multiamide systems might be of importance for molecular interactions in many areas of chemistry and biology. A class of macromolecular ring systems containing various heteroatoms (O,N,S) is widely exploited by supramolecular chemists as a source of models for studying of selectivity of molecular recognition.

Present contribution reports on interactions of amide units in the class of di- and tetraazacoronands. Convenient method of synthesis of the above compounds by reaction of primary α,ω-diamines with methyl esters of α,ω-diacids in methanol[1] yields ring systems with various ring size and number and distribution of ether groups and amide units. We were particularly interested if there is any characteristic hydrogen bond pattern stabilizing conformation of the molecule or the construction of the crystal lattice. In the case of compounds with larger ring size (18- to 30-membered) incorporation of small molecules in order to prevent collaps of the ring's interior were studied.

RESULTS

X-Ray structure analysis performed for 11 compounds showed that hydrogen bond

system always exhibits two- or four-fold symmetry (crystallographic or not), observed also in NMR spectra.

Hydrogen bond patterns analysed using graph-set methodology[2] revealed quite strong system of intra- and intermolecular hydrogen bonds characteristic for this class of compounds. The basic pattern stabilizing ring conformation is that between amide H-atom and ring oxygen located in β-position to the carbonyl C-atom [N_1=2S(5)]. As you might see from Scheme 1 showing molecular conformation of some compounds, if no such oxygen is present (molecules I[3] and III[4]) intermolecular hydrogen bond is preferred. In that case significant distortion of the ring torsion angles from ideal 60,180° values is observed. Planar amide units tend to form dihedral angle of 40-60° with the l.s. plane of the ring. 15-Memberd ring (II)[5] is the only case when amide nitrogens are bonded to the remaining ring oxygen, however the same type of pattern is observed.

One water molecule is present in some 18- and 21-membered rings. With the enlargement of the ring's size the number of water molecules increases. One water molecule is always (except of 24-membered ring) acceptor for the two amide hydrogens, forming rings of two different sizes - N_2=R^1_2(13 or 16). One water H-atom may form additional single or bifurcated hydrogen bond with the remaining ring oxygens with the simplest N_3=C(4) or N_4=R^2_1(4) pattern (see compounds IV[6] and V[7]).

An intermolecular H-bond system formed in the absence of water molecule is that containing chains of N_5=C(4) or N_6=C^2_2(8) pattern. In the presence of water N_7=C(3) pattern is observed between carbonyl and rarely ether oxygens and water molecules.

In conclusion, conformation of the ring system in diazacoronands is highly affected by several characteristic patterns of hydrogen bonds. More studies are in progress to make these findings more general.

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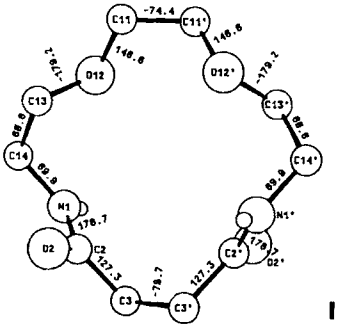

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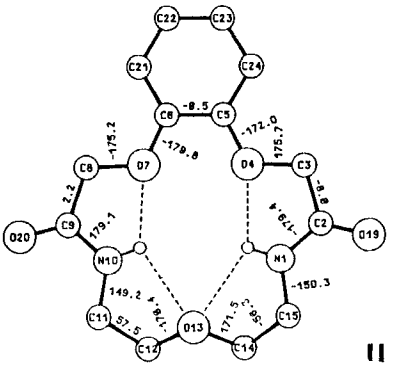

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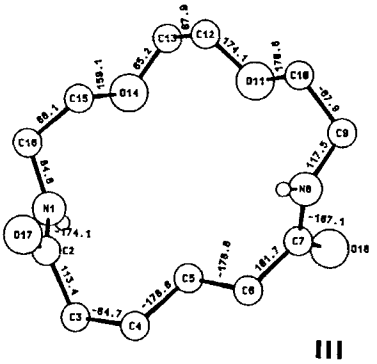

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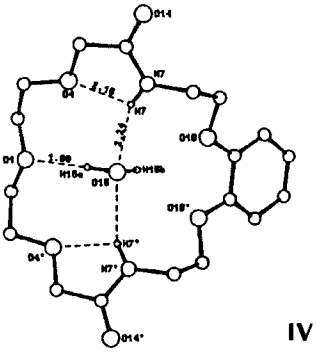

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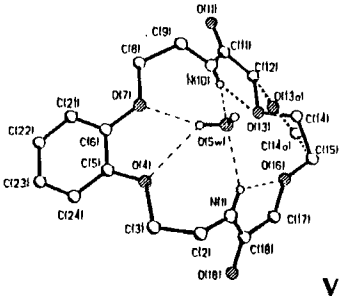

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