## TRIS[2-(TETRAZOL-5-YL)ETHYL]NITROMETHANE, THE FIRST EXAMPLE OF A BRANCHED POLYNUCLEAR TETRAZOLE SYSTEM

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Open chain branched structures ("molecular octopuses") with terminal azolyl groups have been discussed as highly effective polydentate ligands for binding metal atoms in stable complexes [1]. The syntheses of such structures with terminal imidazoline and pyrazolyl groups have been reported, but molecular octopuses with terminal NH-tetrazolyl units have not yet been obtained. Consequently polydentate ligands with NH-tetrazole groups are of considerable interest [2, 3].

We have proposed a simple universal route for the synthesis of branched polynuclear systems containing NH-tetrazoles based on the 1,3-dipolar addition of alkylammonium azides to nitriles, the mechanism of which has been discussed [4]. The use of branched polynitriles as substrates in this reaction has not been examined because of the poor entropy factors. Suitable polyfunctional nitriles may be obtained by cyanoethylation with acrylonitrile of most substrates containing mobile hydrogen atoms [5]. As a first example of this synthetic scheme we synthesized tris[2-(tetrazol-5-yl)ethyl]nitromethane.



The structure of tris(tetraazolylethyl)nitromethane II has been confirmed by IR and <sup>1</sup>H NMR spectroscopy. Elemental analysis results agree with calculated values.

**Tris**[2-(tetrazol-5-yl)ethyl]nitromethane (II,  $C_{10}H_{15}N_{13}O_2$ ). Yield 60%. mp 211°C (dec.). IR Spectrum (KBr): 3200-3000 (NH), 2888 (CH<sub>2</sub>), 1584, 1352 (NO<sub>2</sub>), 1432, 1240, 1108, 1048, 1024 cm<sup>-1</sup> (tetrazole). <sup>1</sup>H NMR Spectrum (200 MHz, DMSO-D<sub>6</sub>): 2.55 (6H, br.s, <u>CH<sub>2</sub>CN<sub>4</sub>H</u>), 3.01 (6H, br.s, <u>CH<sub>2</sub>CH<sub>2</sub>CN<sub>4</sub>H</u>), 4.93 ppm (3H, s, NH). <sup>13</sup>C NMR Spectrum (50.3 MHz, DMSO-D<sub>6</sub>): 155,110 (C-tetrazole), 92.665 (C-NO<sub>2</sub>), 32.020 (<u>CH<sub>2</sub>CH<sub>2</sub>CN<sub>4</sub>H</u>), 17.905 ppm (<u>CH<sub>2</sub>N<sub>4</sub>H</u>).

Analysis of the spacial structure of the nitrile I and the tetrazole II carried out by molecular mechanics (MM2) and quantum chemical calculations (MNDO) revealed the structural characteristics resulting from replacement of the nitrile groups by tetrazoles, for example the major change in the relative positions of the hydrogen atoms in the methylene groups on going from compound I to compound II. This effect is reflected in the nature of the spin-spin interactions between the protons of these groups. For example, in the <sup>1</sup>H NMR spectrum of compound the characteristic triplet of the CH<sub>2</sub> group is observed, but this changes to a broad singlet on replacing the nitrile group by tetrazole (compound II).

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