2-Aminoimidazolines are very good substrates for the synthesis of a fused imidazolidine containing ring systems, e.g., imidazo[1,2-a][1,3,5]triazines or imidazo[2,1-c][1,2,4]triazines. Some of their derivatives have exhibited significant pharmacological activity, especially in the central nervous system, e.g., antinociceptive, antiepileptic or serotonergic activity. 2,3 Based on this observation, we decided to synthesize 1-alkyl-5-(1-naphthyl)-2-aminoimidazolines, and to use it for the synthesis of fused systems. Different alkyl substituents were used to check their effect on the activity of the synthesized fused compounds.

The title 1-methyl-5-(1-naphthyl)-2-aminoimidazoline-2 hydrobromide was synthesized from N1-methyl-1-(1-naphthyl)-1,2-diaminoethane 4 and cyanogen bromide. In order to establish tautomerization of the guanidine fragment and localization of the formal positive charge in the investigated molecule (Scheme 1), an X-ray analysis was undertaken.

A solution of N1-methyl-1-(1-naphthyl)-1,2-diaminoethane (0.1 mol) in 100 ml of 2-propanol was added dropwise into a solution of cyanogen bromide (0.1 mol) in 150 ml of 2-propanol. The mixture was stirred for 4 h at the room temperature, and then under reflux for an additional 4 h. The mixture was kept overnight, precipitation separated and purified by crystallization from a methanol-2-propanol (1:2) mixture. Yield 84%, m.p. 251 – 2˚C [Calcd. %: C 54.91, H 5.27, N

The title compound, C14H16N3Br, crystallizes in the monoclinic system, space group P21/n, with cell constants a = 11.8837(5)Å, b = 8.3762(3)Å, c = 13.9106(6)Å, β = 105.889(4)˚A and Z = 4. The partially saturated imidazoline ring adopts a half-chair conformation. The guanidine part of the molecule is planar with full delocalization of the π-electrons and formal positive charge between three C–N bonds and three possible proton positions.

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13.73; Found %: C 54.92, H 5.15, N 13.66.

Colorless prismatic crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a 1-butanol solution. X-ray data were collected on an Enraf Nonius MACH 4 four-circle diffractometer at room temperature: crystal size, 0.25 × 0.18 × 0.10 mm, ω–2θ scans. The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic temperature factors for non-H atoms. All hydrogen atoms were located from a ∆ρ map, and their coordinates were refined with isotropic displacement parameters taken as 1.5-times those of the respective parent atoms. Details of the crystal data and a structure refinement and selected geometrical parameters are given in Tables 1, 2 and 3. A view of the molecule with numbering of the atoms is shown in Fig. 1.

The three C–N bond lengths in the guanidine part of the title molecule have very similar values of 1.325(5), 1.328(6) and 1.330(6) Å for C2–N1, C2–N21 and C2–N3, respectively, intermediate between the expected single- and double-bond lengths. This suggests that the π-electrons in this system are delocalized between all three C–N bonds, and that the guanidine fragment is a hybrid structure of both tautomeric forms presented in Scheme 1. Similarly, the presence of the three Br−····H+ short interatomic contacts (Br1−H31 = 2.81(6) Å, Br1−H212 = 2.77(7) Å and Br1−H211 = 2.42(6) Å) indicate that the formal positive charge on the aminoimidazoline base is also delocalized between three possible proton positions in the guanidine part of the molecule. The partially saturated imidazoline ring adopts a half-chair conformation with opposite displacements of the C4 and C5 atoms from the ring plane defined by the three N1–C2–N3 atoms of the guanidine moiety location of this ring by –0.183(5) and 0.098(4) Å, respectively. The orientation of the naphthyl substituent in relation to the heterocyclic system is described by a torsion angle (C4–C5–C51–C52) of –27.9(5)°.

References