X-RAY DIFFRACTION EXAMINATION OF THE MOLECULAR STRUCTURE OF GUANAZOLE (3,5-DIAMINO-1H-1,2,4-TRIAZOLE)

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In the case of guanazole, five isomeric forms can exist. From the study of UV and IR spectra, amino-imine [1], diimine [2] and diamine [3] structures have been attributed to guanazole. According to the data of the quantum-chemical calculation of the heat of formation, the diamine asymmetric form is the most probable structure [4]. To unequivocally determine the structure of the guanazole molecule in the crystalline state, we carried out out an x-ray diffraction study.

Guanazole crystallizes in a monoclinic syngony, steric group $P2_1/b$. In the unit cell with parameters a = 10.658 (2), b = 10.837 (2), c = 4.339 (1) Å, γ = 118.83 (2)°, there are four molecules; ρ_{roent} = 1.49 g/cm^3. A tridimensional set of 816 nonzero independent reflections was obtained from a single crystal 0.3 × 0.3 × 0.2 mm in size on a four-circular automatic diffractometer $P2_1$ "Sinteks." The coordinates of the carbon and nitrogen atoms were found directly by the "Roentgen-70" program [5]. The structure has been more precisely specified by taking into account the anisotropy of the thermal vibrations of the atoms by means of a set of x-ray diffraction programs "X-RAY 72" [6] up to R-factor 0.033. The unequivocal localization of the hydrogen atoms on the differential Fourier synthesis showed that guanazole crystallizes in a diamine asymmetric tautomeric form (3,5-diamino-1H-1,2,4-triazole), as also indicated by quantum-chemical calculations [4].

The bond lengths and angles in the guanazole molecule are shown in Fig. 1. All the C–N bonds have an intermediate value between a single and a double bond, and the N–N bond has almost the same value as the single bond. The N–H distances in the guanazole molecule differ

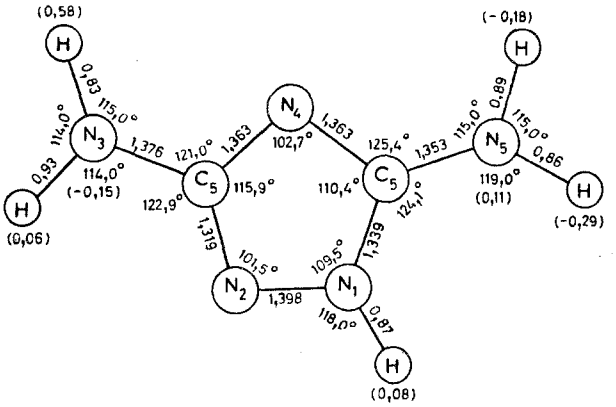

Fig. 1. Bond lengths and angles in the guanazole molecule. Standard deviations for the C–N and N–N bond lengths do not exceed 0.002 Å, for the N–H – 0.02 Å, and the standard deflections for the CNN and NCN angles are 0.2°, for the CNH and NNH angles – 2°. The departures of the atoms from the ring plane are shown in brackets.

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somewhat, probably as the result of nonequivalence of the hydrogen bonds joining the molecules.

The geometry of the triazole ring is similar to that of the ring in aminotriazole [7] and other derivatives of 1,2,4-triazole (see, e.g., [8]). The triazole ring is planar, and the planarity equation, calculated by the method of least squares, has the form: $-0.97x + 10.52y + 5.59z = 7.40$. The two amino groups are inclined towards the plane of the ring at an angle of 29.5° (at N_5) and 21.5° (at N_3). The 1-H hydrogen atom is also deflected from the ring plane.

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