INFRARED SPECTRA AND STRUCTURE OF SOME 3,5-DIAMINO-1,2,4-TRIAZOLES (GUANAZOLES)

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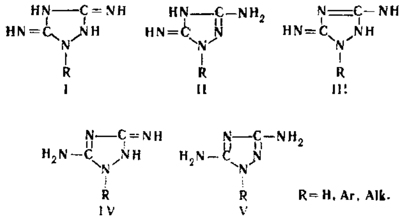
The IR spectra of guanazole and 1-methyl- and 1-phenylguanazoles have been recorded. A comparison of the IR spectra of the products before and after deuteration at the N—H bonds has shown that they have the diamino structure.

Pellizzari [1] isolated a product of the reaction of hydrazine hydrochloride with dicyandiamide which he called guanazole and to which he ascribed the structure 3,5-diiminotetrahydro-1,2,4-triazole. The use of arylhydrazines as one of the components led to the synthesis of 1-arylguanazoles [1–5]. Later, a number of investigations was carried out on the optimum conditions for the reaction [6,7].

Stolle and Dietrich [8] observed that the existence of the following types of structures (I–V) is possible for the guanazoles, and for convenience of illustration they proposed to use the diamine structure V.



R= H, Ar, Alk.

Later, Steck and Nachod [9], studying the UV spectra of the 1-arylguanazoles, suggested that they have the structure of 3(5)-amino-5(3)-imino-1-aryl-1,2,4-triazolines (III or IV); however, they considered that the existence of the diaminotriazole form V could not be excluded. Finally, in 1963 a paper appeared [10] in which, on a basis of the study of the IR spectra, the diimino structure I was ascribed to guanazole and methylguanazole.

As has been shown by Angyal and Angyal [11], chemical methods of establishing structure are unsuitable for aminoheterocycles. Consequently, for a definitive elucidation of the structure of a number of guanazoles in the crystalline state we have made a comparison of their IR spectra before and after deuteration at the N—H bonds. The use of the results of partial [12,13] and exhaustive [14–17] deuteration has been used succesfully for the solution of similar problems.

In the region of the NH stretching vibrations of 1,2,4-triazole there are two absorption bands (Fig. 1). The first of them, at 3400 cm^{-1}, is comparatively diffuse and it can be ascribed to the stretching vibrations of the NH of the ring. The band at 3100 cm^{-1} was previously [19] ascribed to the NH stretching vibrations of the ring but, apparently, incorrectly, since the intensity of this band scarcely changes on deuteration. Thus, the band at 3100 cm^{-1} must apparently be ascribed to the C—H stretching vibrations in the heterocyclic ring.

It is known [16,17,19,20] that in 1,2,4-triazole derivatives with a fixed imino structure there is a strong absorption band in the 1700–1600 cm^{-1} region corresponding to the vibrations of an exocyclic C═N band. There is no absorption in this region in the spectrum of 1,2,4-triazole.

The spectra of guanazole and 1-methyl- and 1-phenylguanazoles that we studied have groups of strong bands in the 3300–3000 cm^{-1} region caused by the symmetrical and antisymmetrical vibrations of the NH_2 groups and also, for guanazole, by the NH vibrations of the ring (Figs. 2a, 3a, and 4a).

After the first deuteration of the compounds studied, the intensity of the bands in the 3000 cm^{-1} region decreased, while in the 2500 cm^{-1} region a new group of bands appeared. No new details of the spectrum appeared in the region of the symmetrical and antisymmetrical vibrations of the NH group.

However, the method of partial deuteration cannot show the structure of the compounds studied unambiguously, and for a definitive proof of the structure we subjected the products to more far-reaching deuteration.

After fivefold deuteration the bands in the region of the NH stretching vibrations had almost disappeared, and in place of them bands had appeared in the 2500 cm^{-1} region which is characteristic for the stretching vibrations of the ND bond (Figs. 2b, 3b, and 4b).

In the region of the deformation vibrations of the amino group in the spectra that we studied, a strong band is found at 1620–1640 cm^{-1} which may be due either to the vibrations of the exocyclic C═N bond (for the diimino structure I [10]) or to the deformation vibrations of the NH_2 group (in the case of the diamino structure V). In addition, it may be regarded as a summary band for the amino-imino structures II–IV.

For the diimino compound I, the replacement of hydrogen by deuterium should not lead to substantial changes in the positions and intensities of the band in the 1620–1640 cm^{-1} region.

In the case of an amino-imino structure (II–IV), there should be a weakening or a splitting (on partial deuteration) in the 1620–1640 cm^{-1} region.

In the case of the diamino structure V, this band should disappear almost competely, with the appearance in the 1100–1200 cm^{-1} region of a band caused by the vibrations of the ND group.

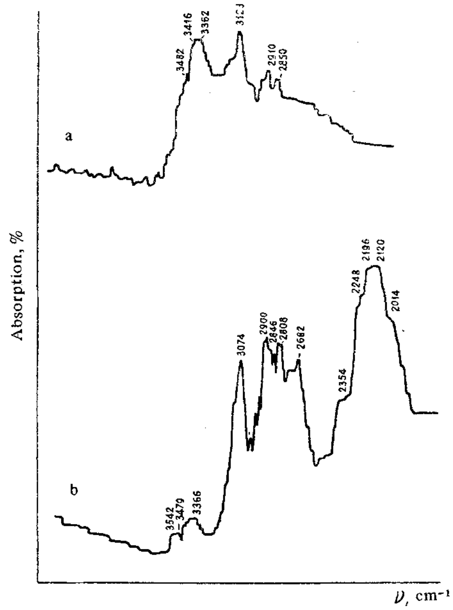


Fig. 1. IR spectra of 1,2,4-triazole in KBr in the region of the NH stretching vibrations: a) before deuteration; b) after deuteration

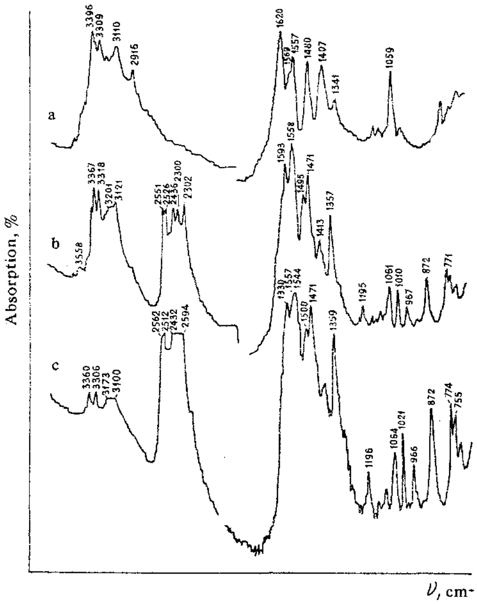


Fig. 2. IR spectra in KBr of 3,5-diamino-1,2,4-triazole (guanazole): a) before deuteration; b) after deuteration.

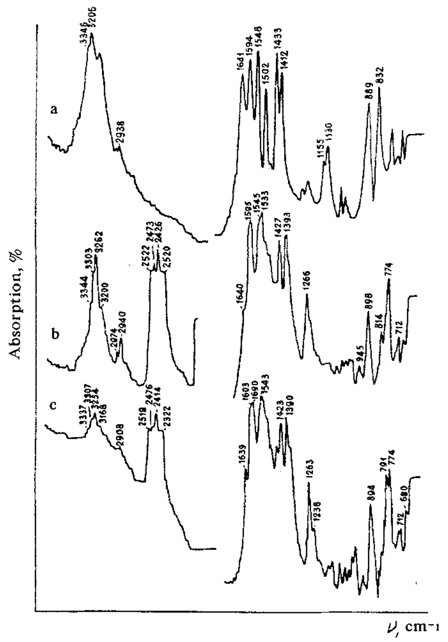


Fig. 3. IR spectra in KBr of 3,5-diamino-1-methyl-1,2,4-triazole: a) before deuteration; b) after deuteration.

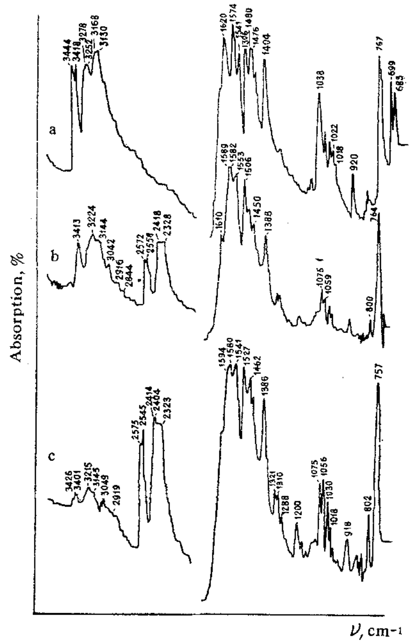


Fig. 4. IR spectra in KBr of 3,5-diamino-1-phenyl-1,2,4-triazole: a) before deuteration; b) after deuteration.

The spectra given in Figs. 1–4 permit the conclusion that a diamino structure of type V, is the most likely in the crystalline state for guanazole and the derivatives of it that have been studied.

EXPERIMENTAL

The compounds studied were obtained by known methods: 1,2,4-triazole with mp 124° C [18], guanazole with mp 204° C [7], and 1-phenylguanazole with mp 174–175° C [5]. 1-Methylguanazole with mp 156° C was obtained in 80% yield from methylhydrazine sulfate and dicyandiamine [5].

The IR spectra were taken on an IKS-14A instrument. The samples were prepared in the form of tablets with potassium bromide. Deuteration was carried out by boiling the substances with heavy water (D_2O) 4-5 times with its subsequent removal by distillation in vacuum.

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