SYNTHESIS AND STRUCTURE OF SOME DIAZONIUM SALTS OF THE 1,2,4-TRIAZOLE SERIES

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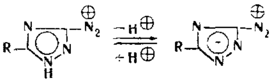
Diazotriazolecarboxylic acid, its methyl ester, and 3-diazonium-5-nitrophenyltriazoles have an internal salt structure. 3-Diazonium-5-methyl- and -5-phenyl-1,2,4-triazoles have been isolated as nitrates, perchlorates, and fluoroborates. All the compounds mentioned exist in strongly acid media as salts of the corresponding acid with diazo cations, but in weakly acid and neutral solutions they exist as zwitterions, formed by elimination of a proton from the imino nitrogen of the heterocycle.

Diazonium salts of the 1,2,4-triazole series have not been investigated to any extent. 3-Amino-1,2,4-triazoles are readily diazotized in mineral acids [1] to give solutions of the diazonium salts, which undergo further conversion into halo [2], nitro [3], and other 1,2,4-triazole derivatives. However no triazolediazonium salts, other than diazotriazolecarboxylic acid [2, 4], have been isolated in the solid state. An internal diazoacylate structure has been assigned [2] to this acid and its ethyl ester [2].

The aim of this work was the preparation of some triazolediazonium salts and the investigation of their structure.

We expected the presence of the electronegative diazonium group in the heterocyclic molecule to result in a considerable increase in the mobility of the imino nitrogen, and consequently lead to diazonium salts with a zwitterion structure (conversion from structure A to structure B).


A B

The formation of this type of diazo compound is seen particularly well in 3-diazopyrazole [5].

The method of diazotization described for aminotriazolecarboxylic acid and its ethyl ester [2, 4] proved unsuitable for m- and p-nitrophenylaminotriazoles, the latter being poorly soluble in HCl. The method given in [6] was more convenient. The bisdiazonium salt from 3,3'-diaminobis-1,2,4-triazol-5-yl was prepared in a similar manner. Diazotization of 3-amino-5-phenyl-1,2,4-triazole in fluoroboric or perchloric acid resulted in the ready isolation of the corresponding phenyltriazolediazonium fluoroborate or perchlorate. These methods, however, proved unsuitable for the preparation of the diazonium salts from 3-amino-5-alkyl-1,2,4-triazoles because of their high solubility and low stability.

The crystalline diazonium nitrate from 3-amino-5-methyl-1,2,4-triazole was obtained by the action of nitrogen oxides on an ether suspension of the amine [7].

The structures of the diazonium salts obtained were confirmed by their elementary analyses, IR spectra, and by their conversion into nitro compounds by the method given in [3] (see table).

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TABLE 1. Diazonium Salts of the 1,2,4-Triazole Series

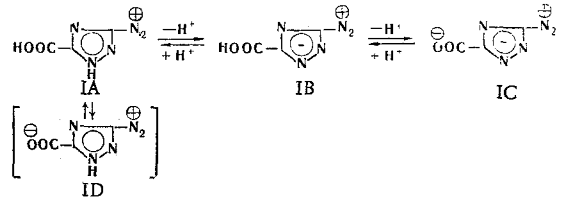
Compound	Name	Molecular formula	Found			Calculated			IR spectrum cm⁻¹ (stretching vibrations of the diazo group)
			Total nitrogen, %	Diazo nitrogen, %	mol wt	Total nitrogen, %	Diazo nitrogen, %	mol wt	
II	Methyl diazotriazolecarboxylate	$C_4H_3N_5O_2$	46,03	18,10	—	45,75	18,30	—	2230
III	3-Diazonium-5-methyl-1,2,4-triazole nitrate	$C_3H_4N_4N_5^+ \cdot NO_3^-$	48,62	15,95	—	48,83	16,27	—	2310
IV	3-Diazonium-5-phenyl-1,2,4-triazole fluoroborate	$C_8H_6N_5^+ \cdot BF_4^-$	27,50	—	—	27,02	—	—	2300 (2295 perchlorate)
V	3-Diazonium-5-(p-nitrophenyl)-1,2,4-triazole	$C_8H_4N_6O_2$	—	12,44	223	—	12,96	216	2220
VI	3-Diazonium-5-(m-nitrophenyl)-1,2,4-triazole	$C_8H_4N_6O_2$	—	12,80	219	—	12,96	216	2200
VII	3,3'-Bisdiazoniumbis-1,2,4-triazol-5-yl	C_4N_{10}	—	28,90	—	—	29,78	—	2220

The high mechanical and thermal sensitivity of the compounds prevented determination of the mp's and, in some cases, the elementary analyses. For these compounds, the diazo nitrogen content was determined by decomposition with sodium nitrite in aqueous solution, and by the mol. wt.

The structures of diazotriazolecarboxylic acid (I), its methyl ester (II), and 3-diazonium-5-methyl-1,2,4-triazole nitrate (III), were investigated by spectral methods. In the IR spectrum of III, the absorption band with a maximum at 2310 cm^{-1} [8] (Fig. 1) was assigned to the stretching vibrations of the diazo group in the diazo cation (structure A). A series of bands of medium intensity in the 1560-1710-cm^{-1} region represented the vibrations of the heterocyclic ring [9]. The wide, very strong band at 1340-1410 cm^{-1} and the weak band at 830 cm^{-1} were attributed to the nitrate ion [10]. Thus, according to the elementary analyses methyl diazotriazolecarboxylate has the zwitterion structure (type B). This is confirmed by its IR spectrum, which clearly shows a shift of the stretching vibration of the diazo group to 2240 cm^{-1}, and a change in its shape (a similar shift is observed in 3-diazopyrazole [5]). The appearance of a band at 1500 cm^{-1} with a simultaneous reduction in the intensity of the band for the heterocycle (1560-1630 cm^{-1}) indicates a transfer of the electron density in the ring, causing loss of the proton from the imino nitrogen to the ring. The presence of an ester group in the spectrum of II was shown by its characteristic absorption at 1740, 1250, and 1050-1070 cm^{-1} [10].

Diazotriazolecarboxylic acid (I) also has the zwitterion structure, but there are two forms in which its bipolar nature may exist (see reaction scheme below): 1) Structure IB, in this case, the IR spectrum of the acid would be very similar to the spectrum of the ester (curve II; or 2) structure ID, in this case, the IR spectrum of I would not contain an acid carbonyl absorption band at 1690-1720 cm^{-1}, but rather a series of wide, strong bands at 1620-1550 and 1400 cm^{-1} due to the carboxylate ion [10]. We see from curve IB (Fig. 1) that the IR spectrum of the acid I still possesses strong bands due to the un-ionized carboxyl at 1710. 1250, and 1090 cm^{-1}, and is very similar to the spectrum of the ester II both with respect to the vibration bands of the diazo group (2240 cm^{-1}), and also in the nature of the absorption curve as a whole. Crystalline diazotriazolecarboxylic acid, therefore, has the structure IB.

The behavior of the acid I in media of differing pH values shows its capacity to undergo protonation. Thus, in weakly alkaline aqueous media, absorption bands due to un-ionized carboxyl (1710 and 1250 cm^{-1}) disappear from the IR spectrum (curve IC, Fig. 1), and bands due to the carboxylate ion appear at 1620 and 1340 cm^{-1}, i.e., structure IC is formed. In this case, the vibrations of the diazo group retain a value characteristic of bipolar ions, 2240 cm^{-1}.



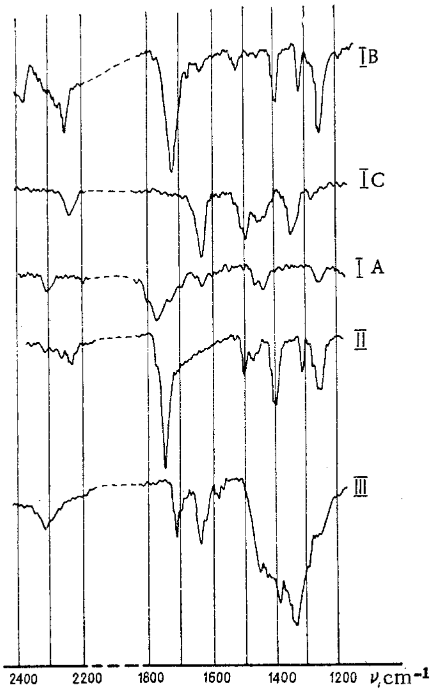


Fig. 1

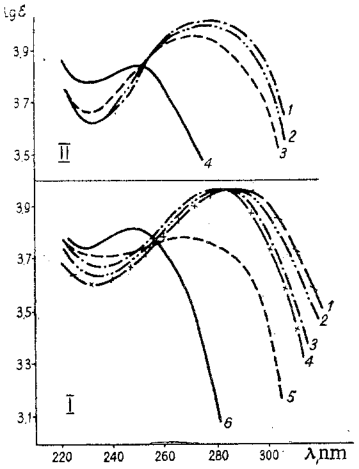


Fig. 2

Fig. 1. IR spectra of (I) diazotriazolecarboxylic acid, (II) its methyl ester, and (III) 3-diazonium-5-methyl-1,2,4-triazole nitrate. IB) Solid film of the diazo acid, IC) solution in NaOH$-D_2O$ (weakly acid medium, IA) solution in $HClO_4-H_2O$, II) solid film of the ester, III) solid film of 3-diazonium-5-methyltriazole nitrate.

Fig. 2. UV spectra of (I) the diazo acid and (II) its methyl ester at various pH values. I. 1) pH 6.8, 2) 4.2, 3) 1.4, 4) 0.8, 5) 35.0% H_2SO_4, 6) 79.8% H_2SO_4. II. 1) pH 1.4, 2) 6.2, 3) 28.3% H_2SO_4, 4) 79.8% H_2SO_4.

In strongly acid aqueous media (perchloric acid solution), the prototropic equilibrium is shifted in the direction of structure IA. The IR spectrum of the diazo acid in perchloric acid (curve IA, Fig 1) shows the presence of a strong band due to the un-ionized carboxyl, with a maximum at 1760 cm^{-1}. The shift of the acid carbonyl to higher frequencies (1760 cm^{-1}), and the disappearance of the band at 1500 cm^{-1}, indicate the protonation of the ring nitrogen atom, which was previously bonded by the delocalized electron pair.

The stretching frequency of the diazo group assumes a value of 2310 cm^{-1}, similar to that of the vibration of the diazo group in 3-diazonium-5-methyl-1,2,4-triazole nitrate, i.e., structure A is formed. 3-Diazonium-5-methyl-1,2,4-triazole nitrate in glycol solution, or in nitromethane-trifluoroacetic acid, preserves the same diazo cation structure as it has in the crystalline state (structure A), but in aqueous solution, the diazo cation rearranges into a bipolar ion, which undergoes further irreversible change.

The UV spectral data for I and II confirm the conclusions drawn from the examination of the IR spectra. In strongly acid media ($H_0 = -7$), in which diazo cations of type IA are present, I and II have absorption maxima at 251 nm, log ε 3.86 (curves I6 and II4, Fig. 2). With a reduction in the acidity, the amino nitrogen dissociates and an internal diazonium salt of the type IB is formed. This is shown in the UV spectrum by a strong bathochromic shift of the absorption maximum to 281 nm (log ε 3.99) for I and 278 nm (log ε 4.05) for II (I, curves 3, 4, and 5, and II, curve 3). It is interesting that a similar strong bathochromic shift (by 40-50 nm) has been observed by us in passing from undissociated nitro-1,2,4-triazoles to their anions [11]. A further reduction in acidity does not cause any change in the spectrum of the ester II, although the spectrum of the diazo acid I shows an additional bathochromic shift of 10 nm (I, curves 1 and 2) resulting from dissociation of the hydrogen of the carboxyl group to give the unusual zwitterionic structure having a triazole ring with an ionized carboxyl group (IC).

The results obtained permit the formulation of a scheme for the prototropic conversions of diazotriazolecarboxylic acid from $H_0 = -7$ to pH = 7 (see scheme on p. 654).

It is noteworthy that the initial loss of a proton from IA is from the nitrogen heteroatom rather than from the carboxyl group, while in 3-nitro-5-carboxyl-1,2,4-triazole, the reverse is true [11]. This phenomenon apparently results from the higher stability of the mesomeric anion of the diazo acid IB compared with the analogous anion from 3-nitro-5-carboxy-1,2,4-triazole.

The results obtained also permit the conclusion that the structures of the diazonium salts in the triazole series in the crystalline state depend on the electronegativity of the substituents in the 5-position of the ring. Thus, 5-methyl- and 5-phenyl-substituted diazoniumtriazoles exist in the crystalline state as normal diazonium salts (fluoroborates, perchlorates, and nitrates). The introduction of a nitro group into the phenyl nucleus leads to an increase in the electronegativity of the substituent, which causes an increase in the lability of the heterocyclic imino hydrogen, and 5-nitrophenyldiazoniumtriazoles exist as internal salts in the crystalline state.

EXPERIMENTAL

Methyl Diazotriazolecarboxylate (II). To a solution of 1.42 g (0.01 mole) of methyl aminotriazolecarboxylate [12] in 15 ml of 10% HCl was added at 0° C 0.8 g of sodium nitrite in 10 ml of water. The precipitate of the diazo compound was filtered off after 20 min, and washed with alcohol and ether to give 0.75 g (50%) of product.

3-Diazonic-5-phenyl-1,2,4-triazole Fluoroborate (and perchlorate) (IV). To a solution of 1.6 g (0.01 mole) of 3-amino-5-phenyl-1,2,4-triazole [13] in 15 ml of 15% HCl was added at 0° C a solution of 0.8 g of sodium nitrite in 5 ml of water. The resulting diazo solution was filtered rapidly, and to the solution was added at 0° C 20 ml of 35% fluoroboric acid (or 20 ml of 50% perchloric acid). The precipitated diazonium salt was filtered off to give 1.55 g (60%). The fluoroborate was purified by dissolution in nitromethane and precipitation at 0° C by the addition of benzene.

3-Diazonium-5-(p-nitrophenyl)-1,2,4-triazole (V). A 1.02-g (0.005 mole) quantity of 3-amino-5-(p-nitrophenyl)-1,2,4-triazole [13] in 15 ml of glacial acetic acid was added to a solution of 0.8 g of sodium nitrite in 5 ml of conc H_2SO_4 at 0° C. After 20 min, 10 ml of water was added with cooling, the mixture was filtered, and the filtrate was diluted with 100 ml of water. The precipitate of the diazo compound was filtered off, and dried in air, to give 1.1 g (50%). The product was purified by precipitation from conc H_2SO_4 with water.

3-Diazonium-5-(m-nitrophenyl)-1,2,4-triazole (VI) (yield 50%), and 3,3-bisdiazoniumbistriazol-5-yl (VII) (yield 60%) were obtained in a similar manner.

3-Diazonium-5-methyl-1,2,4-triazole Nitrate (III). Into a suspension of 0.98 g (0.01 mole) of 3-amino-5-methyl-1,2,4-triazole [14] was passed at 0° C for 3 hr a stream of nitrogen oxides obtained by decomposing sodium nitrite with ferric sulfate in acid solution. The precipitate was filtered off and washed with ether to give 1.2 g (70%) of product. A small amount (in view of its instability) of the diazonium salt was purified by reprecipitation from nitromethane with ether at 0° C.

Determination of Diazo Nitrogen. A weighed amount of the diazonium salt was introduced into a 5% solution of sodium nitrite (100 ml), which was kept at 50° C in a closed thermostatic vessel fitted with a differential manometer filled with xylene.

The calculation was carried out using the following formula:

$$\%\ \text{diazo nitrogen} = 2800 \cdot P/aq,$$

where P is the observed pressure of the xylene column in mm, a is the weight of the diazo compound in g, and q is a constant for the system (pressure in mm developed in the xylene column on introducing 1 mole of nitrogen).

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