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SYNTHESIS AND PROPERTIES OF 1,5-DIAMINOTETRAZOLE

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An effective method was developed for preparation of 1,5-diamino tetrazole from thiosemicarbazide and sodium azide in the presence of lead(II) oxide and ammonium chloride in DMFA. Its physical properties and certain reactions were studied.

1,5-Diaminotetrazole (DAT) is a convenient reagent for a directed synthesis of tetrazole-containing compounds, which find application in certain branches of national economy [1]. However, until now DAT is difficultly accessible. Two synthetic methods for the preparation of DAT have been described: 1) based on the reaction of 5-aminotetrazole with hydroxylamine-O-sulfonic acid, DAT is formed in a low (8.5%) yield in a mixture with the 2,5-diaminotetrazole isomer [2]; 2) based on the reaction of more simple and available compounds — thiosemicarbazide, lead (II) oxide and sodium azide in ethanol in a CO_2 atmosphere [3]. The latter reaction has, however, been practically not studied. The authors do not even report the yield of the product. The stage of isolation of DAT as hydrochloride is labor consuming.

In the present work, we tried to find the optimal parameters of this synthetic path. On reproducing the conditions of [3] it was found that the reaction proceeds incompletely and the unreacted thiosemicarbazide contaminates the desired product by reacting with benzaldehyde, which is used to purify DAT. The end product, DAT hydrochloride, is obtained in a 35-40% yield, and its melting point corresponded to the literature data after multiple recrystallizations. We found that the stage of DAT purification via the benzylidene derivative can be eliminated, and the yield of the desired product could thus be increased to 45-50%, if DAT is isolated by recrystallization from water. By using ammonium azide, passage of carbon dioxide is unnecessary, and the course of the reaction is well controlled, as can be inferred from the evolution of ammonia. However, unreacted ammonium azide interferes with the purification of the product, and the yield of DAT is 34-37%. A mixture of equimolar amounts of sodium azide and ammonium chloride in boiling ethanol behaves similarly, but the yield of DAT is still lower (15-20%). The best results were obtained by using a small excess of this mixture in DMFA, and the yield of DAT thus reaches 60%. The improved method of synthesis makes it possible to obtain DAT easily and rapidly in a good yield.

Little is known of the properties of DAT. Triacetyl [2] and benzylidene [3] derivatives have been described. The IR [4] and PMR spectra [2] of DAT have reported. The PMR spectrum of DAT shows a singlet at normal temperature. At −50°C, two resolved singlets are observed spaced 28 Hz apart. The two amino groups of DAT also differ little with respect to the position in the IR spectrum of the absorption bands of the stretching (3305 and 3215 cm^{-1}) and deformational (1624 cm^{-1}) vibrations both in the crystal (KBr tablet) and in solution (DMSO).

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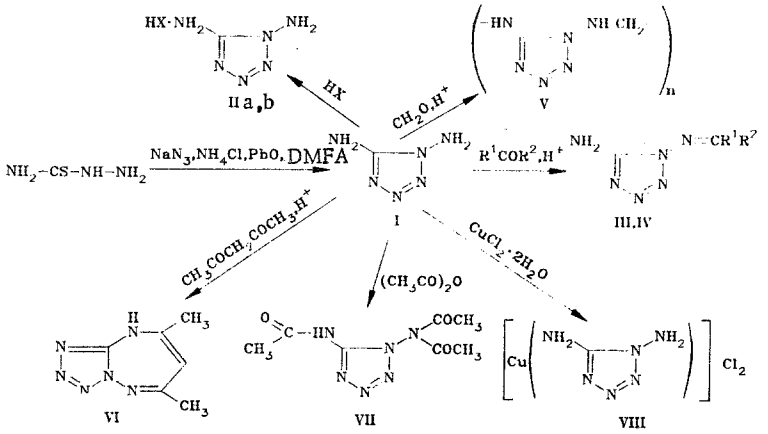
The third band observed in this region at 3145 cm^{-1} should, in our opinion, be assigned to the stretching vibrations of the partially associated amino group [5], and not to the ring N–H bond of the tautomeric imino form of DAT [4]. This agrees with PMR spectral dada, and also with the fact that during successive dilution of the DAT solutions, the intensity of this band decreases considerably.

The amino group in the 1-position is "hydrazinic" in character, so that we can expect a higher reactivity with respect to carbonyl compounds [6], compared with the 5-amino group. For a more reliable relating of the reaction path with respect to the amino group in the position 1 or 5, we studied the chemical properties of DAT in comparison with the properties of 1- and 5-aminotetrazoles (AT). The compounds obtained were identified by elemental analysis, IR and PMR spectroscopy (see experimental part).



II a $X=NO_3$, b $X=C_6H_2N_3O_7$; III $R^1=H$, $R^2=Fc$; IV $R^1=R^2=CH_3$

Like 5-AT, DAT reacts with strong acids as a monohydric base forming stable salts with a 1:1 composition (II). 1-AT does not form similar salts. DAT hydrochloride, nitrate, and picrate have been isolated. The nitrate is sensitive to friction. The PMR spectra of DAT salts show a singlet in the 7.15-7.40 ppm region, corresponding to the absorption of five protons. In the IR spectra of crystalline samples, together with the absorption bands of the free amino group (1-NH_2) in the 3200-3250 cm^{-1} region, there appears a broad band at 3060-3080 cm^{-1}, and several medium-intensity bands in the 2400-2900 cm^{-1} range, which confirms the formation of an ammonium structure [7].

DAT, like 1-AT, readily reacts with carbonyl compounds. Like benzaldehyde [2], ferrocenealdehyde and acetone condense with one of the NH_2 groups of DAT to form the corresponding azomethines (III, IV). Formaldehyde and acetylacetone react with two NH_2 groups, forming in the first case polymeric products V with a molecular weight, estimated from the terminal hydroxyl group content, of 950-1000 nom.u. Like with other heterocyclic ortho-diamines [8], acetylacetone gives with DAT a condensed seven-membered ring – 1H-2,4-dimethyltetrazolo[1,5-b]-1,2,4-triazepine (VI).

The assignment of structure VI, among other possible isomeric structures [9], was chosen based on the analysis of IR and PMR spectra, relative nucleophilicity of the amino groups of DAT, and comparison of the data obtained with the literature data [6, 9]. It should be noted that in the PMR spectrum of compound VI, proton signals of the methine (4.30 ppm) and NH (9.59 ppm) groups were recorded. The IR spectrum of the latter group shows the characteristic absorption bands in the 3100-3300 cm^{-1} region. The more nucleophilic 1-NH_2 group of the initial DAT probably participates in the formation of the triazepine ring ($\nu C=N$ 1625 cm^{-1}).

It is known that the tetrazole ring of several derivatives decomposes by the action of acylating agents with the formation of 1,3,4-oxadiazoles [1]. In boiling acetic anhydride, DAT forms the triacetyl derivative VII, while 5-AT under these conditions, and 1-AT even at room temperature give 5-acetylamino-2-methyl-1,3,4-oxadiazole [2, 10].

DAT has good complexing properties. For example, with copper(II) chloride, it forms a stable 1:1 crystalline complex (VIII), which also distinguishes it from 1- and 5-AT which give with $CuCl_2$ 1:3 [11] and 2:1 complexes, respectively.

EXPERIMENTAL

The PMR spectra were obtained on the Jeol PNS-100 spectrometer (100 MHz) in DMSO-D_6, using HMDS as internal standard. At lower temperatures, the spectra were run in a 4:1 DMFA–ether mixture. The IR spectra were run on the Specord-75IR spectrometer in KBr tablets. The elemental anslysis was carried out on the CHN analyzer (CSSR) using tetrazole as a standard.

1,5-Diaminotetrazole (I). A mixture of 18 g (0.2 mole) of thiosemicarbazide, 16.3 g (0.25 mole) of NaN_3, 13.4 g (0.25 mole) of NH_4Cl, and 89.2 g (0.4 mole) of PbO in 350 ml of DMFA is stirred for 6 h on a boiling water bath. The mixture is filtered while hot, and the filtrate is evaporated off *in vacuo*. The residue is dissolved in 50 ml of hot water, filtered while hot, and cooled slowly. The precipitate is filtered off, washed with cold water, and dried. Yield, 11.8 g (59%), white crystals, mp 186-187°C (dec) (from water). Readily soluble in hot water and in aqueous alcoholic mixtures, acids, and DMFA; moderately soluble in cold water and ethanol; and insoluble in THF, ethyl acetate, methylene chloride, and ether. IR spectrum: 1006, 1084, and 1113 (ring); 1642, 3145, 3215, and 3305 cm^{-1} (NH_2). PMR spectrum: 6.38 (4H, s); at −50°C 6.64 (2H, s); 6.92 ppm (2H, s). Found: C 12.2; H 4.1; N 83.1%. CH_4N_6. Calculated: C 12.0; H 4.0; N 84.0%.

1,5-Diaminotetrazole Nitrate (IIa). A 10 g portion (0.1 mole) of DAT is dissolved at 75°C in a mixture of 16 ml of conc. HNO_3 and 15 ml of water, and the mixture is left to stand at room temperature for crystallization, and then is cooled to 0°C. The precipitate is filtered off and dried in vacuo over P_2O_5. Yield, 15.2 g (93%), white crystals, mp 136-138°C (dec) (from water). PMR spectrum: 7.21 ppm (5H, s). Found: C 7.2; H 3.0; N 59.0%. $CH_4N_6 \cdot HNO_3$. Calculated: C 7.4; H 3.1; N 60.1%.

1,5-Diaminotetrazole Picrate (IIb). A solution of 1.0 g (0.01 mole) of DAT in 15 ml or 95% ethanol is added to 2.3 g of picric acid in 20 ml of ethanol, and the mixture is heated to boiling. The picrate crystallizes on slow cooling. Yield, 2.9 g (88%), yellow crystals, mp 162-164°C (from ethanol). PMR spectrum: 7.36 (5H, s); 8.58 ppm (2H, s, H_{arom}). Found: C 25.3; H 2.0; N 37.9%. $CH_4N_6 \cdot C_6H_3N_3O_7$. Calculated: C 25.5; H 2.1; N 38.3%.

1-Ferrocenylideneamino-5-aminotetrazole (III). A solution of 1.06 g (0.005 mole) of ferrocenealdehyde in 20 ml of ethanol is added to a solution of 0.5 g (0.005 mole) of DAT in 20 ml of 95% ethanol, and then a drop of concentrated H_2SO_4 is added. The precipitate is filtered off, washed and dried. Yield, 1.43 g (97%), red powder, dec. temp. 206-210°C. IR spectrum: 1002, 1066, and 1173 (tetrazole); 1044 (ferrocene); 1600 (CH=N); 1644, 3253, and 3315 (NH_2); 3100 cm^{-1} (CH). PMR spectrum: 3.36 (5H, s, C_5H_5); 4.65 (2H, m, H-3,4); 4.94 (2H, m, H-2,5); 6.98 (2H, s, NH_2); 9.03 ppm (1H, s, CH=N). Found: C 48.5; H 4.0; N 28.0%. $C_{12}H_{12}N_6Fe$. Calculated: C 48.7; H 4.1; N 28.4%.

1-Isopropylideneamino-5-aminotetrazole (IV). A drop of concentrated H_2SO_4 is added to 1.0 g (0.01 mole) of DAT in 25 ml of acetone, and the mixture is boiled for 1 h and then cooled. The precipitate is filtered off, and washed with acetone. Yield, 1.13 g (81%), white crystals, mp 145-147°C (from acetone). IR spectrum: 993, 1042, and 1089 (ring); 1628 (C=N); 1654 (NH_2); 2980 and 3120 (CH_3); 3233 and 3336 cm^{-1} (NH_2). PMR spectrum: 2.11 (3H, s, CH_{3anti}); 2.26 (3H, s, CH_{3syn}); 6.72 ppm (2H, s, NH_2). Found: C 27.8; H 6.3; N 64.3%. $C_4H_8N_6$. Calculated: C 28.1; H 6.3; N 65.6%.

Condensation Product of DAT with Formaldehyde (V). A 15-ml portion of 30% formalin (pH ∿8-8.5) is added to a solution of 5 g (0.05 mole) of DAT in 20 ml of water, and the mixture is heated for 2 h at 80°C. Then 7 ml of concentrated HCl is added and heating is continued for another 30 min. The solution is evaporated *in vacuo*, the residue is dissolved in 50 ml of DMFA, and precipitated by 200 ml of isopropanol. The polymer is filtered off, washed with alcohol and dried in vacuo at 55-60°C. Yield, 4.73 g (80.4%), white powder, decomposition beginning at 161-165°C. IR spectrum: 1022, 1083, and 1138 (ring); 1480 (CH_2); 1617 (NH); 2944 and 3004 cm^{-1} (CH_2). Found: C 21.6; H 3.8; N 71.2; OH 3.5%. $(C_2H_4N_6)_n$. Calculated: C 21.4; H 3.6; N 75.0%.

1H-2,4-Dimethyltetrazolo[1,5-b]-1,2,4-triazepine (VI). Acetylacetone (1.5 g (0.015 mole)) and 3 drops of concentrated HCl are added to 1.0 g (0.01 mole) of DAT in 30 ml of a 1:1 chloroform–ethanol mixture. The mixture is boiled until DAT is completely dissolved (∿30 min). The solution is evaporated *in vacuo*, the residue is washed with a 1:2 mixture of ethanol and ether, and dried. Yield, 1.54 g (92%), orange crystals, mp 204-206°C (dec) (from an isopropanol–chloroform mixture). IR spectrum: 1022, 1086, and 1122 (ring); 1360 and 1439 (CH_3); 1625 (C=N); 2913 and 2955 (CH_3); 3237 cm^{-1}(NH). PMR spectrum: 1.60 (3H, s, CH_3),

1.69 (3H, s, CH_3); 4.30 (1H, s, CH); 9.56 ppm (1H, s, NH). Found: C 43.6; H 4.7; N 50.8%. $C_6H_8N_6$. Calculated: C 43.9; H 4.0; N 51.2%.

1-Diacetylamino-5-acetylaminotetrazole (VII). A solution of 1.0 g (0.01 mole) of DAT in 20 ml of acetanhydride is heated to boiling for 2 h. The product crystallizes on cooling, is filtered off, and dried. Yield, 1.45 g (64%), white crystals, mp 186-188°C (dec) (from ethanol). IR spectrum: 1011, 1081, and 1115 (ring); 1361 and 1416 (CH_3); 1626 (NH); 1696 and 1756 (C=O); 2810 and 2973 (CH_3); 3190 and 3295 cm^{-1} (NH). PMR spectrum: 2.21 (3H, s, CH_3); 2.36 (6H, s, $2CH_3$); 3.34 ppm (1H, s, NH). Found: C 37.4; H 4.3; N 37.0%. $C7H_{10}N_6O_3$. Calculated: C 37.2; H 4.4; N 37.2%.

1,5-Diaminotetrazole Copper(II) Chloride (VIII). A solution of 1.9 g (0.011 mole) of $CuCl_2 \cdot 2H_2O$ in 40 ml of ethanol is added with stirring to 1.0 g (0.01 mole) of DAT in 40 ml of hot 95% ethanol. The complex is filtered off, washed with ethanol, and dried. Yield, 2.26 g (96%), green crystals, mp 186-187°C (dec). IR spectrum: 1027, 1080, and 1156 (ring); 1664, 3160, 3310, and 3415 cm^{-1} (NH_2). Found: Cl 30.0; Cu 27.4%. $CH_4N_6 \cdot CuCl_2$. Calculated: Cl 30.3; Cu 27.1%.

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