

salt solution was filtered into an ice-cold solution of N-methylaniline (1.07 g, 0.01 mol) in 50 ml of water containing 3 ml of concentrated hydrochloric acid. Sodium acetate (5 g) was added to the solution. After 1 hr stirring, the precipitated solid was filtered and washed with water: yield 2.26 g (90%); mp 55–60°. Recrystallization from petroleum ether (bp 30–60°) gave sulfur-colored granules, mp 64–66° with partial decomposition.

***o,o'*-Diazidodiazaminobenzene.**—*o*-Azidoaniline (1.34 g, 0.01 mol) was dissolved in 30 ml of water and 3 ml of concentrated hydrochloric acid. The solution was half-diazotized by the addition of 0.35 g (0.05 mol) of sodium nitrite at 0°. A solution of 5 g of sodium acetate in 50 ml of water was added all at once. The solution was kept cold by the addition of ice. After stirring for 40 min, the solution was allowed to stand overnight at room temperature. The precipitate was filtered and washed with water. Recrystallization from absolute ethanol (charcoal) gave 1.13 g (81%), mp 123°. Thermal decomposition of this solid in refluxing dioxane gave only polymeric products.

The following procedure is typical of that used for the decomposition of the *o*-azidoazobenzenes. Procedure A was used to prepare 2-(2-hydroxy-5-methylphenyl)-, 2-(4-hydroxyphenyl)-, 2-(4-dimethylaminophenyl)-, and 2-(2-hydroxy-1-naphthyl)benzotriazoles.

2-(2-Hydroxy-5-methylphenyl)benzotriazole. A.—In 5 ml of dioxane was placed 0.05 g (0.002 mol) of 2-(*o*-azidophenylazo)-4-methylphenol and the solution was heated. Evolution of nitrogen was noticeable at 65°. After refluxing for a few minutes, the colorless solution was cooled and poured into 50 ml of water, and the precipitated solid was filtered: yield 0.44 g (99%); mp 130–132°. This compound exists in two crystalline forms. When it crystallizes from hot 95% ethanol, rhombohedrons are obtained which melt at 131.5–133°. When crystallization from 95% ethanol occurs at room temperature, long needles are formed which melt at *ca.* 100° when heated rapidly. The melt then solidifies and remelts at 131.5–133°.

B.—2-(2-Nitrophenylazo)-4-methylphenol (0.05 g, 0.019 mol) was dissolved in 80 ml of water containing 1.6 g of sodium hydroxide. The solution was electrolyzed for 1.5 hr using a copper cathode and carbon anode.⁶ The current through the cell varied from 2 to 0.5 A. The temperature during the electrolysis rose to 65°. At the end of this time, the solution was treated with charcoal and filtered, and the filtrate was acidified. The small amount of solid which precipitated was filtered and recrystallized from ethanol, yield 0.04 g (9%). This product had the same melting point characteristics and the same ir spectrum as the compound prepared by thermal decomposition of 2-(2-azidophenylazo)-4-methylphenol.

2-(*N*-Methylanilino)benzotriazole.—*N*-Methyl-*N*-(*o*-azidophenylazo)aniline (0.05 g, 0.002 mol) was decomposed by refluxing it in *m*-xylene (5 ml) for 1 hr. The xylene was distilled off on the steam bath under vacuum. The residual oil solidified on cooling. Recrystallization of the solid from 95% ethanol gave 0.28 g (63%) of the benzotriazole, mp 99–101°.

2-(4-Hydroxy-1-naphthyl)benzotriazole.—*o*-Azidoaniline (2.69 g, 0.02 mol) was dissolved in 60 ml of water containing 6 ml of concentrated hydrochloric acid, cooled to 0°, and diazotized with 1.44 g of sodium nitrite. This solution was added with stirring to a cold solution of 2.88 g (0.02 mol) of 1-naphthol in 100 ml of water containing 2.40 g of sodium hydroxide. The resulting dark red precipitate (3.7 g) was filtered and washed thoroughly with water. This solid was stirred with 52 ml of 3 *N* sodium hydroxide for 1 hr. The dark red base-insoluble solid (A) was then filtered, washed with water, and air dried. The sodium hydroxide solution was treated with charcoal and then filtered. Acidification of the solution with hydrochloric acid gave 1.16 g (20%) of a flesh-colored precipitate (B).

Several recrystallizations of B from aqueous alcohol gave an analytical sample, mp 202–203°. The infrared spectrum of this material showed the azide group to be absent, indicating that the decomposition to the benzotriazole had already occurred. The analysis was correct for 2-(4-hydroxy-1-naphthyl)benzotriazole.

Compound A was very insoluble in all solvents and could not be purified. When 0.11 g of A was refluxed several hours in dioxane, the dark red color was discharged. Cooling of the dioxane solution gave 0.008 g of colorless needles, mp 289–299°. The analysis of the compound is consistent with an empirical

formula of C₂₂H₁₄N₆O. This product is base insoluble, does not give an acetyl derivative with acetyl chloride, and does not show an OH absorption in its infrared spectrum.

Anal. Calcd for C₂₂H₁₄N₆O: C, 69.83; H, 3.73; N, 22.21. Found: C, 69.81; H, 3.94; N, 21.98.

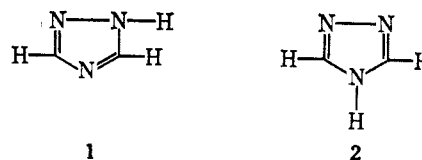
Nuclear Magnetic Resonance Studies of Triazoles. I. Tautomerism of 1,2,4-Triazole^{1a}

LINDA T. CREAGH^{1b} AND PRICE TRUITT

Department of Chemistry, North Texas State University,
Denton, Texas 76203

Received January 25, 1968

If tautomerism involving only N–H hydrogen is considered, all triazoles, tetrazoles, and unsymmetrically substituted imidazoles and pyrazoles can exist in at least two tautomeric forms similar in form to 1 and 2.



Under appropriate conditions proton magnetic resonance has been shown to provide valuable information as to the nature of tautomerism in heterocycles.² Previous publications concerning the nmr spectrum of 1,2,4-triazole have either not treated the problem of tautomerism³ or worked in solvents contaminated with water.⁴

Experimental Section

Proton magnetic resonance data was taken with a Varian A-60 spectrometer equipped with a Varian Model V-6057 variable temperature accessory. Temperature given was accurate to $\pm 2^\circ$. Each spectrum was taken a minimum of five times with the indicated chemical shift determined by weighted average. Concentrations given as percentages are weight per unit weight and are accurate to 0.0001 g. Concentrations given in terms of moles are accurate to $\pm 0.01 M$. Each sample contained tetramethylsilane (TMS) as an internal reference.

The solvents used were spectroscopy grade hexadeuteriodimethyl sulfoxide (DMSO-*d*₆) and reagent grade hexamethylphosphoramide (HMPT). The DMSO-*d*₆ was dried by distillation at reduced pressure from sodium sulfate and kept in an anhydrous nitrogen atmosphere. The HMPT was purified by distillation at reduced pressure and stored in an anhydrous nitrogen atmosphere. The nmr tubes used were filled in an anhydrous nitrogen atmosphere and stored with pressure caps in a calcium chloride desiccator. No changes in the spectra due to water were observed over an interval of 6 months.

(1) (a) This work was supported by Research Grant No. CY3908, from the National Institutes of Health and a North Texas State University Faculty Grant. (b) Address inquiries to this author at Texas Instruments Incorporated, Richardson, Tex.

(2) (a) S. Gronowitz and R. A. Hoffman, *Ark. Kemi*, **16**, 459 (1960); (b) D. O'Brien and J. Gates, Jr., *J. Org. Chem.*, **31**, 1538 (1966); (c) J. Pople, W. Schneider, and H. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 223; (d) D. W. Moore and A. G. Whittaker, *J. Amer. Chem. Soc.*, **82**, 5007 (1960); (e) C. L. Habraken and J. A. Moore, *J. Org. Chem.*, **30**, 1892 (1965); (f) L. Tensmeyer and C. Ainsworth, *ibid.*, **31**, 1878 (1966).

(3) (a) R. Child, *J. Heterocycl. Chem.*, **2**, 98 (1965); (b) M. Hauser and O. Logush, *J. Org. Chem.*, **29**, 972 (1964); (c) G. B. Barlin and T. J. Battersham, *J. Chem. Soc., Sect. B*, 516 (1967); (d) K. T. Potts and R. M. Huseby, *J. Org. Chem.*, **31**, 3538 (1966); (e) H. Zimmermann, *Z. Electrochem.*, **66**, 440 (1961).

(4) W. Frieberg and C. F. Kroger, *Tetrahedron Lett.*, 2109 (1967).

(6) See Table I, footnote g.

1,2,4-Triazole was purchased from Aldrich Chemical Co., Milwaukee, Wis. Purification was accomplished by sublimation followed by storage in an anhydrous nitrogen atmosphere.

Discussion

The nmr spectrum of liquid 1,2,4-triazole, examined just above the melting point (125°) of the compound, consists of two singlets at 13.9 and 7.85 ppm with relative intensities of 1:2 (see Table I). The upfield signal corresponds to the C-3 and C-5 hydrogens. This assignment is in agreement with corresponding assignments for 1,2,4-triazoles.^{3b,d}

TABLE I
CHEMICAL SHIFTS FOR 1,2,4-TRIAZOLE

Solvent	Temp, °C	Signal assignments ^a	
		C-H	N-H
Neat	125	7.85	13.9
DMSO- <i>d</i> ₆ (3.8%)	37	8.25	13.9
HMPT (4.3%)	37	8.17	15.1

^a In parts per million from tetramethylsilane (TMS). Although all the signals are downfield from TMS, the negative sign has been omitted from the resonance assignments for convenience.

The downfield N-H signal in 1,2,4-triazole is very sharp due to rapid exchange of this proton.⁵ This is supported by the coalescence of the N-H signal on addition of water.⁶

The spectrum of 1,2,4-triazole in anhydrous DMSO-*d*₆ (10.3%, 37°) is essentially similar to that observed for liquid 1,2,4-triazole. The C-3 and C-5 hydrogen peak is shifted downfield to 8.25 ppm and the N-H resonance occurs at 13.9 ppm as a very broad signal. A comparison of the chemical shifts for 1,2,4-triazole in solvent and as a pure liquid is given in Table I.

In carefully distilled hexamethylphosphoramide (HMPT), two distinct C-H peaks are observed at temperatures below 0° (see Table II). In a 4.3% solution, a maximum separation of 56 Hz is observed at -34°.

TABLE II
TEMPERATURE DEPENDENCE OF 1,2,4-TRIAZOLE NMR SPECTRA^a

Temp, °C	Signal assignments	
	N-H	C-H
37	15.0	8.17
10	15.09	8.03 (broad)
0	15.10	8.95, 8.59
-10	15.15	8.72, 7.87
-34	15.25	8.85, 7.92

^a 4.3% in HMPT. Chemical shifts are in parts per million relative to TMS.

In the absence of rapid inter- or intramolecular exchange, the spectra of 1 and 2 would be expected to be different due to symmetry considerations. In the unsymmetrical isomer, 1, the C-3 hydrogen is in a region of greater electron density than the C-5 hydrogen which is adjacent to the ring hydrogen and, as a result, the downfield peak of the high-field doublet is assigned to the C-3 hydrogen. This assignment parallels designations made for hydrogens found in similar chemical environments.⁷

(5) M. Takeda and E. Stejskal, *J. Amer. Chem. Soc.*, **82**, 25 (1960).

(6) F. Duderck, R. Degrote, J. Delannoy, R. Nasielski-Hinken, and J. Nasielski, *Bull. Soc. Chim. Belg.*, **74**, 119 (1965).

The intensity of the low-field N-H signal in 1,2,4-triazole in HMPT solutions remains constant relative to the intensity of the C-H signals with changes in temperature indicating that the N-H hydrogen is not exchanging with the solvent or with traces of water. The N-H resonance shifts downfield with decreasing temperature due to increasing intermolecular hydrogen bonding at lower temperatures.⁸

The nmr spectrum shows that at -34° there is only (1H)-1,2,4-triazole (1). From potentiometrically determined ionization constants of 1- and 4-alkyltriazoles, Froger and Freiberg⁹ estimated the tautomeric ratio of (1H)- to (4H)-1,2,4-triazole to be 5-10:1 (20°, 0.01 M in water). Quantitative calculations of the π -electron densities in the neutral 1,2,4-triazole nucleus yield various values of the electron density on N-1 and N-4 due to differences in the choice of parameters.¹⁰ Atkinson and Polya found values of 1.136 for N-1 and 1.093 for N-4¹¹ which agree with the result of the qualitative assignment of electron density based on the nmr results.

In order to corroborate the assignments made for the nmr spectra of 1,2,4-triazole, the N-methyl derivatives were prepared by the procedure of Pellizzari and Soldi.¹² The nmr spectrum of 1-methyl-1,2,4-triazole (3) consists, in HMPT at 37°, of a singlet at 3.64 (three hydrogens) and two singlets at 8.01 and 8.70 ppm each equivalent to one hydrogen. The upfield peak in this group is ascribed to the C-5 hydrogen in 3 because the local diamagnetic shielding from the electron-donating methyl group would be expected to cause an upfield shift of an adjacent proton.¹³ The nmr spectrum of 4-methyl-1,2,4-triazole (4) in HMPT at 37° is composed of singlets at 3.64 (three hydrogens) and 8.20 ppm (one hydrogen). At -40° the spectra were shifted downfield so that the low field singlets occur at 8.02 and 8.93 (3) and 8.34 ppm (4) with the same relative intensities as above. The low field signal of 4 is found to occur in the region of the averaged signals for the carbon-bound hydrogens in 1,2,4-triazole.

That the local diamagnetic screening and electron density for N-1 and N-4 in 1,2,4-triazole are very similar¹⁴ is shown by the fact that the methyl resonance of 3 and 4 are the same.

The mean half-life of the N-H hydrogen on N-1 at about 10° is estimated^{15,2c} to be 4×10^{-3} sec by using the separation of the C-H peak at -34° as the maximum separation.

The N-1 hydrogen multiplicity in 1,2,4-triazole cannot be distinguished at -34° due to the broadness of the N-H hydrogen resonance resulting from quadrupole effects associated with the N¹⁴ nucleus.

Registry No.—1, 288-89-1; 3, 6086-21-1; 4, 10570-40-8.

(7) W. Paudler and J. Barton, *J. Org. Chem.*, **31**, 1720 (1966).

(8) G. Korinek and W. Schneider, *Can. J. Chem.*, **35**, 1157 (1955).

(9) C. F. Froger and W. Freiberg, *Chimia*, 161 (1967).

(10) K. Potts, *Chem. Rev.*, **61**, 109 (1961).

(11) M. Atkinson and J. Polya, *J. Chem. Soc.*, 3319 (1954).

(12) Pellizzari and Soldi, *Gazz. Chim. Ital.*, **35**, 375 (1900), as cited by F. Richter from F. K. Beilstein, "Handbuch der organischen Chemie," Vol. 26, Edwards Bros., Ann Arbor, Mich., 1942, pp 141, 16, and II35.

(13) P. Corio and D. Dailey, *J. Amer. Chem. Soc.*, **77**, 3043 (1956).

(14) A. Katritzky, *Advan. Heterocycl. Chem.*, **2**, 121 (1963).

(15) J. Happe, *J. Phys. Chem.*, **65**, 72 (1961); H. Gutowsky and C. Holm, *ibid.*, **25**, 1128 (1956); A. Allerhand, H. Gutowsky, J. Jones, and R. Minzer, *J. Amer. Chem. Soc.*, **88**, 3185 (1966).