

Synthesis and Characterization of 5-Dinitromethyltetrazole

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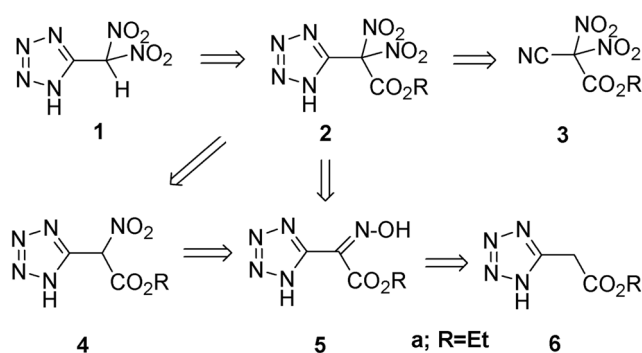
Even though various explosives have been continuously developed, higher performance and lower sensitivity have been a keen concern in weapon system.¹ Recently 1,1-diamino-2,2-dinitroethylene (FOX-7) was prepared and showed similar performance, but lower sensitivity to both friction and impact compared with RDX.²

5-Dinitromethylidene-1,4-dihydro-1H-tetrazole consists of same functional groups as FOX-7.^{3,4} 5-Dinitromethylidene-1,4-dihydro-1H-tetrazole, a tautomer of 5-dinitromethyltetrazole (**1**), was synthesized before FOX-7 was introduced.⁵ Its various salts and *N*-methyl derivatives were prepared from 5-dinitromethyltetrazole (**1**),^{5,6} and the monosodium salt of **1** was also from FOX-7.⁷ In the synthesis of tetrazoles containing dinitromethyl moiety, trinitroacetone nitrile has been mainly employed.^{5,6} Due to easy decomposition, trinitroacetone nitrile should be handled with utmost care, and kept in solution.

Tetrazole-tetrazoline (1,4-dihydro-1H-tetrazole) tautomerism was readily observed, in addition to two tautomeric forms of 1-H and 2-H tetrazole rings. When -OH and -SH were substituted at C-5, tetrazoline forms were predominant.⁸ While 1-phenyl tetrazolylcyanoacetate was confirmed as in the form of tetrazoline,⁹ 5-dinitromethyltetrazole (**1**) was depicted as in tetrazole form.^{5,6} In this paper, we report an useful synthetic method of 5-dinitromethyltetrazole, and discuss its tautomerism.

Since known methods were encountered some difficulties in the preparation of 5-dinitromethyltetrazole (**1**), other schemes should be developed for the scale-up process. In the synthesis of FOX-7, various starting materials such as 2-methylimidazole, 2-methoxy-2-methylimidazolidine-4,5-dione, and 2-methylpyrimidine-4,6-dione (4,5-dihydroxy-2-methylpyrimidine) were nitrated and then hydrolyzed to give FOX-7 by somewhat different process.^{2,10} Since the methyl group was converted to dinitromethylidene moiety in all methods, nitration of 5-methyltetrazole was attempted to afford 5-dinitromethylidene-1,4-dihydro-1H-tetrazole, but this reaction failed to proceed, and most of the starting material was recovered.

Several compounds consisted of dinitromethylene moiety were synthesized in a reaction of FOX-7 with amino compounds *via* transamination³ or 1,1-dihalo-2,2-dinitroethylene with amino compounds *via* substitution.⁴ Since a suitable amine may be 2-tetrazene, which is metastable at room temperature, 5-dinitromethyltetrazole might be hardly



Scheme 1. A Retrosynthesis of 5-Dinitromethyltetrazole.

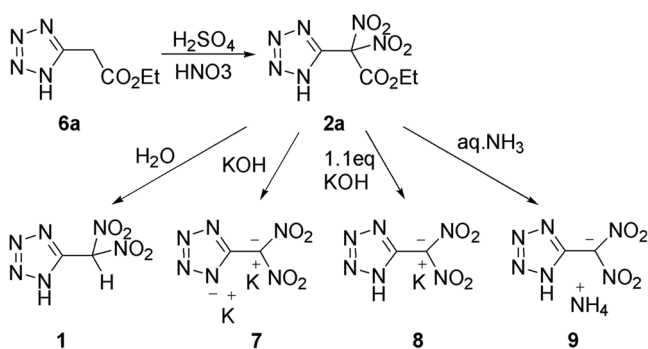
prepared from FOX-7.¹¹ Although treatment of 3,3-diazido-2-cyanoacrylates with substituted amines afforded dihydro-tetrazolidene moieties,⁹ diazodinitro compounds might not be useful for the large scale synthesis of 5-dinitromethyltetrazole.

A retrosynthesis is outlined in Scheme 1. Dinitromethyl tetrazole **2** may be afforded in the reaction of cyanoacetate **3** with azide salts, and then alkoxy carbonyl moiety is removed to prepare 5-dinitromethyltetrazole. Otherwise, tetrazole ring will be formed, and two nitro groups are introduced stepwise, and then alkoxy carbonyl moiety is removed.

Alkyl cyanodinitroacetate (**3**) was readily available,¹² and used in many reactions.¹³ Although the reaction of a nitrile with an azide generally gave a tetrazole, nitrile **3** has not been employed in the preparation of the corresponding tetrazole (**2**).^{5,6,14} We tried to carry out the reaction of ethyl cyanodinitroacetate (**3a**) with sodium azide, and could not earn any good result. Moreover, preparation and purification of nitrile **3a** were not suitable for a large scale synthesis.¹²

Although the synthesis of ethyl 5-tetrazolylidene-1,4-dihydro-1H-tetrazole (**1**) has not been reported, ethyl 5-tetrazolylidene-1,4-dihydro-1H-tetrazole (**4a**) was prepared from ethyl 5-tetrazolylacetate (**6a**).⁶ Compound **4a** could be converted to dinitro **2a** by the oxidative nitration which was employed in the synthesis of 1,3,3-trinitroazetidine.¹⁵

By the known method of a dinitro group from an oxime one, we could prepare ethyl 5-tetrazolylidene-1,4-dihydro-1H-tetrazole (**1**) in the reaction of ethyl 5-tetrazolylacetate oxime (**5a**) with a mixture of nitric acid and sulfuric acid (mixed acids).¹⁶ Two nitro groups were directly introduced at the methylene position in the treatment of methyl cyanoacetate with mixed acids to give nitrile **3** (R = Me) in 36% yield, and the



Scheme 2. Synthesis of 5-Dinitromethyltetrazole and Its salts.

reaction became progressively troublesome with increasing size of the alkyl group.^{12,17} We carried out the reaction of commercially available ethyl 5-tetrazolylacetate (**6a**) with mixed acids and obtained ethyl 5-tetrazolyl-2,2-dinitroacetate (**2a**) in high yield, resulting that two nitro groups were successfully introduced in one pot reaction.

When ethyl 5-tetrazolyl-2,2-dinitroacetate (**2a**) was treated with water, 5-dinitromethyltetrazole (**1**) was readily given. Hydrolysis followed by decarboxylation was taken place completely within 2 h at 50 °C. In the treatment of **1** with KOH, dipotassium salt **7** and monopotassium **8** were obtained even in lower temperature, depending upon the equivalent of KOH.¹⁸ Meanwhile, only mono salt **9** was given in the reaction of ammonia.⁵ 5-Dinitromethyltetrazole (**1**) was also afforded by an acid treatment of the salts.⁶

This process would be much more efficient and safer than the previous methods. Preliminary experiments showed that these compounds have some explosive properties.

Tetrazole-tetrazoline tautomerism was generally observed. X-ray analysis revealed that 1-phenyltetrazolidene cyanoacetate exists in the form of tetrazoline.⁹ But dinitromethyltetrazole was depicted as in tetrazole form without proper experimental data in the previous papers.^{5,6}

In IR spectra, a NO₂ group generally shows higher asymmetric mode and lower symmetric one. When an electron withdrawing group is attached to the same carbon, the asymmetric frequency is raised, and the symmetric one is lowered. Conjugation to NO₂ causes lowering of both modes. Nitroethane absorbs at 1558 and 1368 cm⁻¹, dinitroethane at 1587 and 1337 cm⁻¹, and nitroethylene at 1527 and 1363 cm⁻¹.¹⁹ Since ethyl tetrazolylacetate (**6a**) absorbs at 1394 and 1332 cm⁻¹, which is close to the symmetric mode, we focused on the asymmetric mode to investigate the distribution of tautomers. Ethyl tetrazolyl-2,2-dinitroacetate (**2a**) absorbed at 1594 cm⁻¹, which was higher than that of dinitroethane as expected. Strong absorptions occurred at 1587 cm⁻¹ for 2-methyl-5-dinitro-methyltetrazole⁶ and 1560, 1500 cm⁻¹ for 2-dinitromethylenebenzimidazole.⁴ Since the frequency of 5-dinitromethyltetrazole (**1**) was 1585 and 1521 cm⁻¹,⁶ similar to 2-dinitromethylenebenzimidazole, we might consider that major portion of the compound in solid state exists in the tetrazoline form.

To investigate the tautomer in solution, we analyzed UV spectra. Several absorptions were observed for conjugated

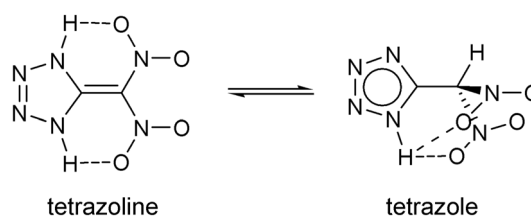


Figure 1. Energy Differences Between Two Forms: (a) RHF/6-31G(d) Calculation, $\Delta E = 0.75$ kcal/mol; (b) B3LYP/6-31G(d) Calculation, $\Delta E = 3.90$ kcal/mol.

dinitro compounds. 1,1-Bisdimethylamino-2,2-dinitroethylene absorbed at 264, 302, 340 nm, and 2-dinitromethylenebenzimidazole at 240, 320, 335 nm.⁴ The absorptions of tetrazole **6a** and dinitrotetrazole **2a** appeared around 225 nm, but that of 5-dinitromethyltetrazole (**1**) in methanol was 227, 304, 360 nm. Therefore, some parts of 5-dinitromethyltetrazole (**1**) existed in the tetrazoline form. Interestingly, dipotassium salt **7** absorbed at 230, 361 nm. The proton absorption of **1** appeared at 12.9 ppm in DMSO-*d*₆, 8.2, 11.4 ppm in CH₃CN-*d*₃, and 8.8, 8.9 ppm in acetone-*d*₆, respectively. In addition to UV data, the predominant form in solution depends on solvent properties.

On the basis of the molecular orbital calculations using RHF/6-31G(d) and B3LYP/6-31G(d),²⁰ the energy of tetrazoline form is lower by 0.75 or 3.90 kcal/mol than that of tetrazole one. In the case of tetrazoline form, two hydrogen bonds stabilize the structure, resulting in the ring and two nitro groups lie in the same plane. Meanwhile, the tetrazole ring preserves aromaticity, and H attached ring nitrogen lies between two nitro groups, and forms weak hydrogen bonds. Therefore, the energy difference is so small that the molecule may exist in the mixture of two forms.

In summary, ethyl 5-tetrazolyl-2,2-dinitroacetate (**2a**) was readily prepared from commercially available **6a** and converted to 5-dinitromethyltetrazole (**1**), which exists in a mixture of tetrazole and tetrazoline forms. Predominant tautomeric form could be dependent on the state such as in solution or in solid.

Experimental Section

General. ¹H/¹³C NMR spectra were recorded on Varian Oxford 200 or Unitynova 400 instruments. Infrared (FTIR) spectra were recorded on a Nicolet 5700 FT-IR spectrophotometer, ν max in cm⁻¹. Samples were recorded as a KBr disc. Ultraviolet spectra were recorded on a Lambda 40 UV-Visible Spectroscopy instrument. High resolution mass spectra were recorded on JMS-AX505 WA mass spectrometer (JEOL). Melting points were performed on recrystallized solids and recorded on a SRS OptiMelt or electrothermal 9100 melting point apparatus and were uncorrected.

Ethyl 5-Tetrazolyl-2,2-dinitroacetate (2a). Ethyl 5-tetrazolylacetate (**6a**, 10.0 g, 0.064 mol) was dissolved into sulfuric acid (98%, 50.0 mL, *d* = 1.84, 0.92 mol). The solution was cooled to 15 °C, and nitric acid (95%, 16.2 g, 0.244 mol) was added dropwise over 30 min. After stirring for 2 h at rt, the

reaction mixture was poured into ice water (200 g). The precipitate was filtered to give a crude product as a pale yellow solid (10.3 g, 65%). The mother liquid was extracted with ethyl acetate, and the organic layer was washed with water and brine, dried over MgSO_4 , and concentrated *in vacuo*, to give an additional crude product as a pale yellow solid (4.81 g, 31%): mp 78-80 °C (EtOH, dec); IR (KBr) 1773, 1594, 1314, 1244, 1047, 838 cm^{-1} ; UV (MeOH) λ_{max} 225 nm; ^1H NMR (DMSO- d_6 , 200 Hz) δ 1.30 (t, 3H), 4.57 (q, 2H), 12.3 (br, 1H); ^{13}C NMR (DMSO- d_6) δ 13.7, 67.1, 112.9, 152.3, 156.2; HRMS (FAB) m/z calcd for $\text{C}_5\text{H}_7\text{N}_6\text{O}_6$ ($\text{M}+\text{H}^+$) 247.0428, found 247.0429.

5-Dinitromethyltetrazole (1). Ethyl 5-tetrazolyldinitroacetate (**2a**, 10.0 g, 0.041 mol) was dissolved into water (100 mL), and the mixture was stirred for 2 h at 50 °C. The aqueous mixture was concentrated *in vacuo* until a solid appeared. The precipitate was filtered to give a crude product as a pale yellow solid (5.80 g, 82%): mp 122-123 °C (MeOH- CHCl_3 , dec); IR (KBr) 3226, 1585, 1521, 1384, 1218, 1050, 1018, 835, 754 cm^{-1} ; UV (MeOH) λ_{max} 227, 304, 360 nm; ^1H NMR (DMSO- d_6 , 200 Hz) δ 12.9 (br); ^{13}C NMR (DMSO- d_6) δ 121.6, 149.1.

General Procedure for 5-Tetrazoyldinitromethylide salts.^{5,6} To a solution of ethyl 5-tetrazolyldinitroacetate in CH_3OH , KOH or NH_4OH was added. After stirring for 3 h at rt, the mixture was evaporated and the residue was washed with ether to give almost pure salt in high yield.

Dipotassium salt of 5-Dinitromethyltetrazole (7): mp 284-290 °C (H_2O -MeOH, dec); IR (KBr) 1525, 1443, 1368, 1234, 1197, 1124, 1018, 826, 750 cm^{-1} ; UV (MeOH) λ_{max} 230, 361 nm; ^{13}C NMR (DMSO- d_6) δ 128.5, 155.2.

Potassium salt of 5-Dinitromethyltetrazole (8): mp 167-171 °C (H_2O , dec); IR (KBr) 3215, 1525, 1479, 1420, 1362, 1317, 1245, 1194, 1114, 1052, 837, 752 cm^{-1} ; UV (MeOH) λ_{max} 229, 357 nm; ^{13}C NMR (DMSO- d_6) δ 121.8, 149.7.

Ammonium salt of 5-Dinitromethyltetrazole (9): mp 217 °C (H_2O , dec); IR (KBr) 3215, 1526, 1479, 1402, 1361, 1245, 1183, 1142, 1113, 1052, 998, 837, 752 cm^{-1} ; UV (MeOH) λ_{max} 230, 361 nm; ^{13}C NMR (D_2O) δ 126.7, 154.2.

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