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1-METHYL-5-NITROTETRAZOLE AND 2-METHYL-5-NITROTETRAZOLE

PART 1

SYNTHESIS, CHARACTERISATION AND DETECTION, AND MOLECULAR COMPLEX

Robert J. Spear

Approved for Public Release

JUNE, 1980

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ABSTRACT

The preparation of two novel castable primary explosives, 1-methyl-5-nitrotetrazole (1) and 2-methyl-5-nitrotetrazole (2), is described. Both are prepared from tetrazol-5-amine monohydrate (3). The only practical synthesis of (1) is methylation of (3) to 1-methyltetrazol-5-amine (5) and 2-methyltetrazol-5-amine (6), followed by separation and diazotization of (5) in the presence of excess nitrite. Although (2) can be prepared similarly from (6), the route via sodium 5-nitrotetrazole dihydrate (4) is preferable both for yield and ease of purification. This latter reaction also produces (1) but crystallisation yields only (2) and a second product which has been shown not to be (1), as previously reported, but a 1:1 complex of (1) and (2). Some initial data relating to the nature of the complex are described. (1) and (2) have been characterised spectroscopically and chromatographically, and methods for their qualitative and quantitative detection are described.

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16. ABSTRACT (if this is security classified, the announcement of this report will be similarly classified):

The preparation of two novel castable primary explosives, 1-methyl-5-nitrotetrazole (1) and 2-methyl-5-nitrotetrazole (2), is described. Both are prepared from tetrazol-5-amine monohydrate (3). The only practical synthesis of 1 is methylation of 3 to 1-methyltetrazol-5-amine (5) and 2-methyltetrazol-5-amine (6), followed by separation and diazotization of 5 in the presence of excess nitrite. Although 2 can be prepared similarly from 6, the route via sodium 5-nitrotetrazole dihydrate (4) is preferable both for yield and ease of purification. This latter reaction also produces 1 but crystallisation yields only 2 and a second product which has been shown not to be 1, as previously reported, but a 1:1 complex of 1 and 2. Some initial data relating to the nature of the complex are described. 1 and 2 have been characterised spectroscopically and chromatographically, and methods for their qualitative and quantitative detection are described.

CONTENTS

1-METHYL-5-NITROTETRAZOLE AND 2-METHYL-5-NITROTETRAZOLE

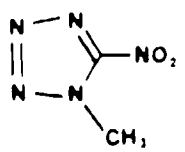
PART 1

SYNTHESIS, CHARACTERISATION AND DETECTION, AND MOLECULAR COMPLEX

1. INTRODUCTION

The most commonly used primary explosive for detonators or initiators in explosive trains, lead azide, decomposes hydrolytically on prolonged storage [1a]. In recent years, a concerted research effort has been directed towards developing primary explosives which match lead azide in performance and safety in handling but possess superior long term storage properties. The class of compounds which has yielded the most promising results is the tetrazoles, particularly the mercuric and silver salts of 5-nitrotetrazole [2-6]. Apart from the widely used stab sensitizer tetrazene [1b,7], organic tetrazoles, i.e., tetrazoles which are not metal salts, have been the subject of only limited study and the evidence available at present is insufficient to give an accurate assessment of the potential of such species as initiating explosives.

A study of the isomeric organic tetrazoles 1-methyl-5-nitrotetrazole (1) and 2-methyl-5-nitrotetrazole (2) was therefore initiated. A detailed investigation of the explosive behaviour of 1 and 2 under hot wire initiation had previously been reported [8] and limited explosive and sensitivity data had been published for 2 [4]. The data from both studies indicated



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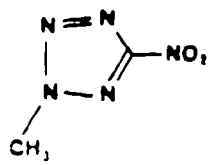


2

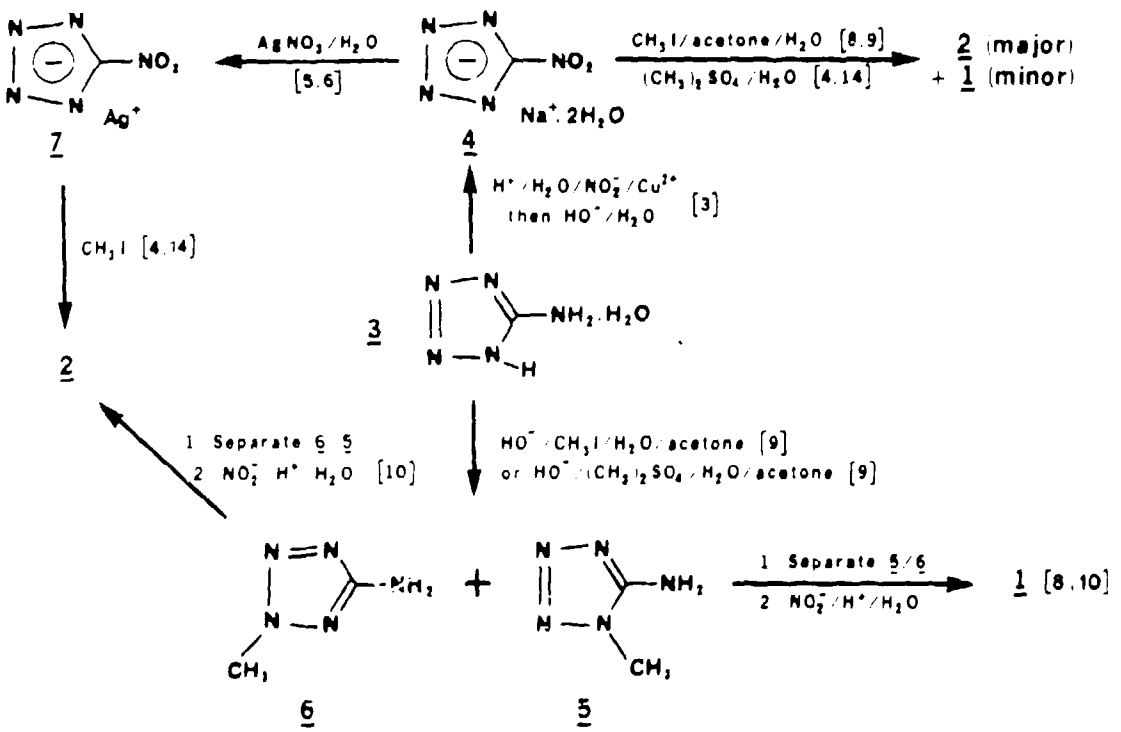
that 2 had explosive properties consistent with those of a primary explosive, but the data for 1 were so limited that no firm conclusions could be drawn. A further point of practical and theoretical interest is that both 1 and 2 are solids of low melting point (m.p. 40-1°C and 84-85.5°C respectively), thus are potentially castable, and could fall within the very limited list of primary explosives which melt below their ignition temperature.

Although both 1 and 2 have been synthesised from tetrazol-5-amine monohydrate (3, see Scheme 1) via a number of intermediates [4,8-10,14], repetition of the published methods revealed deficiencies either in product yield or method of purification, or both. No previous attempt has, indeed, been made to determine the optimum method for synthesising either 1 or 2. A further complication is that all syntheses rely, at some stage, on separation of isomeric mixtures, and no methods are currently available whereby minor amounts of 1 could be detected in a sample of 2 or vise versa; such impurity levels could have significant effects on explosive properties. The investigation of the synthesis, characterisation and detection of 1 and 2, particularly with providing answers to the deficiencies mentioned above, is described in this report. A subsequent report will deal with their explosive and thermal properties.

2. RESULTS AND DISCUSSION

2.1 Synthesis

The syntheses of 1 and 2 which have been reported in the literature are shown in Scheme 1 below :



Scheme 1 - Syntheses of 1-methyl-5-nitrotetrazole (1) and 2-methyl-5-nitrotetrazole (2) as reported in literature references.

2.1.1 *1-methyl-5-nitrotetrazole (1)*

Henry and Finnegan [9] first reported the isolation of 1 as a minor product from methylation of sodium 5-nitrotetrazole dihydrate (4), the major product being 2. This product was not 1, however, but a 1:1 complex of 1 and 2, as will be shown later in this report.

The only unequivocal synthesis of 1 has been via 1-methyltetrazol-5-amine (5) [8,10]. Methylation of 3 produced 5 and the isomeric 2-methyltetrazol-5-amine (6) which were separated by their differential solubilities [9]. Bagal et al. [10] first reported the conversion of 5 to 1 by acid catalysed diazotisation in the presence of excess nitrite in 57.5% yield, although whether this refers to crude or purified material was not clear. Indeed Tarver et al. [8], in repeating the procedure, obtained a much lower yield; 5 (5 g) gave crude 1 (1.5 g, 23%). Repetition of this experimental procedure in these laboratories resulted in only moderate to low yields of 1 (Table 1, entries 1-4) prior to purification.

Two experimental modifications which potentially could increase the yield of 1 were addition of cupric ion which can catalyse substitution of diazonium by nitro functions [11], and increase of nitrite concentration by decreasing total reaction volume. The presence of cupric ion has the further advantage of minimising build-up of the potentially explosive 1-methyltetrazole-5-diazonium intermediate; tetrazole-5-diazonium is extremely hazardous [12] and will detonate in aqueous solution when the concentration exceeds 1% [13]. A number of experimental variations were tried (Table 1, entries 5-9) and all gave yields significantly increased over the original conditions. Further reduction in total volume for ease of handling in a large scale synthesis could presumably be achieved.

Lower reaction temperature should lead to longer lifetime of the diazonium intermediate, facilitating replacement by nitro rather than decomposition into unwanted products. When the reaction was carried out at 15-19°C, comparable yields were obtained to the higher temperature reactions (Table 1, entries 10,11) but the reaction was extremely slow. Nitrogen was still being evolved after eight hours and did not cease till the next day, hence the higher temperature reaction was considered preferable.

A major problem encountered in all syntheses was that of purification. The procedure used by Bagal et al. [10], i.e., recrystallisation from ether, was found to be very unsatisfactory as 1 tended to oil out and was invariably yellow in colour; Tarver et al. [8] resorted to filtration chromatography prior to purification. In this work, both problems were overcome by firstly adding decolourising charcoal to an ether solution of crude 1, filtering, then adding 10-15% by volume of light petroleum and finally allowing the solution to crystallise at - 15°C. This procedure consistently gave a good recovery of 1 as long colourless crystals (Table 1); variations in recovery reflect the difficulty of recrystallisation. The optimum experimental conditions and work-up, corresponding to entry 7, Table 1, are given in Section 3.

It should be noted that the melting point of 1 obtained here, 40-1°C, is significantly lower than reported previously (55-6°C [10] and 52°C [8]. The structure and purity of 1 was confirmed by microanalysis, spectroscopy,

differential scanning calorimetry (DSC) and thin layer chromatography (TLC) (see subsequent sections) and it must be concluded that the melting points have previously been misreported. Both references cite the original (incorrect) melting point [9] which may explain the discrepancy.

2.1.2 2-methyl-5-nitrotetrazole (2)

Methylation of 4 with either iodomethane in aqueous acetone [8,9] or dimethylsulfate in water [4,14], or of silver 5-nitrotetrazole (7) with iodomethane [4,14], gave 2 in yields ranging from 36-53%. These reactions are not specific, 1 being formed as a minor product. The only specific synthesis, acid catalysed diazotisation of 6 in the presence of excess nitrite, was reported to give 2 in 76.5% yield [10]. An investigation of the preparation of 2 via 6 and via methylation of 4 with iodomethane was initiated. Methylation of 7 was discounted because 7 is a sensitive primary explosive [5,6] and would have to be formed via 4, thus involving an additional step.

a. 2 Via Diazotisation of 6

Bagal et al. [10] reported the conversion of 6 to 2 by acid catalysed diazotisation in the presence of excess nitrite at 45°C. The yield claimed was 76.5%, although whether this represents crude or purified material was not stated. Repetition of this procedure gave a comparable yield of crude product (Table 2, entry 1). Addition of cupric ion, increased nitrite ion concentration or lower reaction temperature had no effect on the crude yield (Table 2, entries 2-8). The reaction at 15-19°C, as in the analogous 5 to 1 conversion, required 24 hours for completion. The smaller reaction volumes should be advantageous for scale-up procedures.

The major problem encountered in all syntheses was contamination by two bright yellow impurities (TLC, silica gel, dichloromethane, R_f 0.07, 0.09 c.f. 2, 0.48). These impurities were not removed by recrystallisation or decolourising charcoal, resulting in a yellow product which melted 2-4°C below the literature values [4,8,10].

A partial solution to this problem was to chill the reaction mixture at 0°C for an hour, filter the resulting colourless crystals of 2 then recrystallise. This recovered about 60% of the crude yield while the remainder, extracted from the aqueous solution, was a yellow semi-crystalline mass which could be purified only to a yellowish low melting state. A further improved procedure was achieved when 2 was found to sublime under water pump pressure at 100°C. The optimum experimental procedure, corresponding to entry 5, Table 2, is detailed in Section 3.

b. 2 Via Methylation of 4

Methylation of 4 with iodomethane in aqueous acetone is reported to give 2 in 47.2% [9] and 35.8% [10] yield. The corresponding methylation with dimethylsulfate in water afforded a slightly higher yield (53%) [4] but the more difficult work-up procedure, together with the known toxicity of dimethylsulfate, led to the choice of iodomethane as methylation reagent.

Methylation of 4 with 1 mole equivalent of iodomethane for 3 hours gave moderate yields of crude product (Table 3, entries 1,2). Increase of reflux time to 6 hours gave a substantial increase (entry 3) while the addition of a second mole equivalent of iodomethane after an initial reflux period further increased the yield (entries 4,5). Larger scale reactions (entries 6-10) also gave higher yields, probably reflecting greater net loss of product from the smaller scale reactions (2 sublimes, as noted above, and could be slowly lost during evaporation of solvent in vacuo). Addition of a third mole equivalent of iodomethane (entry 9) did not affect the yield. The procedure originally published [8,9] involved initially using 1.35 mole equivalents of iodomethane*, then a further 0.41 mole equivalents* after 3.5 hours. The yield of crude product was 65.0%*.

All reactions gave both 2 and 1 with 2 predominating. The ratio 2:1, calculated from the areas under the respective NMR absorption peaks (see Section 2.2.4), is detailed in Table 3 for entries 1-5 and 10. The ratios show some variation over the series but the differences probably reflect lack of reproducibility of NMR peak areas.

Recrystallisation of the crude material from toluene-light petroleum afforded a mixture of two crystalline types, 2 as clusters of white platelets, with a few larger yellow-tinged rhombohedral crystals which were readily separated manually. Sublimation at 100°C at water pump pressure partially removed 1 as it sublimed much slower than 2. Recrystallisation of the sublimed crystals then afforded pure 2 in high yield (Table 3). The yields are significantly higher than procedures previously reported [4,9,10]. Both experimental methods are described in Section 3.

2.1.3 Molecular Complex of 1 and 2

The rhombohedral crystals obtained as minor product in the methylation of 4 had the same melting point and crystal type as the product isolated from this reaction, and incorrectly identified as 1 by Henry and Finnegan [9]. Analysis of the product by TLC revealed the presence of *both* 1 and 2 in approximately equal amounts. The NMR spectrum of a deuterochloroform solution showed only absorptions due to the methyl protons of 1 and 2 in a ratio of 1:1. Furthermore, if a hot equimolar solution of 1 and 2 in toluene-light petroleum was allowed to crystallise, only the rhombohedral crystals were formed and in high yield (see Section 3).

$$\underline{1}\ (\text{mp.}40\text{-}1^{\circ}\text{C}) + \underline{2}\ (\text{mp.}85\text{-}6^{\circ}\text{C}) \xrightarrow[\text{2. Allow to crystallise}]{\text{1. Equimolar, dissolve in hot toluene - light petroleum}} \text{rhombohedral crystals } (\text{mp.}56.5\text{-}58^{\circ}\text{C})$$

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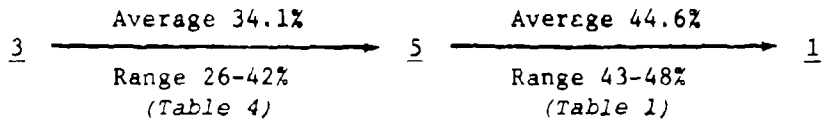
* It was assumed, in the original work [9], that the sodium 5-nitrotetrazole was a tetrahydrate but it has subsequently been shown to be a dihydrate [3], thus affecting the quoted yields and iodomethane equivalents.

That the crystals melt sharply, with a melting point intermediate between that of 1 and 2, and consist of 1 and 2 in equimolar quantities, suggests that this product is a 1:1 molecular complex. This suggestion is further reinforced by the DSC trace, which shows a single sharp endotherm at 56-58.5°C and no endotherm corresponding to melting either of 1 or 2. Attractive forces between the isomers must not be strong, since the complex dissociates at 100°C during sublimation, with 2 subliming much faster than 1 and hence affording a partial separation, and on a TLC plate. The complex also appears to dissociate in polar solvents, as evidenced from its NMR spectrum; further spectral properties will be discussed in the following sections.

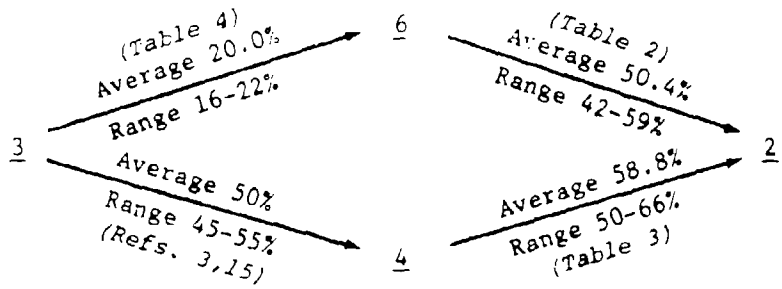
2.1.4 Comparison of Alternative Syntheses of 1 and 2

The only practical synthesis of 1 is by diazonium displacement through 5. The yield for the overall conversion from 3 averages 15.2% (Tables 4 and 1). Although 1 is produced in the methylation of 4, it is only a minor component and can only be isolated as the 1:1 complex of 1 and 2. Separation of 1 from 2 cannot be achieved by recrystallisation or sublimation, but could be achieved chromatographically.



Overall: Average 15.2% Range 11-20%

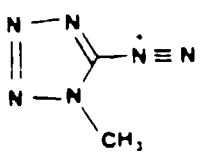
In contrast, the conversion of 3 to 2 is reasonably straightforward via either 4 or 6. The latter conversion is hampered by the low yield in the methylation of 3; both 5 and 6 are formed in the ratio of approximately 1.4:1 (from the NMR spectrum of the crude reaction mixture). This ratio is maintained throughout separation and purification (Table 4), giving an average overall yield of 20.0%, comparable with that reported by Henry and Finnegan [9]. The diazotisation and replacement proceeds in an average yield of 50.4% (Table 2), giving an overall conversion of only 10.1%.



Overall: via 6 Average 10.1% Range 7-13%
via 4 Average 29.4% Range 23-36%

The route via 4 has the advantage of the higher yield in the first step, the conversion of 3 to 4. This step is quite straightforward using the procedure of Gilligan and Kamlet [3] and their quoted yield, 45-55%, was consistently reproduced in these laboratories [15]. Yield in the following methylation is high (Table 3) giving an overall average from 3 of 29.4%. This procedure should consistently give higher returns than 29.4% since the best yields for the 4 to 2 conversion were obtained using the refined sublimation work-up (Section 3). The higher yield, coupled with the easier work-up in the final step, clearly favours synthesis of 2 via 4 but the route via 6 is acceptable provided 6 is readily available, e.g., if both 1 and 2 were required, necessitating concurrent synthesis of 5 and 6.

An unexpected feature of the preparation of 1 and 2 by diazonium displacement was the significantly higher crude yield of 2 from 6 (Table 2) relative to 1 from 5 (Table 1), although this difference is not so marked in the purified yields. One possible answer is that 5 reacts more readily to 1-methyltetrazole-5-diazonium (8) than does 6 to 2-methyltetrazole-5-diazonium (9), but 8 is considerably less stable than 9 and tends to fragment into low molecular weight units, a competing reaction to attack by nitrite ion. Such a suggestion is supported by TLC analysis of the crude 2



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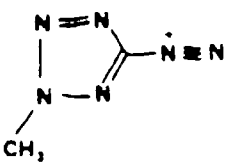

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obtained from 6, where significant amounts of polar impurities such as nitrosamines* are observed, while crude 1 from 5 was much cleaner.

A further intriguing observation is that the conversion of 5 to 1 is catalysed by copper ions whereas that of 6 to 2 is not. It is currently thought that displacement of diazonium salts by nitrite ion is a radical process [16] whereby the catalyst transfers an electron to the diazonium ion and subsequent attack occurs on the aryl radical formed by loss of nitrogen. An ionic mechanism cannot be ruled out in some systems [16] and the catalysis results observed here could suggest competing ionic and radical pathways. Further research, such as the use of different catalytic salts, seems warranted.

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* No attempt was made to isolate these intermediates owing to their potential explosive and carcinogenic properties.

2.2 *Characterisation and Detection of 1 and 2*

In order that explosives be accurately identified and analysed, a wide range of data from experimental testing must be available. One such data base exists; a recent, extensive report of spectroscopic and chromatographic data for a number of frequently used explosives and nitrotoluene isomers [17]. Accordingly, 1 and 2 were subjected to a comprehensive series of experimental tests, both as a means of characterisation and identification, and more specifically, for their independent assay to check for contamination arising from syntheses which were not isomerically specific.

2.2.1 Thin Layer Chromatography (TLC)

A TLC investigation of 1 and 2 was carried out using silica gel as adsorbent. The results for three solvents which gave acceptable separation and reasonable R_f values are given in Table 5. Tetrazoles are quite polar compounds, with the 1-substituted isomers having significantly higher dipole moments than the corresponding 2-isomers [13]. Thus, for any set of conditions, 2 would be expected to have a higher R_f value than 1, as is observed for dichloromethane (Table 5). However, this order is reversed in diethylether and ethylacetate (Table 5). A number of other 1- and 2-methyl-5-substituted tetrazole isomers were examined under identical conditions, and no such reversal is noted. There appears to be no satisfactory explanation for this unusual observation.

Detection of 1 and 2 when adsorbed on silica gel was investigated using a variety of techniques (Table 6). The most convenient method was found to be irradiation with 254 nm UV light using plates impregnated with fluorescent indicator (entry 3) where both isomers gave strong fluorescence. Both $TiCl_3$ followed by DMAB (entry 8) and KOH in methanol followed by Griess' reagent (entry 9) gave distinct colouration, but the former test is preferable due to the widely differing colours and development times observed between 1 and 2. A number of methods failed because 2 gave unsatisfactory results.

Both 1 and 2 can thus readily be qualitatively analysed by TLC. The characteristic colour differences should be useful for identification while the R_f values, particularly the reversal in dichloromethane relative to diethyl ether and ethyl acetate, are also extremely characteristic. Since both 1 and 2 absorb in the UV region (see below) high performance liquid chromatography (HPLC) should be amenable to quantitative determination of 1 and 2 in mixtures.

2.2.2 Ultraviolet (UV) Spectra

Tetrazole and alkyl tetrazoles exhibit only end absorption in the 180-220 nm region [13]. Both 1 and 2 follow this pattern despite the presence of the conjugative nitro group: 1, λ_{max} 214 nm, ε 6490 (ethanol); 216,6770 (methylcyclohexane); 2, 215, 7290 (ethanol); 214, 8480 methylcyclohexane). The UV spectra are nearly identical.

2.2.3 *Infrared (IR) Spectra*

The IR spectra of 1 and 2 as KBr discs are quite similar. Both exhibit dominant absorptions due to the NO_2 group stretching and bending vibrations; 1, 1510, 1350, 840 cm^{-1}; 2, 1560, 1330, 845 cm^{-1}, and strong peaks probably due to C=N stretching vibrations at 1570 cm^{-1} for 1 and 1560 cm^{-1} for 2 (this latter peak is particularly strong as it overlaps with the NO_2 asymmetric stretching vibration. The tetrazole ring is characterised by an absorption near 1300 cm^{-1} , due to N-N=N stretching vibrations and skeletal vibrations ranging from 970-1100 cm^{-1} where two to four bands are usually observed [18,19]. Indeed, the spectrum of 1 shows two bands at 988 and 1032 cm^{-1} while 2 exhibits three bands at 1026, 1040 and 1072 cm^{-1}. The absorption at 988 cm^{-1} in 1 and 1072 cm^{-1} in 2 are in regions with no obscuring bands in the other isomer and can be used as a quick qualitative check for the presence of 2 in 1 and vice versa. The N-N=N stretching vibration is unfortunately obscured by the very strong NO_2 symmetric stretching vibration in both 1 and 2.

The IR spectrum of the 1:1 complex, whether recorded as a KBr disc or as a melted film at 95°C, is essentially a composite of the individual spectra of 1 and 2. Such behaviour is typical of weakly polar diamagnetic adducts or π-complexes [20] where there are no major structural or electronic changes to the individual molecules making up the complex.

2.2.4 *Proton NMR Spectra*

Proton NMR spectra of a wide range of 5-substituted-1- and 2-alkyltetrazoles have been extremely useful for distinguishing between isomers since the chemical shift of the alkyl substituent is dependent on its location in the ring [21]. It can be seen from the limited amount of data available for N-methyltetrazoles that the methyl protons of a 2-methyl group resonate 0.09-0.34 ppm downfield from the methyl protons in the corresponding 1-isomer [21]. The data obtained for 1 and 2 in deuterochloroform continue this trend: 1, 10% w/v, δ 4.43 ppm; ∞-dilution, δ 4.45 ppm; 2, 10% w/v, δ 4.50 ppm, ∞-dilution, δ 4.51 ppm. The methyl protons are the most deshielded, while the chemical shift difference is the smallest, yet observed for any tetrazole isomeric pair. The former results from the substantial electron withdrawal by the nitro group, while the latter reflects the local anisotropy from the neighbouring nitro group on the methyl group of 1. Although the chemical shift difference between 1 and 2 is small, the signals are still readily resolved and, as such, proton NMR represents the best technique studied here for quantitatively determining ratios of 1 and 2 and detecting contamination of one by the other.

3. EXPERIMENTAL

All melting points are uncorrected. Infrared spectra were recorded on either a Unicam SP 1000 or Perkin Elmer 125 Infrared Spectrophotometer, ultraviolet spectra were recorded on a Varian Superscan 3 UV-Visible Spectrophotometer and proton magnetic resonance spectra were recorded at 60 MHz on a Varian HA 60 IL spectrometer with tetramethylsilane as internal reference. The microanalysis was performed by the Australian Microanalytical

Service, CSIRO, Melbourne. Thin layer chromatographic analyses were performed on either Merck Pre-coated silica gel 60 F_{254} plates, thickness 0.25 mm, with fluorescent indicator, or Eastman Chromatogram Sheet, 13179 silica gel, without fluorescent indicator. All chemicals were commercially available except those whose syntheses are described below, and tetrazol-5-amine monohydrate (3) and sodium 5-nitrotetrazole dihydrate (4) which were available from previous studies. Phase separating paper was Whatman 1_S^P.

Note: Both 1 and 2 are quite impact sensitive (F of I values 23 and 22 respectively) and all manipulation should be with wooden or paper (not metal) spatulas. 2 also appears to have allergenic properties leading to dermatitis and gloves should be used for handling during preparation.

Methylation of Tetrazol-5-amine monohydrate (3)

Methylation of 3 with iodomethane was carried out exactly as described by Henry and Finnegan [9]. 2-Methyltetrazol-5-amine (6) was isolated by treating the benzene extracts with light petroleum (b.p. 80-100°C) and allowing to crystallise at 0°C, then filtering and concentrating the mother liquors. 6 was thus obtained as colourless crystals, m.p. 102-104.5°C, lit. [9] m.p. 104.5-105.5°C.

1-Methyltetrazol-5-amine (5) was isolated by twice recrystallising the benzene insoluble material from water, again as previously described [9]. 5 was obtained as colourless needles, m.p. 226-8°C, lit. [9] m.p. 226-8°C. The yields of 5 and 6 obtained in all experimental runs are shown in Table 4.

1-Methyl-5-nitrotetrazole (1) via Diazotisation of 5

A solution of 5 (4.00 g), 98% sulfuric acid (8.0 cm^3) and cupric sulfate pentahydrate (0.5 g) in water (120 cm^3) was added dropwise, over a period of 90 minutes, to a stirred solution of sodium nitrite (42.4 g) in water (150 cm^3) held at 45 ± 2°C. After addition was completed, the solution was stirred for an additional hour, during which time evolution of nitrogen ceased, and then allowed to cool to room temperature. The reaction mixture was extracted with dichloromethane (3 x 50 cm^3), the organic extracts were washed with saturated aqueous sodium bicarbonate, dried by filtration through fluted phase separating paper and the solvent removed in vacuo to leave a brown oil (2.97 g, 57.0%).

The oil was dissolved in diethyl ether under reflux (approx. 50 cm^3), decolourising charcoal was added and the then colourless solution was filtered. Light petroleum (b.p. 40-60°) was added to the hot solution till permanent cloudiness was just reached (approx. 10 cm^3 required), diethyl ether was added dropwise to clear and further additions were made till the solution reached room temperature. The solution was seeded with 1 and allowed to stand overnight at - 15°C. Filtration gave 1 as long colourless crystals (1.85 g), m.p. 40-1°C, lit. 55-6°C [10], 52°C [8] (see note Section 2.1.1). Found: C, 18.5; H, 2.4; N, 54.3. $C_2H_3N_5O_2$ requires C, 18.6; H, 2.4; N, 54.3. Further material (0.66 g, m.p. 39-40.5°C) was obtained by repetition of recrystallisation on the oil remaining after evaporation of the mother liquors. Total yield 2.51 g, 48.2%.

2-Methyl-5-nitrotetrazole (2) via Diazotisation of 6

A solution of 6 (2.00 g), 98% sulfuric acid (4.0 cm^3) and cupric sulfate pentahydrate (0.4 g) in water (60 cm^3) was added dropwise, over 90 minutes, to a stirred solution of sodium nitrite (21.2 g) in water (80 cm^3) held at 45 ± 2°C. After addition was completed, the solution was stirred for an additional hour at 45 ± 2°C, then allowed to cool and refrigerated for 2 hours. The resultant colourless crystals were filtered under suction and allowed to dry overnight. Yield = 1.15 g. The crystals were purified by sublimation at water pump pressure (2.0 kPa, 15 mm Hg) on a steam bath to give 2 as colourless irregular plates, 1.07 g, m.p. 84-85.5°C, lit. m.p. 85-6°C [8,9], 86-7°C [10].

The filtrate was extracted with dichloromethane (2 x 25 cm), the extracts were washed with saturated sodium bicarbonate solution and dried by filtration through fluted phase separating paper. Removal of solvent gave yellow oily crystals (0.85 g) which were sublimed as above to give slightly yellowish plates. Recrystallisation by dissolution in the minimum of hot toluene, adding light petroleum (b.p. 80-100°C) to incipient cloudiness, allowing to cool and finally refrigerating overnight gave 2 (0.37 g), slightly less pure than the above crop, m.p. 83-84.5°C.
Total yield = 1.44 g, 55.2%.

2 via Methylation of sodium 5-nitrotetrazole dihydrate (4)

A solution of iodomethane (1.65 g) in acetone (20 cm^3) was added to 4 (2.00 g) in water (5 cm^3). The resulting solution was heated under reflux for 8 hours, further iodomethane (1.65 g) was added and heating was continued overnight. After cooling, the reaction mixture was extracted with dichloromethane (50 cm^3 then 20 cm^3) and the combined extracts were washed with 10% aqueous sodium metabisulfite, then dried by filtration through phase separating paper. Removal of solvent gave a slightly yellow crystalline product (1.25 g) which was purified by sublimation under water pump pressure (2.0 kPa, 15 mm Hg) on a steam bath. The cold finger was removed every 60 minutes and the crystals adhering to it were gently scraped off. Sublimation was continued for 3 hours, then the combined crystals were recrystallised by dissolving in the minimum hot toluene (approx. 12 cm^3) on a water bath, adding light petroleum (b.p. 80-100°C) till the solution was just cloudy (approx. 10 cm^3) and then adding toluene dropwise to clear the solution. The solution was cooled to room temperature, refrigerated overnight and filtered under suction to yield 2 as sparkling colourless plates (0.99 g, 66.4%), m.p. 84.5-86°C, lit. m.p. 85-6°C [8,9], 86-7°C [10].

Alternative procedure for purification : The crude product from methylation (1.22 g) was recrystallised as described above using an additional hot filtration of the toluene solution. The crystals were isolated by suction filtration, and inspection of the crystals revealed two types which were separated manually. The major component was 2 as colourless irregular plates, (0.78 g, 52.4%), m.p. 84-85.5°C. The minor component (0.19 g, 12.9%) consisted of large colourless rhombohedra, m.p. 56.5-58°C which were identified as a 1:1 molecular complex of 1 and 2 (see Section 2.1.3). Henry and Finnegan [9] report m.p. 57.5-58°C for this product, incorrectly identified as 1.

Preparation of the 1:1 complex of 1 and 2

A mixture of 1 (0.25 g) and 2 (0.25 g) was dissolved in hot toluene (10 cm^3), light petroleum (b.p. 80–100°C, 7.5 cm^3) was added and the solution was allowed to cool. Overnight refrigeration followed by filtration gave the 1:1 complex of 1 and 2 as colourless rhombodhedra, m.p. 56.5-58°C, identical with those obtained above in the methylation of 4.

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TABLE 1

PREPARATION OF 1-METHYL-5-NITROTETRAZOLE (1) VIA DIAZOTISATION OF 1-METHYLTETRAZOL-5-AMINE (5) : EXPERIMENTAL CONDITIONS AND YIELDS

Entry	Solution A[a]				Solution B[a]		Temp. (°C)	Yield of 1 (g, %[b])	
	5 (g)	98% H_2SO_4 (cm^3)	$CuSO_4.5H_2O$ (g)	H_2O (cm^3)	$NaNO_2$ (g)	H_2O (cm^3)		Crude product	Purified
1	1.00	3.4	-	60	10.6	100	45 ± 2	0.424(32.6)	0.24(18.4)
2	4.00	13.6	-	240	42.4	400	45 ± 2	1.894(36.4)	1.42(27.3)
3	3.45	11.7	-	205	36.6	345	45 ± 2	2.007(44.7)	1.58(35.2)
4	1.00	3.4	-	60	10.6	100	45 ± 2	0.635(48.7)	0.49(37.6)
5	1.00	2.0	0.1	30	10.6	75	45 ± 2	0.724(52.4)	0.56(43.0)
6	2.00	4.0	0.2	60	21.2	100	45 ± 2	1.459(56.0)	1.13(43.4)
7	4.00	8.0	0.5	120	42.4	150	45 ± 2	2.970(57.0)	2.51(48.2)
8	1.71	3.4	0.25	50	18.1	65	45 ± 2	1.165(52.3)	0.92(42.5)
9	2.00	4.0	0.3	60	21.2	70	45 ± 2	1.615(62.0)	1.15(44.2)
10	1.00	2.0	0.15	30	10.6	40	17 ± 2	0.840(64.5)	0.62(47.6)
11	3.275	6.55	0.5	100	35.0	125	17 ± 2	2.463(57.8)	1.86(43.6)

a See Experimental Section; b % Yields in parentheses.

TABLE 2

PREPARATION OF 2-METHYL-5-NITROTETRAZOLE (2) VIA DIAZOTISATION OF 2-METHYLTETRAZOL-5-AMINE (6) : EXPERIMENTAL CONDITIONS AND YIELDS

Entry	Solution A[a]				Solution B[a]		Temp. (°C)	Yield of 2 (g, %[b])	
	6 (g)	98% H_2SO_4 (cm^3)	$CuSO_4.5H_2O$ (g)	H_2O (cm^3)	$NaNO_2$ (g)	H_2O (cm^3)		Crude product	Purified
1	1.00	3.4	-	60	10.6	100	45 ± 2	0.985(75.6)	0.565(43.4)[c]
2	1.00	2.0	0.1	30	10.6	75	45 ± 2	0.991(76.1)	0.656(50.4)[c]
3	1.00	2.0	0.15	30	10.6	40	45 ± 2	1.025(78.7)	0.610(46.8)[c]
4	3.00	6.0	0.5	90	31.8	110	45 ± 2	3.023(77.4)	2.04(52.2)[d]
5	2.00	4.0	0.4	60	21.2	80	45 ± 2	2.00(76.7)	1.44(55.2)[e]
6	1.00	2.0	0.15	30	10.6	40	17 ± 2	0.96(73.7)	0.77(59.1)[d]
7	3.00	6.0	0.5	90	31.8	110	17 ± 2	2.805(71.8)	1.865(47.7)[d]
8	3.00	6.0	0.5	90	31.8	110	17 ± 2	3.02(77.4)	1.62(41.5)[d]

[a] See Experimental Section.

[b] Yields in parentheses.

[c] Product isolated by extraction then recrystallisation, contaminated by yellow impurity (see text).

[d] Product fractionated by filtration then extraction, then separately recrystallised (see text).

[e] Product fractionated by filtration then extraction, separately sublimed and the extracted fraction subsequently recrystallised.

TABLE 3

METHYLATION OF SODIUM 5-NITROTETRAZOLE DIHYDRATE (4) WITH IODOMETHANE

EXPERIMENTAL CONDITIONS AND YIELDS

Entry	Experimental Conditions			Crude Product (g,%)[a]		Purified Product (g,%)[a]	
	4 (g)	CH_3I (g)	Procedure	Total 2 + 1	Ratio 2:1	2	Complex
1	0.2	0.165	3 hour reflux	0.068(45.6)	5.0:1	[b]	
2	0.2	0.165	3 hour reflux	0.066(44.2)	5.3:1	[b]	
3	0.2	0.165	6 hour reflux	0.079(53.0)	5.0:1	[b]	
4	0.2	0.165 + 0.165	3 hour reflux, add 2nd equiv., 3 hour reflux	0.106(71.1)	6.0:1	[b]	
5	0.2	0.165 + 0.165	15 hour reflux, add 2nd equiv., 8 hour reflux	0.110(73.7)	5.4:1	[b]	
6	2.0	1.65 + 1.65	8 hour reflux, leave o/night, add 2nd equiv., 8 hour reflux	1.217(81.6)		0.781(52.4)[c]	0.193(12.9)[c]
7	2.0	1.65 + 1.65	as entry 6	1.125(75.4)		0.74(49.6)[c]	0.12(8.0)[c]
8	2.52	2.1 + 2.1	as entry 6	1.717(91.3)		1.124(59.8)[c]	0.094(5.0)[c]
9	2.0	1.65 + 1.65 + 1.65	8 hour reflux, add 2nd equiv. and leave o/night, add 3rd equiv. and reflux 2 hours.	1.25(83.8)		0.99(66.4)[d]	[b]
10	2.0	1.65 + 1.65	6 hour reflux, cool, add 2nd equiv. and leave o/night, 2 hours reflux.	1.30(87.2)	5.0:1	0.98(65.7)[d]	[b]

[a] % Yields in parentheses.

[b] No attempt to isolate product.

[c] Isolated by recrystallisation followed by manual separation of 2 and the molecular complex (see text).

[d] Isolated by sublimation followed by recrystallisation.

TABLE 4

YIELDS OF 1-METHYLTETRAZOL-5-AMINE (5) AND 2-METHYLTETRAZOL-5-AMINE (6) OBTAINED FROM METHYLATION OF TETRAZOL-5-AMINE MONOHYDRATE (3)

Experiment	Reactant	Products	
	3 (g)	5(g, %)[a]	6(g, %)[a]
1	8.50	2.54(31.1)	1.68(20.6)
2	8.50	3.40(41.6)	1.66(20.3)
3	8.50	2.65(32.4)	1.68(20.8)
4	25.50	11.39(46.5)	5.10(20.8)
5	8.50	2.71(33.5)	1.77(21.7)
6	8.50	2.69(32.9)	1.29(16.0)
7	34.00	8.44(25.8)	6.35(19.4)
8	25.50	7.01(28.6)	4.93(20.1)

a % Yields are shown in parentheses.

TABLE 5

TLC R_f VALUES FOR 1-METHYL-5-NITROTETRAZOLE (1) AND 2-METHYL-5-NITROTETRAZOLE (2) USING SILICA GEL ADSORBENT

Solvent	R_f 1	R_f 2
dichloromethane	0.35	0.48
ethyl acetate	0.62	0.56
diethyl ether	0.83	0.74

TABLE 6

COLOUR AND SPECTROPHOTOMETRIC TESTS FOR DETECTION OF 1-METHYL-5-NITROTETRAZOLE (1) AND 2-METHYL-5-NITROTETRAZOLE (2) ON SILICA GEL TLC PLATES

Test (TLC Plates without fluorescent indicator unless specified)	Result	
	1	2
UV light, 254 nm	no flucrescence	no fluorescence
UV light, 366 nm	dark purple fluorescence	very faint fluorescence
UV light, fluorescent indicator, 254 nm	strong purple fluorescence	strong purple fluorescence
UV light, fluorescent indicator, 366 nm	no fluorescence	no fluorescence
Iodine	dark brown stain	very faint stain
Spray with 98% H_2SO_4, allow to dry, heat at 180°C for 30 minutes	dark brown stain	brown stain
Spray with 10% KOH in methanol	no colour	no colour
Spray with 12.5% $TiCl_3$ in 15% HCl in H_2O, air dry, spray with 0.25% dimethylaminobenzaldehyde (DMAB) in 30% HOAc in H_2O, then heat at 105°C for 15 minutes	pinkish grey spot with orange surround, develops slowly on heating	bright yellow spot, develops immediately on spraying with DMAB
Spray with 10% KOH in methanol, heat at 105°C for 20 minutes, then spray with Griess' reagent	pink-orange colour	orange-brown colour
Spray with 1.5% diphenylamine in methanol, then UV light, 254 nm, 15 minutes	no colour	no colour
Spray with bromocresol green (Merck spray reagent, 0.05%)	pale blue-grey spot on blue background	no colour distinguishable from background

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