# Crystal and Molecular Structure of 3-Hydrazino-1-Hydrazinothio- Carbonyl Pyrazoline (TNT3)

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*The crystal and molecular structure of 3-Hydrazino-1-Hydrazinothio-carbonyl pyrazoline (TNT3), $C_4H_{10}N_6S$ has been determined with $MoK_{\alpha\alpha}$ diffractometer data by direct methods. The compound crystallized in the monoclinic space group $P2_1/c$, with a = 6.925(1), b=13.675(3), c=8.190(2)Å and $\beta$=108.14(3)º. The structure was refined by full matrix least squares methods to R=0.047 using 917 reflections. The pyrazoline ring was found to be planner and delocalized. The amino groups connected to N7 and to N9 is extended and trans.*

## Introduction

Pyrazoline and its derivatives have not been found in nature. The addition of aliphatic diazo compounds to olefins lead to pyrazolines. Also the addition of hydrazine or its derivatives on α, β- unsaturated aldehydes or ketones yields pyrazoline [1].

Pyrazoline derivetives was found to have potential antipyretic analgesic [2,3,4], anti-inflammatory [5], and antimicrobial properties [6]. Pyrazoline dervivatives was found to exhibit a cytoxic activity [7], inhibitory activity of platelet aggregation [8], herbicide activity [9]. Pyrazoline interest extended to dyes and dye couplers [10]. In the present work X-ray crystal structure analysis has been undertaken in order to confirm the chemical structure also the molecular packing of the molecules.

## Experimental

The crystals of 2-hydrazino-1-hydrazinothio-carbonyl pyrazoline (TNT3) were kindly supplied by Dr. G. A. El-hity, Chemistry Department, Faculty of Science, Tanta University. The crystals are thin colorless plates elongated along the a-axis. When examined between crossed nicols, they show straight extinction parallel to the plate length. The density of the crystals were found to be 1.53 gm/cm$^3$ and that one calculated 1.532(4) gm/cm$^3$, corresponding to four molecules of ($C_9$ $H_{10}$ $N_6$ S) in the unit cell. A crystal of dimensions $0.3\times0.2\times0.25$ mm was chosen and mounted in random orientation on head of the four circle diffractometer of the kind KM4 point detector, constructed by Kuma, Poland and implemented at Masaryk University, Faculty of Science, Berno, Czech Republic. Least square refinement using 20 reflections with $15\le\theta\ge20^\circ$ was carried out from which an orientation matrix for data collection was derived as well accurate cell parameters were obtained to be: a=6.925(1), b=13.675(3), c=8.190(2)Å and β=108.14(3)$^o$. The data were collected with $MoK_\alpha$ (λ=0.71073) radiation. Data were collected to maximum 2θ of 48$^o$. A total of 1235 reflections were collected of which 1071 were unique. The linear absorption coefficient is 0.38 mm$^{-1}$ for $MoK_{\alpha\alpha}$ radiation. Therefore no absorption correction was made. The structure was solved by direct methods technique using the program SHELX86 [11]. A total of 11 non-hydrogen atoms were located from an E-map. The structure was refined by full matrix least squares calculations using the program SHELX-93 [12]. Several cycles of isotropic refinement reduced the reliability factor R to 0.12. Anisotropic full matrix least squares was followed and after several cycles R converged to 0.07. The hydrogen atoms were located from difference map except those connected to N7 and N9, Then included in the

refinement in geometrically assigned positions riding in the heavy atoms with individual thermal parameters. Further cycles of least squares led to the final structure with R1-factor of 0.047 for 917 reflections greater than $3\sigma(F_o)$. Atomic Scattering curves were taken from Cromer and Waber [13].

## Result and Discussion

The final fractional coordinates for the non-hydrogen atoms of the molecule TNT3 are listed in Table (1). Anisotropic thermal parameters for the non-hydrogen atoms are given in Table (2). The numbering scheme is shown in Fig. (1). Bond lengths and bond angles are given in Table (3) & (4) respectively. Selected torsion angles are listed in Table (5), using the program PARST88 [14].

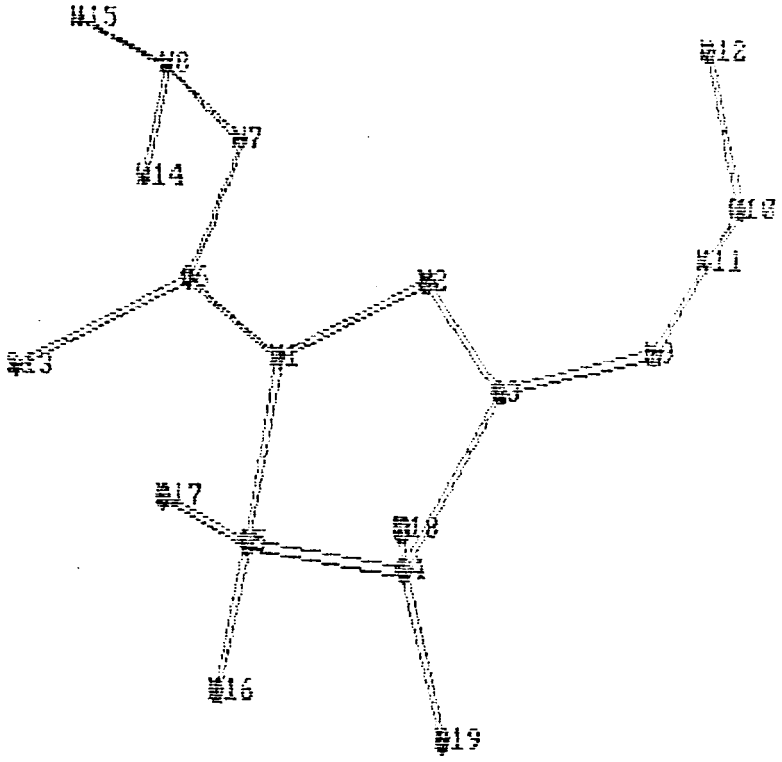


**Fig. (1) :** The numbering scheme of TNT3.

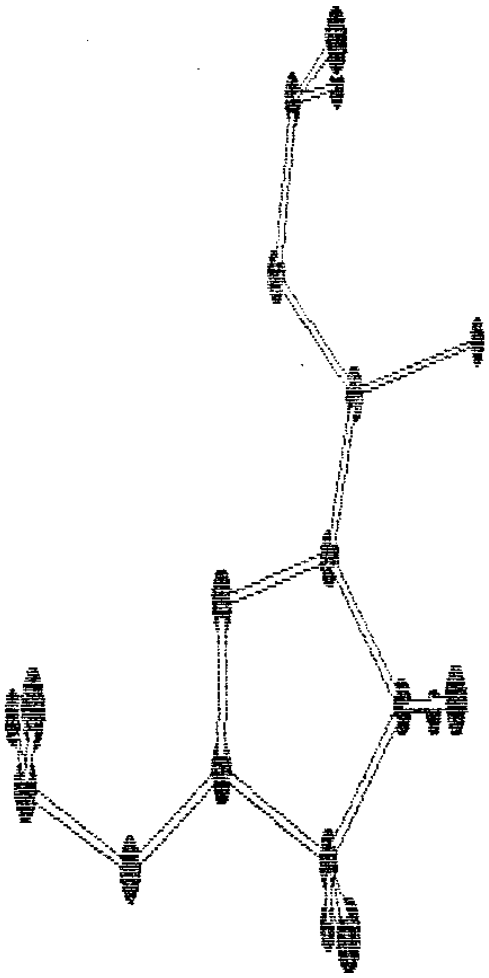

**Fig.(2):** The molecular geometry of TNT3

Computer drawing illustrating the molecular geometry of the molecule using the program MOLDRAW [15] is shown in Fig. (2). The molecular packing of the molecules is shown in Fig. (3).

The amine groups connected to N7 and that connected to N9 are trans and extended, the torsion angles found to be N1-C6-N7-N8=178° and C4-C3-N9-N10=176°. It was noticed that the single bond lengths in the ring are shorter than usual values; the expected values for C-C=1.543(3), C-N= 1.465(2) and N–

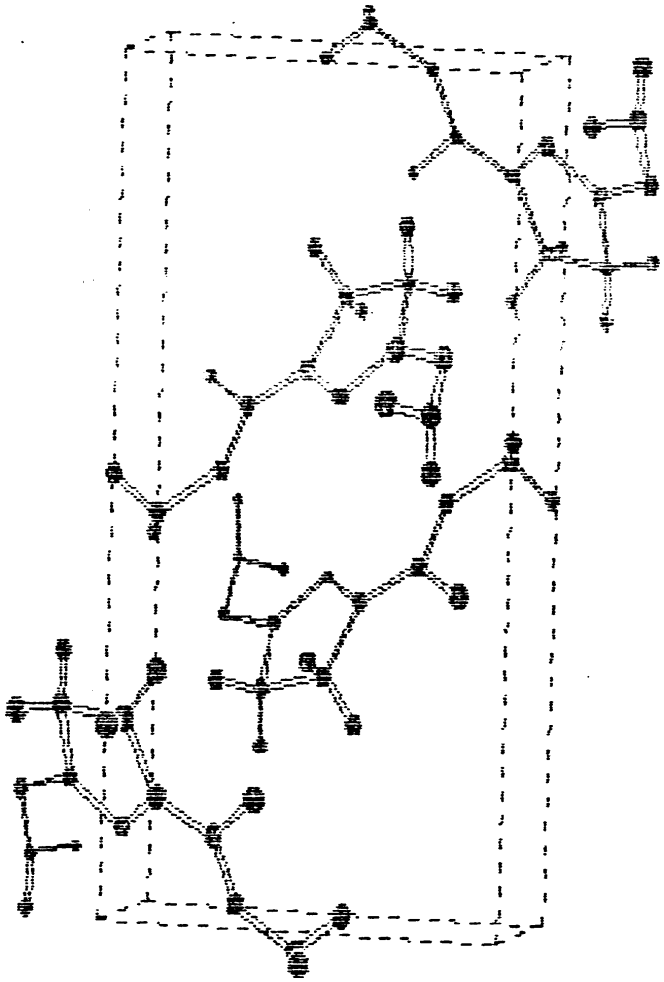

**Fig. (3):** The packing of the molecules of TNT3.

N =1.442(2) Å [16]. The single bond lengths in the ring are N1-N2=1.327(5), C3-C4=1.499(5), C4-C5=1.503(5) and N1-C5= 1.469(5) Å, indicating partial single bond character. Also N2=C3 =1.283 Å, the expected value is 1.242Å [16] showing partial double bond character. Consequently, the atoms in the ring are approximately planners. This is due to delocalization of bonds, such a feature was noticed by NMR and UV spectroscopy studies on tetrazole compounds [17]. Also torsion angles calculation showed that the ring is planar; he following table shows the asymmetry parameters $\Delta C_s$ and $\Delta C_2$ of this ring [18].

| | |
|---|---|
| $\Delta Cs^{N1}$ | 1.0 |
| $\Delta C2^{1,5}$ | 0.4 |

The bond lengths of the side chain moieties N1-C6, C6-N7 and C3-N9 are 1.327(5), 1.340(5) and 1.348(5) Å are in good agreement with that found in 1 - Phenyl- 3 - Methyl-5 - pyrozolene Perchlorate (ES1) and 3 -Amino-2-(4-metylphenylamino) quinazoline - 4(3H) - one (TNT2) [19-20]. The bond length C6-S13 is 1.693(4) Å. Bond angles C4-C3-N9 and C5-N1-C6, are 120.0(3) and 126.7(3)º suggesting the side chain moieties are approximately in the same plane. The intermolecular forces are mainly due to Van der Waals interactions. The packing of the molecules is shown in Fig. (3).

**Table (1)**
Fractional coordinates and their esd's for TNT3.

| **Atoms** | **X** | **Y** | **Z** |
|---|---|---|---|
| **N1** | 0.5061(5) | 0.3691(2) | 0.4252(4) |
| **N2** | 0.7100(4) | 0.4015(2) | 0.4845(4) |
| **C3** | 0.8017(6) | 0.3455(3) | 0.6104(4) |
| **C4** | 0.6733(6) | 0.2667(3) | 0.6510(5) |
| **C5** | 0.4704(6) | 0.2823(3) | 0.5174(5) |
| **C6** | 0.3727(5) | 0.4125(3) | 0.2926(5) |
| **N7** | 0.4416(4) | 0.4881(2) | 0.2226(4) |
| **N8** | 0.3195(5) | 0.5391(2) | 0.0774(4) |
| **N9** | 0.9957(5) | 0.3574(2) | 0.7102(4) |
| **N10** | 1.1226(5) | 0.4272(2) | 0.6603(4) |
| **S13** | 0.1285(1) | 0.3739(1) | 0.2199(1) |

**Table (2)**
Anisotropic temperature factor and their esd's for TNT3

| Atoms | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| N1 | 0.007(2) | 0.015(2) | 0.022(2) | 0.003(1) | 0.004(1) | 0.002(1) |
| N2 | 0.005(2) | 0.016(2) | 0.021(2) | 0.001(1) | 0.004(1) | 0.001(1) |
| C3 | 0.014(2) | 0.013(2) | 0.017(2) | -.001(1) | 0.006(1) | 0.001(1) |
| C4 | 0.015(2) | 0.019(2) | 0.032(2) | 0.008(1) | 0.006(1) | 0.007(1) |
| C5 | 0.012(2) | 0.016(2) | 0.030(2) | 0.005(1) | 0.009(1) | 0.000(1) |
| C6 | 0.009(2) | 0.013(2) | 0.021(2) | -.004(1) | 0.008(1) | 0.000(1) |
| N7 | 0.011(2) | 0.020(2) | 0.016(2) | 0.005(1) | 0.002(2) | 0.001(1) |
| N8 | 0.017(2) | 0.024(2) | 0.019(2) | 0.006(1) | 0.004(1) | 0.001(1) |
| N9 | 0.012(2) | 0.019(2) | 0.026(2) | 0.002(1) | 0.003(1) | 0.003(1) |
| N10 | 0.009(2) | 0.019(2) | 0.025(2) | 0.003(1) | 0.004(1) | 0.003(1) |
| **S13** | 0.008(1) | 0.017(1) | 0.030(1) | -.001(1) | 0.003(1) | 0.002(1) |

**Table (3)**
Bond lengths and their esd's for TNT3

| Atoms | Bond length | Atoms | Bond length |
|---|---|---|---|
| **N1-N2** | 1.414(4) | C6-S13 | 1.693(4) |
| **N2-C3** | 1.283(5) | C3-N9 | 1.348(4) |
| **C3-C4** | 1.499(5) | N9-N10 | 1.418(4) |
| **C4-C5** | 1.503(5) | | |
| **C5-N1** | 1.469(4) | | |
| **N1-C6** | 1.327(5) | | |
| **C6-N7** | 1.340(5) | | |
| **N7-N8** | 1.411(5) | | |

**Table(4)**
Bond angles and their esd's for TNT3

| Atoms | Angles | Atoms | Angles |
|---|---|---|---|
| **N1-N2-C3** | 106.3(3) | C3-N9-N10 | 120.5(3) |
| **N2-C3-C4** | 115.4(3) | C5-N1-C6 | 126.7(3) |
| **C3-C4-C5** | 102.7(3) | N2-N1-C6 | 120.5(3) |
| **C4-C5-N1** | 102.8(3) | N2-C3-N9 | 124.4(3) |
| **C5-N1-N2** | 112.8(3) | C4-C3-N9 | 120(3) |
| **N1-C6-N7** | 122.7(3) | | |
| **C6-N7-N8** | 122.9(3) | | |
| **N1-C6-S13** | 120.9(3) | | |

**Table (5)**
Selected torsion angles

| Atoms | Angles | Atoms | Angles |
|---|---|---|---|
| **C3-C4-C5-N1** | -2.6 | C5-N1-C6-N7 | -176.6 |
| **C4-C5-N1-N2** | 3.5 | N1-C6-N7-N8 | 177.7 |
| **C5-N1-N2-C3** | -2.9 | N2-N1-C6-N7 | -1.1 |
| **N1-N2-C3-C4** | 1.0 | N2-N1-C6-S13 | 179.6 |
| **N2-C3-C4-C5** | 1.1 | | |
| **C4-C3-N9-N10** | 175.7 | | |
| **N2-C3-N9-N10** | -8.8 | | |
| **C5-N1-C6-S13** | 4.1 | | |

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