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Synthesis and Crystal Structure of 4-Methyl-5-nitro-1,2,3-triazole

HUAN HUO, BO-ZHOU WANG, JUN DONG*, LIN MA and CHENG ZHOU

Xi'an Modern Chemistry Research Institute, Xi'an 710065, Shaanxi Province, P.R. China

*Corresponding author: Tel: +86 29 88291536; E-mail: dyks_@sohu.com

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4-Methyl-5-nitro-1,2,3-triazole was synthesized from ethyl 2,2-dinitroacetate by cyclization. The structure of the compound was characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, elementary analysis and X-ray single-crystal diffraction analysis. The title compound ($C_3H_4N_4O_2$, Mr = 129.11) was crystallized in orthorhombic system, Pbca space group with a = 8.7139(17), b = 9.8198(19), c = 12.889(3)Å, V = 1102.9(4) Å^3, Z = 8, Dc = 1.555 g/cm^3, λ = 0.071073 Å, μ(MoK$_\alpha$) = 0.131 mm^{-1}, F(000) = 536, S = 1.021, R = 0.0490 and wR = 0.1468 for 1559 observed reflections with I > 2σ(I).

Keywords: Organic chemistry, 1,2,3-Triazole compound, Crystal structure, Synthesis.

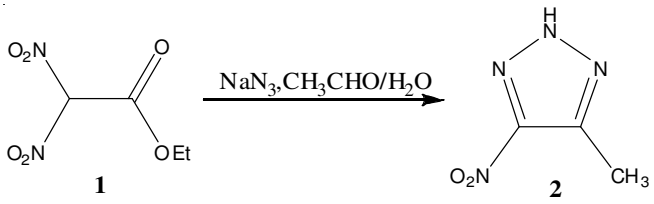
INTRODUCTION

Recently, 1,2,3-triazoles units are interesting structural framework found in all kinds of energetic materials and medicament[1-3]. 4-Methyl-5-nitro-1,2,3-triazole is an important organic intermediate, which has been employed to design and synthesize numerous energetic compounds. For example, taking 4-methyl-5-nitro-1,2,3-triazole as primary substances, 4-amino-5-nitro-1,2,3-triazole (ANTZ) was synthesized[4,5], it was identified as a kind of potential high performance insensitive explosive and has some desirable attributes, including a high nitrogen content of 54 %, high density 1.837 g/cm^3, combustion heat of 1350.5 kJ/mol and relatively low sensitivity to shock or impact-included ignition with H_{50} of 154 cm, which can be used as a main insensitive energetic component of cast explosives and propellants to substitute TATB, RDX or HMX. In order to confirm the molecular structure of compound **2**, its single crystals were grown and its crystal structure was characterized by single-crystal X-ray diffraction analysis.

EXPERIMENTAL

Ethyl 2,2-dinitroacetate was prepared and purified from a reported method[6] by Xi'an Modern Chemistry Research Institute and other reagents were purchased from commercial sources. ^{1}H NMR and ^{13}C NMR were obtained in $CDCl_3$ on a Bruker AV500 NMR spectrometer. Infrared spectra were obtained from KBr pellets on a Nicolet NEXUS870 Infrared spectrometer in the range of 4000-400 cm^{-1}. Elemental analyses (C, H and N) were performed on a VARI-El-3 elemental analyzer.

Synthesis and characterization: Using ethyl 2,2-dinitroacetate **1** as the starting material, our target compound **2** was synthesized *via* cyclization with a yield of 18.2 % outlined in **Scheme-I**.



1 2

Scheme-I: Synthetic route for the title compound

Ethyl 2,2-dinitroacetate (6.6 g, 30 mmol, yield of 93 %), 45 mL water were mixed in a three-necked round-bottomed flask with a stirrer. To the reaction mixture, 40 % acetaldehyde (7.9 g, 45 mmol) and NaN_3 (5.8 g, 90 mmol) were added in turn and adjusted to pH 4 by 70 % sulfuric acid. After stirring for 2 h at 80 °C, adjusted to pH 2 by 20 % sulfuric acid and stirred for another 1 h at 100 °C. After cooling to room temperature, the mixture was put into a beaker and 20 % NaOH was added with stirring until the pH =7-8. The final mixture was extracted with ether. The organic phase was combined and dried over $MgSO_4$. The white product was obtained after evaporating the solvent and then recrystallized from 1,2-dichloroethane to give the pure solid product 0.8 g in a yield of 18.2 %. m.p.: 177-179 °C. Analysis Calculated (%) for $C_3H_4N_4O_2$: N, 43.75; C, 28.12; H, 3.13. Found (%) N, 42.12; C, 28.37; H, 3.217. IR(KBr, ν_{max}, cm^{-1}): 3090 (N-H) 1522, 1368, (-NO_2),

1606, 1449 (triazole); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.60(s, 3H, CH_3), 1.95(s, 1H, NH); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 151.90 (CNO_2), 137.16 (CCH_3), 10.16 (CH_3).

X-ray crystal structure determination: White crystals of 4-methyl-5-nitro-1,2,3-triazole were recrystallized from 1,2-dichloroethane to give satisfactory crystals for X-ray determination. The unit cell determination and data collection were performed with a MoK_α radiation (λ = 0.71073 Å) on a Bruker Smart APEX-CCD diffractometer equipped with a ϕ-ω scan mode in the range of $3.16 \le \theta \le 25.09°$ at 296(2) K. A total of 5062 reflections were collected with 982 unique ones (Rint = 0.0170), of which 982 observed reflections with $I > 2\sigma(I)$ were used in the succeeding refinements. Acrystal with dimensions of 0.31 × 0.23 × 0.17 mm was used. Diffraction data were collected for 878 unique reflections with $-8 \le h \le 10$, $-11 \le k \le 11$ and $-15 \le l \le 13$. Absorption correction was not used. The structure was solved by direct methods using SHELXS program of the SHELXL-97 package and refined with SHELXL package[7,8]. The final refinement was performed by full-matrix least-squares method with anisotropic thermal parameters on F^2 for the non-hydrogen atoms. Crystal data and refinement results are summarized in Table-1. Crystallographic data for the structural analysis have beendeposited in the Cambridge Crystallographic Data Center, CCDC No. 932815.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT DETAILS

Formula	$C_3H_4N_4O_2$
Formula weight	129.11
T (K)	296(2)
λ (Å)	0.71073
Crystal system	Orthorhombic
Space group	Pbca
a (Å)	8.7139(17)
b (Å)	9.8198(19)
c (Å)	12.889(3)
α (º)	90
β (º)	90
γ (º)	90
Volume (Å^3)	1102.9(4)
Z	8
Dc (g/cm^3)	1.555
F (000)	536
θ range/(º)	3.16 to 25.09
Reflections collected/unique	5062 / 982
Refinement method	Full-matrix least-squares on F^2
GOF on F^2	1.093
Final R indexes ($I > 2\sigma(I)$)	$R_1 = 0.0490$, $wR_2 = 0.1468$
Final R indexes (all data)	$R_1 = 0.0527$, $wR_2 = 0.1535$
Largest diff peak and hole (e Å^{-3})	0.573 and -0.491

RESULTS AND DISCUSSION

The selected bond lengths and bond angles are given in Table-2. A displacement ellipsoid plot with atomic numbering scheme and a perspective view of the crystal in a unit cell are shown in Figs. 1 and 2, respectively.

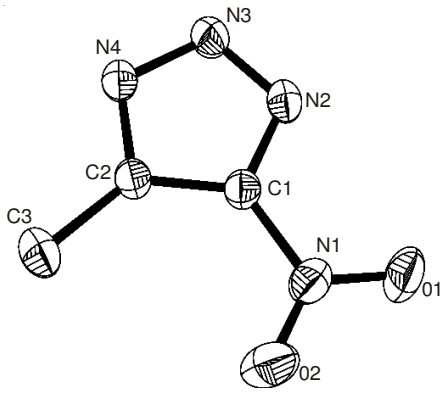


Fig. 1. Molecular structure for the title compound with atomic numbering scheme

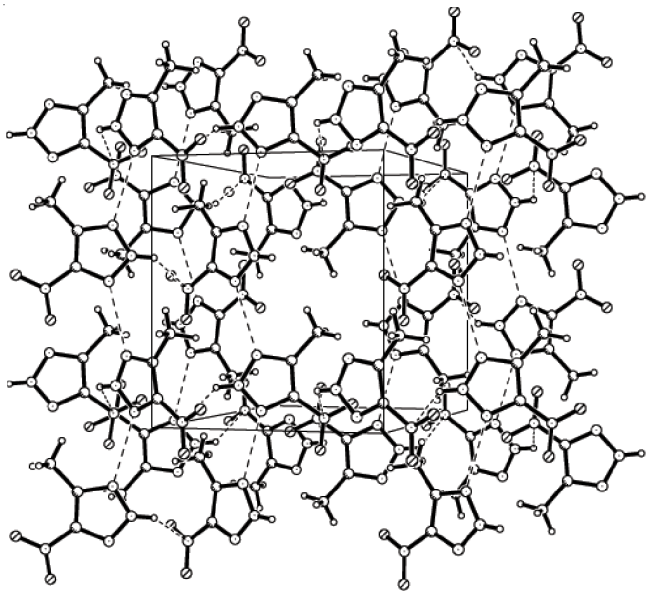


Fig. 2. View of crystal packing down the b axis for the title compound

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (º) FOR THE TITLE COMPOUND

Bond	Dist.	Bond	Dist.	Bond	Dist.
N(1)-O(2)	1.216(3)	N(2)-C(1)	1.347(3)	C(1)-C(2)	1.369(3)
N(1)-O(1)	1.230(2)	N(3)-N(4)	1.342(2)	C(2)-C(3)	1.480(3)
N(1)-C(1)	1.425(3)	N(3)-H(3)	0.8600	C(3)-H(3A)	0.9600
N(2)-N(3)	1.291(2)	N(4)-C(2)	1.337(2)	C(3)-H(3B)	0.9600
Angle	**(º)**	**Angle**	**(º)**	**Angle**	**(º)**
O(2)-N(1)-O(1)	124.44(19)	C(2)-N(4)-N(3)	112.00(16)	C(2)-C(3)-H(3A)	109.5
O(2)-N(1)-C(1)	117.82(19)	N(2)-C(1)-C(2)	110.81(17)	C(2)-C(3)-H(3B)	109.5
O(1)-N(1)-C(1)	117.72(19)	N(2)-C(1)-N(1)	120.42(18)	H(3A)-C(3)-H(3B)	109.5
N(3)-N(2)-C(1)	107.44(16)	C(2)-C(1)-N(1)	128.76(18)	C(2)-C(3)-H(3C)	109.5
N(2)-N(3)-N(4)	107.70(16)	N(4)-C(2)-C(1)	102.04(16)	H(3A)-C(3)-H(3C)	109.5
N(2)-N(3)-H(3)	126.1	N(4)-C(2)-C(3)	123.82(19)	H(3B)-C(3)-H(3C)	109.5
N(4)-N(3)-H(3)	126.1	C(1)-C(2)-C(3)	134.13(19)		

TABLE-3
SELECTED TORSION ANGLES (º)

Angle	(º)	Angle	(º)
C(1)-N(2)-N(3)-N(4)	0.0(2)	O(1)-N(1)-C(1)-C(2)	173.8(2)
N(2)-N(3)-N(4)-C(2)	0.1(2)	N(3)-N(4)-C(2)-C(1)	-0.2(2)
N(3)-N(2)-C(1)-C(2)	-0.1(2)	N(3)-N(4)-C(2)-C(3)	179.3(2)
N(3)-N(2)-C(1)-N(1)	-179.38(17)	N(2)-C(1)-C(2)-N(4)	0.2(2)
O(2)-N(1)-C(1)-N(2)	171.98(19)	N(1)-C(1)-C(2)-N(4)	179.34(18)
O(1)-N(1)-C(1)-N(2)	-7.1(3)	N(2)-C(1)-C(2)-C(3)	-179.1(2)
O(2)-N(1)-C(1)-C(2)	-7.1(3)	N(1)-C(1)-C(2)-C(3)	0.0(4)

In the crystal, the bond lengths N(1)-C(1), N(2)-C(1), N(4)-C(2) was 0.1425(3) Å, 0.1347(3) Å, 0.1337(2) Å, respectively, which were longer than C-C single bond (0.1273 Å) and shorter than C-C double bond (0.1471 Å) (Table-2). Furthermore, the methyl groups and nitryl on C3 and N1 deviate from the planarity of the 1,2,3-triazole ring only slightly, for example the torsion angle of 179.3(2)°, -179.38(17) for N(3)-N(4)-C(2)-C(3) and N(3)-N(2)-C(1)-N(1), respectively, were twisted 0.7 and 0.62 out of plane. Of notable interest are all atoms of the title molecular on one and the same plane nearly (Table-3). The results show that there is one of conjugate system between 1,2,3-triazole ring and the bond of C(2)-C(3) and C(1)-N(1), result that the title molecular shows a good aromaticity and stability.

Conclusion

4-Methyl-5-nitro-1,2,3-triazole was synthesized and characterized by IR, ^{13}C NMR, MS and elemental analysis. X-ray single-crystal diffraction analysis indicated that the title molecule shows a good aromaticity, the C and N atom are involved in same plan with the 1,2,3-triazole ring, which further stabilize the structure.

REFERENCES

1. M.B. Talawar, R. Sivabalan, N. Senthilkumar, G. Prabhu and S.N. Asthana, *J. Hazard. Mater*., **113**, 11 (2004).
2. Z.-Y. Yan, Y.-B. Zhao, M.-J. Fan, W.-M. Liu and Y.-M. Liang, *Tetrahedron*, **61**, 9331 (2005).
3. R. Wang, H. Gao, C. Ye and J.M. Shreeve, *Chem. Mater*., **19**, 144 (2007).
4. Z.-Y. Wang, *Chinese J. Energ. Mater.*, **11**, 227 (2003).
5. K.T. Finlty, Triazole-1,2,3 in Chemistry of Heteroccklic Compounds (1980).
6. H. Huo, B.-Z. Wang and Q. Liu, *Chem. Reagent*, **31**, 490 (2009).
7. G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany (1997).
8. G.M. Sheldrick, SHELXTS-97, Program for Crystal Structure Solution, University of Göttingen, Germany (1997).