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

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Received: 16 August 2013;

Accepted: 24 December 2013;

Published online: 16 July 2014;

AJC-15563

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 ^1H NMR, ^{13}C NMR, FT-IR, elementary analysis and X-ray single-crystal diffraction analysis. The title compound ($\text{C}_5\text{H}_4\text{N}_4\text{O}_2$, Mr = 129.11) was crystallized in orthorhombic system, Pbc_a space group with $a = 8.7139(17)$, $b = 9.8198(19)$, $c = 12.889(3)\text{Å}$, $V = 1102.9(4)\text{Å}^3$, $Z = 8$, $D_c = 1.555\text{ g/cm}^3$, $\lambda = 0.071073\text{ Å}$, $\mu(\text{MoK}\alpha) = 0.131\text{ mm}^{-1}$, $F(000) = 536$, $S = 1.021$, $R = 0.0490$ and $wR = 0.1468$ for 1559 observed reflections with $I > 2\sigma(I)$.

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 medicament¹⁻³. 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 method⁶ by Xi'an Modern Chemistry Research Institute and other reagents were purchased from commercial sources. ^1H 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 $4000\text{--}400\text{ cm}^{-1}$. 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.

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 $80\text{ }^\circ\text{C}$, adjusted to pH 2 by 20 % sulfuric acid and stirred for another 1 h at $100\text{ }^\circ\text{C}$. 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.: $177\text{--}179\text{ }^\circ\text{C}$. Analysis Calculated (%) for $\text{C}_5\text{H}_4\text{N}_4\text{O}_2$: 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, ($-\text{NO}_2$),

1606, 1449 (triazole); ^1H 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 ($\lambda = 0.71073 \text{ \AA}$) on a Bruker Smart APEX-CCD diffractometer equipped with a ϕ - ω scan mode in the range of $3.16 \leq \theta \leq 25.09^\circ$ at 296(2) K. A total of 5062 reflections were collected with 982 unique ones ($R_{\text{int}} = 0.0170$), of which 982 observed reflections with $I > 2\sigma(I)$ were used in the succeeding refinements. A crystal with dimensions of $0.31 \times 0.23 \times 0.17 \text{ mm}$ was used. Diffraction data were collected for 878 unique reflections with $-8 \leq h \leq 10$, $-11 \leq k \leq 11$ and $-15 \leq l \leq 13$. 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 been deposited in the Cambridge Crystallographic Data Center, CCDC No. 932815.

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 ($\text{\AA}$) AND BOND ANGLES ($^\circ$) 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	($^\circ$)	Angle	($^\circ$)	Angle	($^\circ$)
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 (°)

Angle	(°)	Angle	(°)
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 nitril 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, ¹³C 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.

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