



Synthesis and Crystal Structure of 1,2,4-Triazol-5(4H)-one Derivative

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A new triazole compound, $C_{17}H_{15}N_3OCl_2$, has been synthesized and the crystal structure was determined by a single crystal X-ray diffraction study. The crystal symmetry is monoclinic, space group $P2(1)/n$, with $a = 8.1479(17)$ Å, $b = 7.9177(17)$ Å, $c = 25.774(5)$ Å, $\alpha = 90^\circ$, $\beta = 92.976(4)^\circ$, $\gamma = 90^\circ$. An extensive three-dimensional network was observed due to the π - π interactions.

Key Words: Crystal structure, Synthesis, 1,2,4-Triazole.

INTRODUCTION

In recent years, heterocyclic ring systems has received considerable attentions in medicine and agriculture¹⁻⁵, because of their various types of biological activities. Among them, 1,2,4-triazole compounds are playing an important role. They have a rather wide bioactive spectrum, such as fungicidal⁶, insecticidal⁷, bactericidal⁸, herbicidal⁹, anti-cancer¹⁰, etc. Also, the 1,2,4-triazol-5(4H)-one contain amide group, which also exhibited various biological activities¹¹⁻¹³. Since the first triazolinone herbicide-azafenidin was commercialized successfully, a large variety of triazolinone derivatives have been synthesized, such as amicarbazone¹⁴, azafenidin¹⁵, sulfentrazone¹⁶ and carfentrazone-ethyl, are commercially available. Then in the following years, numerous research were evoked on the effort to develop other 1,2,4-triazole-based analogues.

In view of these facts and as a part of our work on the synthesis and biological activity of heterocycles, so herein we report the synthesis and characterization of triazole derivative.

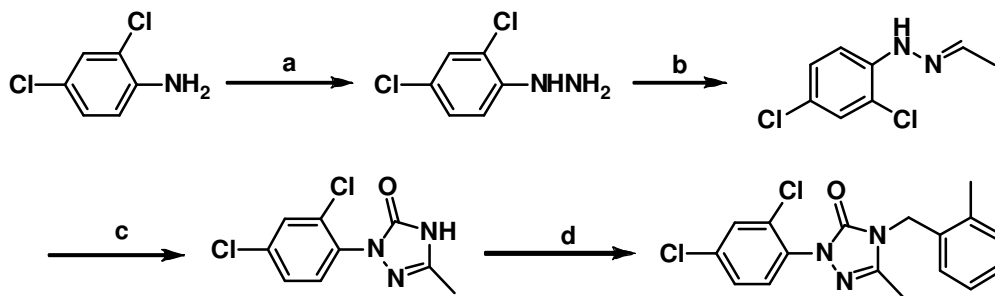
EXPERIMENTAL

All reagents are analytical grade. Melting points were determined using an X-4 apparatus and uncorrected. ¹H NMR spectra were measured on a Bruker AC-P500 instrument using TMS as an internal standard and $CDCl_3$ as solvent. Elemental analyses were performed on a Vario EL elemental analyzer. Crystallographic data of the compound was collected on a Bruker SMART 1000 CCD diffractometer.

Synthesis: The synthetic route was according the reference⁹ as shown in **Scheme-I**. To a mixture of 2-(2,4-dichlorophenyl)-5-methyl-2,4-dihydro-1,2,4-triazol-3-one (0.50 g, 2.0

mmol) and anhydrous potassium carbonate (0.35 g, 2.5 mmol) in DMF (10 mL), *o*-methyl benzyl chloride (2.1 mmol) in DMF (2 mL) was added dropwise. The resulting mixture was stirred at room temperature for 2 h and then CH_2Cl_2 (30 mL) was added and the organic layer was separated, washed with water and the solvent was then evaporated *in vacuo* to afford 1,2,4-triazol-5(4H)-one derivative. 1-(2,4-Dichlorophenyl)-3-methyl-4-(2-methylbenzyl)-1H-1,2,4-triazol-5(4H)-one: white crystal, yield, 81.1 %; m.p. 78-79 °C; ¹H NMR ($CDCl_3$), δ 7.02-7.54 (m, PhH, 7H), 4.91 (s, CH_2 , 2H), 2.37 (s, CH_3 , 3H), 2.10 (s, CH_3 , 3H). Found %: C, 58.60; H, 4.45; N, 12.01. $C_{17}H_{15}N_3OCl_2$ Calculated: C, 58.63; H, 4.34; N, 12.07.

Crystal structure determination: The prism-shaped single crystal of 1,2,4-triazol-5(4H)-one derivative was obtained by recrystallization from EtOH. The crystal with dimensions of 0.28 mm × 0.24 mm × 0.20 mm was mounted on a Bruker SMART 1000 CCD area-detector diffractometer with a graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) by using a Phi scan modes at 294(2) K in the range of $2.6^\circ \leq \theta \leq 20.4^\circ$. A total of 9048 reflections were collected, of which 3356 were independent ($R_{int} = 0.053$) and 1571 were observed with $I > 2\sigma(I)$. The calculations were performed with SHELXS-97 program¹⁷ and the empirical absorption corrections were applied to all intensity data. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were determined with theoretical calculations and refined isotropically. The final full-matrix least squares refinement gave $R = 0.0782$ and $wR = 0.2059$ ($w = 1/[\sigma^2(F_o^2) + (0.0423P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$, $S = 1.01$, $(\Delta/\sigma)_{max} = 0.0010$, $\Delta\rho_{max} = 0.31$ and $\Delta\rho_{min} = -0.31 e \text{ \AA}^{-3}$. Atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-ray crystallography¹⁸.



a. 1. NaNO_2 , 2. SnCl_2/HCl ; b. CH_3CHO ; c. 1. NaOCN , HAc , 2. NaOCl ; d. DMF , $o\text{-MePhCH}_2\text{Cl}$, r.t.

Scheme-I: The synthetic route of title compound

TABLE-1
SELECTED BOND LENGTHS (Å), ANGLES (°) AND TORSION ANGLES [°] FOR THE TITLE COMPOUND

Bond lengths	Å	Bond angles	°	Torsion angles	°
Cl(2)-C(5)	1.728(3)	C(7)-N(1)-C(6)	124.6(2)	C(6)-N(1)-N(2)-C(8)	-166.7(2)
O(1)-C(7)	1.214(3)	C(8)-N(2)-N(1)	103.9(2)	C(2)-C(1)-C(6)-N(1)	179.2(3)
N(1)-C(7)	1.372(3)	C(8)-N(3)-C(7)	108.3(2)	C(4)-C(5)-C(6)-C(1)	-0.2(4)
N(1)-N(2)	1.396(3)	C(8)-N(3)-C(10)	129.7(3)	Cl(2)-C(5)-C(6)-C(1)	179.5(2)
N(1)-C(6)	1.414(3)	N(3)-C(10)-C(11)	114.4(2)	C(4)-C(5)-C(6)-N(1)	-179.3(2)
N(2)-C(8)	1.295(3)	C(1)-C(6)-N(1)	120.4(3)	Cl(2)-C(5)-C(6)-N(1)	0.4(3)
N(3)-C(8)	1.371(3)	C(5)-C(6)-N(1)	120.3(3)	C(7)-N(1)-C(6)-C(1)	113.0(3)
N(3)-C(7)	1.387(3)	O(1)-C(7)-N(1)	129.0(3)	N(2)-N(1)-C(6)-C(1)	-83.5(3)
N(3)-C(10)	1.454(3)	O(1)-C(7)-N(3)	128.2(3)	C(7)-N(1)-C(6)-C(5)	-67.9(3)
C(1)-C(6)	1.369(4)	N(1)-C(7)-N(3)	102.8(3)	N(2)-N(1)-C(6)-C(5)	95.6(3)
C(11)-C(12)	1.377(4)	N(2)-C(8)-N(3)	112.5(3)	N(2)-N(1)-C(7)-O(1)	179.5(3)

RESULTS AND DISCUSSION

Chemistry and spectroscopic properties: Compound **3** was synthesized at 0–5 °C. Compound **4** was prepared according to the reported method⁹. The structures of all intermediates and title compounds were confirmed by elemental analysis and ^1H NMR, X-ray diffraction analysis. The IR spectrum of the title compound shows an absorption band at 1711 cm^{-1} originated from the stretching vibration of C=O stretching vibration. The signal of C=N aromatic double bonds appeared at 1583 cm^{-1} . In the ^1H NMR spectrum of title compound, the CH_2 proton signals were observed at δ 4.91 ppm as a singlet. Also the two methyl groups are observed at δ 2.10 ppm and 2.37 ppm as a singlet respectively.

Crystal structure: The selected bond lengths, bond angles and dihedral angles in Table-1. The molecular structure of the title compound is shown in Fig. 1. The molecular packing of the molecule is shown in Fig. 2. The π - π stacking is shown in Fig. 3.

Generally, the bond lengths and angles (Table-1) of title compound are within normal ranges. However, the C7-N1 bond [$1.372(3)\text{ Å}$] is shorter than a normal C-N single bond (1.47 Å), which shows that C7-N1 is conjugated with the N2-C8 double bond. The C7=O1 bond length (Table-1) is comparable with those of similar C=O double bonds found in 1,2,4-triazole rings.

As shown in Fig. 1, the triazole ring (N1, N2, C8, N3, C7) (two phenyl rings (C1, C2, C3, C4, C5, C6 and C11, C12, C13, C14, C15, C16)) is fairly planar with plane equation $7.652x + 0.822y + 7.171z = 2.0855$ ($0.676x + 5.675y + 17.711z = 4.5981$; $-0.456x + 7.879y + 2.148z = 2.8182$) and the largest

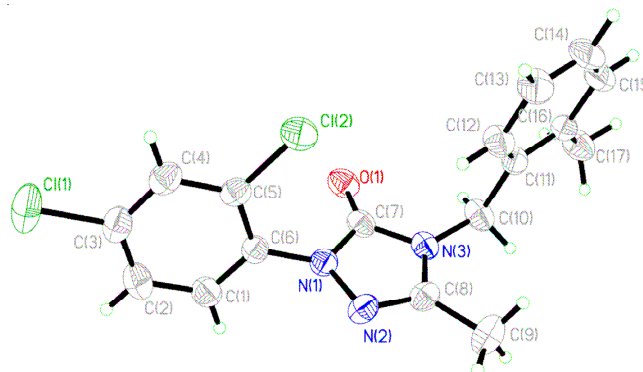


Fig. 1. Molecular structure of the title compound, showing displacement ellipsoids drawn at the 30% probability level

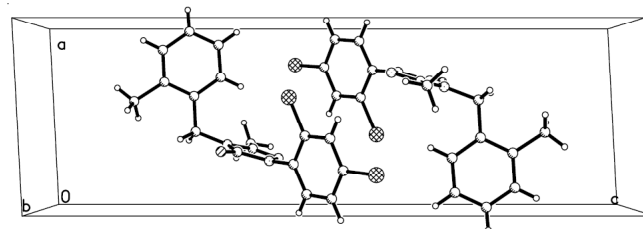


Fig. 2. Pack of title compound

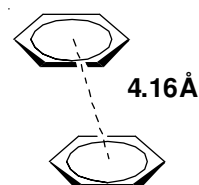


Fig. 3. Face-to-face π - π stacking

deviation from the least squares plane is 0.0048 nm (0.0013 nm and 0.0031 nm). Meanwhile, the triazole ring is vertically with both the phenyl ring (C1~C6) and the other phenyl ring with the respective dihedral angles of 97.4° and 76.7°. The dihedral angle of two phenyl rings is 40.1°.

In the intermolecular face-to-face π - π stacking pattern of the title compound, it is worth mention that the two molecules of each stacking unit are centrosymmetric, which can be proved by the relative position of the two phenyl rings of the two molecules: the centroid distance of them is 4.16 Å. These interactions are estimated to play a role in stabilizing the crystal structure.

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