



Synthesis, Thermal Behaviours and Crystal Structure of 1,1'-Dioxide-7,7'-bis(terfurazan[3,4-b:3,4'-d:3'',4''-f]azepine)

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1,1'-Dioxide-7,7'-bis(terfurazan[3,4-b:3,4'-d:3'',4''-f]azepine) was synthesized from 3,4-bis(4-nitrofurazan-3-yl)furoxan by cyclization and nitration with a yield of 25.7 % and its structure and intermediate were characterized by ^1H NMR, ^{13}C NMR, FT-IR and elementary analysis. Its single crystal was obtained and its crystal structure was studied by X-ray single-crystal diffraction analysis. The title compound ($\text{C}_{18}\text{H}_{12}\text{N}_{14}\text{O}_{10}$, $M_r = 584.42$) crystallizes in trigonal system, P3(2) space group and constituted one 1,1'-dioxide-7,7'-bis(terfurazan[3,4-b:3,4'-d:3'',4''-f]azepine) and two acetone molecules, with $a = 15.460$ (18), $b = 15.460$ (18), $c = 9.603$ (11) Å, $V = 1988$ (4) Å³, $Z = 3$, $D_c = 1.465$ g/cm³, $\lambda = 0.071073$ Å, $\mu(\text{MoK}\alpha) = 0.123$ mm⁻¹, $F(000) = 894$, $S = 1.022$, $R = 0.0720$ and $wR = 0.1838$. In DSC and TG-DTG techniques suggest that there are two main decomposition peaks at 288.7 and 338.7 °C. The results show that the title compound had favorable thermal stability.

Keywords: Organic chemistry, 1,1'-Dioxide-7,7'-bis(terfurazan[3,4-b:3,4'-d:3'',4''-f]azepine), Crystal structure, Synthesis.

INTRODUCTION

The research efforts in the field of energetic materials have been focused on high nitrogen compounds that paid much more attention owing to their unique characteristics, such as high density and high specific volume¹⁻³. Of these, furazan and furoxan rings served as an efficient build-block to enhance the performance of energetic materials⁴⁻⁶. 3,4-Bis(4-nitrofurazan-3-yl)furoxan (DNTF) represents one of the most successful example of an embodiment in practice the idea of nitro-1,2,5-oxadiazole moiety usage for the design of novel high density, high energy materials⁷. 3,4-Bis(4-nitrofurazan-3-yl)furoxan is a novel high energy density material with crystal density of 1.937 g/cm³ and the detonation velocity corresponding to $\rho = 1.937$ g/cm³ is about 9250 m/s. Furthermore, DNTF is not only an energetic compound but also an important explosive intermediate. Especially owing to the reactive nitro groups in DNTF molecule, a variety of new energetic compound could be derived. For example, in alkaline condition, bifurazano[3,4-b:3'4'-f] furoxano[3'',4''-d] oxacycloheptatriene was synthesized from DNTF by intramolecular etherification under alkaline condition⁸ and 7-amino-7H-ter[1,2,5]oxadiazolo[3,4-b:3,4'-d:3'',4''-f]azepine-1-oxide was synthesized from DNTF and hydrazine hydrate by cyclization⁹.

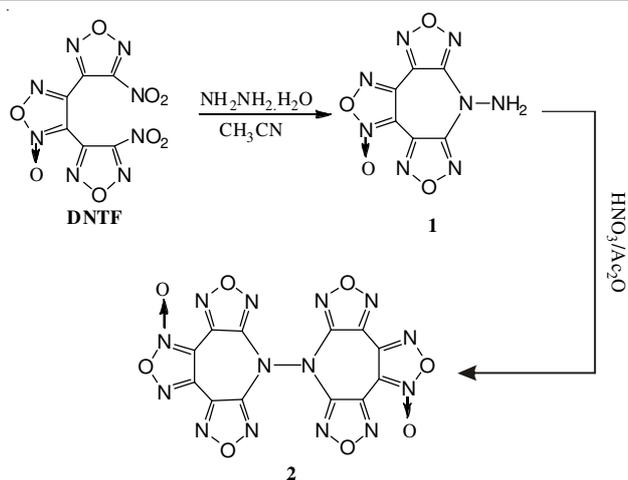
In literature⁹, an energetic material 1,1'-dioxide-7,7'-bis(terfurazan[3,4-b:3,4'-d:3'',4''-f]azepine) (**2**) was synthe-

sized using DNTF as starting material through cyclization and nitration. In order to confirm the molecular structure of compound **2**, its single crystals were firstly grown and its crystal structure was characterized by single-crystal X-ray diffraction analysis. The performances of physico-chemical and detonating and thermal behaviors of the compound **2**, were studied by calculation, DSC and TGA in the first and the results show that the compound **2** was identified as a kind of potential high performance insensitive explosive and has some desirable attributes. Therefore, it has the potential for possible use as an energetic ingredient of propellants and explosives from the point of view of the above mentioned high performance.

EXPERIMENTAL

3,4-Bis(4-nitrofurazan-3-yl)furoxan was prepared and purified by Xi'an Modern Chemistry Research Institute and other reagents were purchased from commercial sources. ^1H NMR and ^{13}C NMR were obtained in DMSO-*d*₆ 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 DNTF as the starting material, our target compound **2** was synthesized *via* cyclization and with a yield of 25.7 % outlined in **Scheme-I**.



Scheme 1 Synthetic route for the title compound 2

Synthesis of compound 1: DNTF(10 g, 35 mmol), 50 mL CH₃CN were mixed in a three-necked round-bottomed flask with a stirrer. To the reaction mixture, 80 % NH₂NH₂·H₂O (4.4 g, 70 mmol) was added dropwise. After NH₂NH₂·H₂O was added completely, it was stirred for another 4 h at 20 °C. The white precipitate was filtered and 5.3 g solid was obtained with a yield of 60.2 % and a purity of 99 %. Analysis calculated (%) for C₆H₂N₈O₄: N, 44.80; C, 28.81; H, 0.81. Found (%) N, 44.63; C, 28.73; H, 0.91. IR (KBr, ν_{\max} , cm⁻¹): 3324, 3241 (NH₂), 1638, 1613, 1584, 1556 (furan), 1527, 1475, 1448 (furoxan); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ : 105.75, 133.94, 136.03, 144.93, 155.85, 156.19.

Synthesis of compound 2: 100 % Nitric acid (10 mL) and compound 1 (1 g, 4.3 mmol) were mixed in a three-necked round-bottomed flask with a stirrer at -10 °C. To the reaction mixture, acetic oxide (5 mL) was added dropwise. After acetic oxide was added completely, it was stirred for another 6 h at 0-5 °C. The final mixture was put into ice water and then the white precipitate was filtered to obtain 0.4 g solid with a yield of and 42.7 %. Analysis calculated (%) for C₁₂N₁₄O₈: N, 41.88; C, 30.78. Found (%) N, 41.46; C, 30.37. IR (KBr, ν_{\max} , cm⁻¹): 1658, 1617, 1596 (furan), 1568, 1527, 1476 (furoxan), 1030 (N-N); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ : 106.04, 135.33, 137.25, 144.64, 150.78, 151.21.

X-ray crystal structure determination: White crystals of 1,1'-dioxide-7,7'-bis(terfurazan[3,4-b:3,4'-d:3'',4''-f]azepine). 2CH₃COCH₃ (C₁₈H₁₂N₁₄O₁₀) were recrystallized from acetone and water (V:V = 1:1) in order to give satisfactory crystals for X-ray determination. There are two equivalent ATA molecules and one equivalent chloride salt 6 molecule in the crystal unit.

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 $1.52 \leq \theta \leq 28.08^\circ$ at 296(2) K. A total of 7320 reflections were collected with 5141 unique ones ($R_{\text{int}} = 0.0651$), of which 8141 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 384 unique reflections with $-18 \leq h \leq 17$, $-19 \leq k \leq 20$ and $-11 \leq l \leq 12$. Absorption correction was not used. The structure was solved by direct methods using

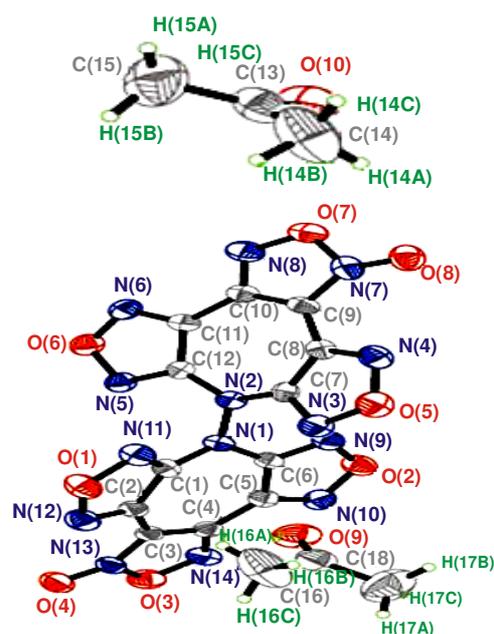
SHELXS program of the SHELXL-97 package and refined with SHELXL package^{10,11}. The final refinement was performed by full-matrix least-squares method with anisotropic thermal parameters on F^2 for the non-hydrogen atoms. Crystal data and refinement results are summarized in Table-1. Crystallographic data for the structural analysis have been deposited in the Cambridge Crystallographic Data Center, CCDC No. 932814.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT DETAILS

m.f.	C ₁₈ H ₁₂ N ₁₄ O ₁₀
m.w.	584.42
T (K)	296(2)
λ (Å)	0.71073
Crystal system	Trigonal
Space group	P3(2)
a (Å)	15.460(18)
b (Å)	15.460(18)
c (Å)	9.603(11)
Volume (Å ³)	1988(4)
Z	3
Dc (g/cm ³)	1.465
F (000)	894
θ range (°)	1.52 to 28.08
Reflections collected/unique	7320 / 5141
Refinement method	Full-matrix least-squares on F^2
GOF on F^2	1.022
Final R indexes ($I > 2\sigma(I)$)	$R_1 = 0.0720$, $wR_2 = 0.1838$
Final R indexes (all data)	$R_1 = 0.1060$, $wR_2 = 0.2136$
Largest diff peak and hole (e Å ⁻³)	0.426 and -0.381

RESULTS AND DISCUSSION

The selected bond distances 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 2. 2CH₃COCH₃ with atomic numbering scheme

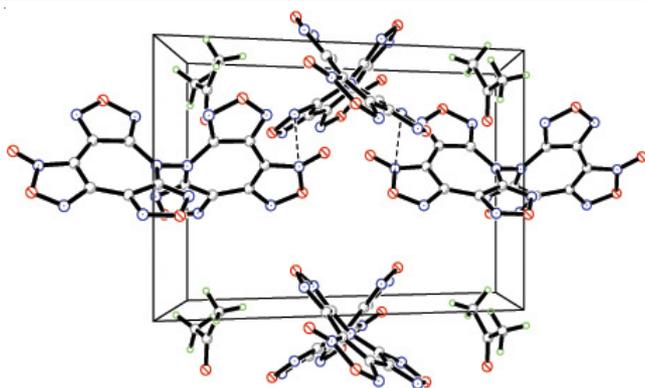


Fig. 2. View of crystal packing down the b axis for the title compound **2**. $2\text{CH}_3\text{COCH}_3$

According to X-ray diffraction structural determination, the bond lengths and bond angles in the furazan rings are generally normal and each ring is almost planar^{12,13}. In the title compound **2**. $2\text{CH}_3\text{COCH}_3$ molecular structure, the azepine ring, plane A from C(1), C(2), C(3), C(4), C(5), C(6) and N(1), $0.5246x - 0.3903y - 0.7566z = -6.5384$, since the torsion angles of C(1)-C(2)-C(3)-C(4), C(2)-C(3)-C(4)-C(5), C(3)-C(4)-C(5)-C(6) and C(4)-C(5)-C(6)-N(1) are 12.4° , -1.2° , -11.5° and -2.1° , respectively. The furazan ring, plane B from N(11), C(1), C(2), N(12) and O(1), $0.6083x - 0.4621y - 0.6453z = -7.0605$. The furazan ring, plane C from O(2), N(10), C(5), C(6) and N(9), $0.3995x - 0.3623y - 0.8421z = -5.9702$. The furoxan ring, plane D from C(4), N(14), O(3), N(13), O(4) and C(3), $0.4368x - 0.5256y - 0.7300z = -7.0605$. The angle

between A and B, A and C, A and D were 8.986° , 8.835° , 9.377° , respectively, which indicates that the plane A, B, C and D are almost co-planer. The other side of the molecular, the azepine ring, plane E from C(7), C(8), C(9), C(10), C(11), C(12) and N(2) is $-0.5232 + 0.3908 - 0.7573 = 2.7367$, since the torsion angles of C(7)-C(8)-C(9)-C(10), C(8)-C(9)-C(10)-C(11), C(9)-C(10)-C(11)-C(12) and C(10)-C(11)-C(12)-N(2) are 12.7° , -0.9° , -12.4° and -1.9° , respectively. The furazan ring, plane F from C(8), C(7), N(3), N(4) and O(5), $-0.6135x + 0.4545y - 0.6458z = 3.8146$. The furazan ring, plane G from O(6), N(10), C(5), C(6) and N(9), $-0.4009 + 0.3605 - 0.8422 = 1.9686$. The furoxan ring, plane H from N(8), O(7), N(7), C(9), C(10) and O(8), $-0.4442x + 0.5193y - 0.7301z = 2.8460$. The angle between E and F, E and G, E and H are 9.004° , 8.716° , 8.789° , respectively, which indicates that the plane E, F, G and H are almost in the same plane. Furthermore, the angle between the two azepine rings, the plane A and E is 81.607° , which shows that the plane A is almost perpendicular to the plane E (Table-3).

Physico-chemistry and detonation properties: These decomposition temperature were obtained by the tests and the other performances were obtained by calculation, in which detonation properties were calculated by Gaussian 98 program¹⁴. It was found that the title compound **2** and its intermediate compound **1** had better performances, some main properties of that the title compound **2** were obtained by calculation or test as follows: Density 1.96 g/cm^3 , detonation velocity 8728 m s^{-1} , enthalpy of formation 1282 kJ mol^{-1} and its decomposition point 288.7°C (Table-4).

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

Bond	Dist.	Bond	Dist.	Bond	Dist.	Bond	Dist.
C(1)-N(11)	1.291(6)	C(6)-N(9)	1.300(6)	C(11)-N(6)	1.322(7)	O(5)-N(4)	1.384(7)
C(1)-N(1)	1.415(6)	C(6)-N(1)	1.401(6)	C(11)-C(12)	1.458(7)	O(5)-N(3)	1.415(6)
C(1)-C(2)	1.449(7)	C(7)-N(3)	1.313(6)	C(12)-N(5)	1.308(6)	O(6)-N(6)	1.360(6)
C(2)-N(12)	1.319(7)	C(7)-N(2)	1.400(6)	C(12)-N(2)	1.388(6)	O(6)-N(5)	1.408(6)
C(2)-C(3)	1.437(7)	C(7)-C(8)	1.452(7)	O(1)-N(11)	1.383(6)	O(7)-N(8)	1.375(7)
C(3)-N(13)	1.333(6)	C(8)-N(4)	1.301(6)	O(1)-N(12)	1.401(7)	O(7)-N(7)	1.469(6)
C(3)-C(4)	1.428(7)	C(8)-C(9)	1.456(7)	O(2)-N(10)	1.364(6)	O(8)-N(7)	1.193(6)
C(4)-N(14)	1.345(7)	C(9)-N(7)	1.354(7)	O(2)-N(9)	1.400(6)	N(1)-N(2)	1.395(5)
C(4)-C(5)	1.449(7)	C(9)-C(10)	1.388(7)	O(3)-N(14)	1.354(6)	—	—
C(5)-N(10)	1.318(7)	C(10)-N(8)	1.336(7)	O(3)-N(13)	1.455(6)	—	—
C(5)-C(6)	1.456(7)	C(10)-C(11)	1.464(7)	O(4)-N(13)	1.204(6)	—	—
Angle	(°)	Angle	(°)	Angle	(°)	Angle	(°)
N(11)-C(1)-N(1)	121.6(4)	N(1)-C(6)-C(5)	129.6(4)	N(5)-C(12)-C(11)	108.9(4)	C(12)-N(5)-O(6)	105.5(4)
N(11)-C(1)-C(2)	110.1(4)	N(3)-C(7)-N(2)	120.7(4)	N(2)-C(12)-C(11)	129.8(4)	C(11)-N(6)-O(6)	107.1(4)
N(1)-C(1)-C(2)	128.3(4)	N(3)-C(7)-C(8)	110.3(4)	O(10)-C(13)-C(15)	119.2(9)	O(8)-N(7)-C(9)	136.1(5)
N(12)-C(2)-C(3)	123.5(4)	N(2)-C(7)-C(8)	128.9(4)	N(11)-O(1)-N(12)	111.0(4)	O(8)-N(7)-O(7)	118.1(5)
N(12)-C(2)-C(1)	107.7(4)	N(4)-C(8)-C(7)	108.2(4)	N(10)-O(2)-N(9)	111.4(4)	C(9)-N(7)-O(7)	105.8(4)
C(3)-C(2)-C(1)	128.8(4)	N(4)-C(8)-C(9)	124.8(4)	N(14)-O(3)-N(13)	109.6(4)	C(10)-N(8)-O(7)	105.4(5)
N(13)-C(3)-C(4)	105.7(4)	C(7)-C(8)-C(9)	127.0(4)	N(4)-O(5)-N(3)	111.5(4)	C(6)-N(9)-O(2)	105.3(4)
N(13)-C(3)-C(2)	126.2(5)	N(7)-C(9)-C(10)	106.8(4)	N(6)-O(6)-N(5)	111.0(3)	C(5)-N(10)-O(2)	106.5(4)
C(4)-C(3)-C(2)	128.2(4)	N(7)-C(9)-C(8)	123.5(5)	N(8)-O(7)-N(7)	108.6(4)	C(1)-N(11)-O(1)	105.8(4)
N(14)-C(4)-C(3)	112.2(4)	C(10)-C(9)-C(8)	129.7(4)	N(2)-N(1)-C(6)	116.7(3)	C(2)-N(12)-O(1)	105.5(4)
N(14)-C(4)-C(5)	121.9(5)	N(8)-C(10)-C(9)	113.4(4)	N(2)-N(1)-C(1)	117.6(4)	O(4)-N(13)-C(3)	134.1(5)
C(3)-C(4)-C(5)	125.9(4)	N(8)-C(10)-C(11)	121.1(5)	C(6)-N(1)-C(1)	124.4(3)	O(4)-N(13)-O(3)	118.8(4)
N(10)-C(5)-C(4)	123.9(5)	C(9)-C(10)-C(11)	125.5(4)	C(12)-N(2)-N(1)	116.6(3)	C(3)-N(13)-O(3)	107.2(4)
N(10)-C(5)-C(6)	107.6(4)	N(6)-C(11)-C(12)	107.5(4)	C(12)-N(2)-C(7)	124.4(4)	C(4)-N(14)-O(3)	105.4(4)
C(4)-C(5)-C(6)	128.5(4)	N(6)-C(11)-C(10)	124.5(4)	N(1)-N(2)-C(7)	117.5(4)	—	—
N(9)-C(6)-N(1)	121.1(4)	C(12)-C(11)-C(10)	128.0(4)	C(7)-N(3)-O(5)	103.7(4)	—	—
N(9)-C(6)-C(5)	109.2(4)	N(5)-C(12)-N(2)	121.2(4)	C(8)-N(4)-O(5)	106.4(4)	—	—
N(1)-C(6)-C(5)	—	—	—	—	—	—	—

TABLE-3
SELECTED TORSION ANGLES (°)

Angle	(°)	Angle	(°)	Angle	(°)	Angle	(°)
N(11)-C(1)-C(2)-N(12)	1.4(5)	N(4)-C(8)-C(9)-C(10)	-168.3(5)	C(6)-N(1)-N(2)-C(12)	113.4(4)	C(9)-C(10)-N(8)-O(7)	-1.5(6)
N(1)-C(1)-C(2)-N(12)	-175.9(4)	C(7)-C(8)-C(9)-C(10)	12.7(8)	C(1)-N(1)-N(2)-C(12)	-79.3(5)	C(11)-C(10)-N(8)-O(7)	179.2(4)
N(11)-C(1)-C(2)-C(3)	-179.1(4)	N(7)-C(9)-C(10)-N(8)	0.7(5)	C(6)-N(1)-N(2)-C(7)	-80.0(5)	N(7)-O(7)-N(8)-C(10)	1.7(5)
N(1)-C(1)-C(2)-C(3)	3.6(8)	C(8)-C(9)-C(10)-N(8)	179.9(5)	C(1)-N(1)-N(2)-C(7)	87.3(5)	N(1)-C(6)-N(9)-O(2)	-176.7(4)
N(12)-C(2)-C(3)-N(13)	11.8(7)	N(7)-C(9)-C(10)-C(11)	179.9(4)	N(3)-C(7)-N(2)-C(12)	156.0(5)	C(5)-C(6)-N(9)-O(2)	0.5(5)
C(1)-C(2)-C(3)-N(13)	-167.7(5)	C(8)-C(9)-C(10)-C(11)	-0.9(7)	C(8)-C(7)-N(2)-C(12)	-28.3(7)	N(10)-O(2)-N(9)-C(6)	-0.3(5)
N(12)-C(2)-C(3)-C(4)	-168.1(5)	N(8)-C(10)-C(11)-N(6)	-11.3(7)	N(3)-C(7)-N(2)-N(1)	-9.4(6)	C(4)-C(5)-N(10)-O(2)	178.9(4)
C(1)-C(2)-C(3)-C(4)	12.4(7)	C(9)-C(10)-C(11)-N(6)	169.6(4)	C(8)-C(7)-N(2)-N(1)	166.3(4)	C(6)-C(5)-N(10)-O(2)	0.4(5)
N(13)-C(3)-C(4)-N(14)	0.7(5)	N(8)-C(10)-C(11)-C(12)	166.7(5)	N(2)-C(7)-N(3)-O(5)	176.0(4)	N(9)-O(2)-N(10)-C(5)	-0.1(5)
C(2)-C(3)-C(4)-N(14)	-179.4(4)	C(9)-C(10)-C(11)-C(12)	-12.4(7)	C(8)-C(7)-N(3)-O(5)	-0.4(5)	N(1)-C(1)-N(11)-O(1)	175.7(4)
N(13)-C(3)-C(4)-C(5)	178.9(4)	N(6)-C(11)-C(12)-N(5)	-0.3(5)	N(4)-O(5)-N(3)-C(7)	0.2(6)	C(2)-C(1)-N(11)-O(1)	-1.8(5)
C(2)-C(3)-C(4)-C(5)	-1.2(7)	C(10)-C(11)-C(12)-N(5)	-178.5(4)	C(7)-C(8)-N(4)-O(5)	-0.4(5)	N(12)-O(1)-N(11)-C(1)	1.7(5)
N(14)-C(4)-C(5)-N(10)	-11.8(7)	N(6)-C(11)-C(12)-N(2)	176.4(4)	C(9)-C(8)-N(4)-O(5)	-179.5(4)	C(3)-C(2)-N(12)-O(1)	-179.8(4)
C(3)-C(4)-C(5)-N(10)	170.2(4)	C(10)-C(11)-C(12)-N(2)	-1.9(8)	N(3)-O(5)-N(4)-C(8)	0.1(6)	C(1)-C(2)-N(12)-O(1)	-0.3(5)
N(14)-C(4)-C(5)-C(6)	166.4(5)	N(9)-C(6)-N(1)-N(2)	9.7(6)	N(2)-C(12)-N(5)-O(6)	-176.5(4)	N(11)-O(1)-N(12)-C(2)	-0.8(5)
C(3)-C(4)-C(5)-C(6)	-11.5(7)	C(5)-C(6)-N(1)-N(2)	-166.9(4)	C(11)-C(12)-N(5)-O(6)	0.4(5)	C(4)-C(3)-N(13)-O(4)	179.2(5)
N(10)-C(5)-C(6)-N(9)	-0.6(5)	N(9)-C(6)-N(1)-C(1)	-156.7(4)	N(6)-O(6)-N(5)-C(12)	-0.5(5)	C(2)-C(3)-N(13)-O(4)	-0.7(8)
C(4)-C(5)-C(6)-N(9)	-179.0(4)	C(5)-C(6)-N(1)-C(1)	26.7(7)	C(12)-C(11)-N(6)-O(6)	-0.1(5)	C(4)-C(3)-N(13)-O(3)	0.1(5)
N(10)-C(5)-C(6)-N(1)	176.3(5)	N(11)-C(1)-N(1)-N(2)	-11.0(6)	C(10)-C(11)-N(6)-O(6)	178.3(4)	C(2)-C(3)-N(13)-O(3)	-179.8(4)
C(4)-C(5)-C(6)-N(1)	-2.1(8)	C(2)-C(1)-N(1)-N(2)	166.1(4)	N(5)-O(6)-N(6)-C(11)	0.4(5)	N(14)-O(3)-N(13)-O(4)	179.8(4)
N(3)-C(7)-C(8)-N(4)	0.5(6)	N(11)-C(1)-N(1)-C(6)	155.3(5)	C(10)-C(9)-N(7)-O(8)	179.7(5)	N(14)-O(3)-N(13)-C(3)	-0.9(5)
N(2)-C(7)-C(8)-N(4)	-175.5(5)	C(2)-C(1)-N(1)-C(6)	-27.7(7)	C(8)-C(9)-N(7)-O(8)	0.5(9)	C(3)-C(4)-N(14)-O(3)	-1.3(5)
N(3)-C(7)-C(8)-C(9)	179.7(4)	N(5)-C(12)-N(2)-N(1)	9.3(6)	C(10)-C(9)-N(7)-O(7)	0.4(5)	C(5)-C(4)-N(14)-O(3)	-179.5(4)
N(2)-C(7)-C(8)-C(9)	3.7(8)	C(11)-C(12)-N(2)-N(1)	-167.0(4)	C(8)-C(9)-N(7)-O(7)	-178.9(4)	N(13)-O(3)-N(14)-C(4)	1.3(5)
N(4)-C(8)-C(9)-N(7)	10.8(7)	N(5)-C(12)-N(2)-C(7)	-156.3(4)	N(8)-O(7)-N(7)-O(8)	179.2(5)	-	-
C(7)-C(8)-C(9)-N(7)	-168.2(5)	C(11)-C(12)-N(2)-C(7)	27.4(7)	N(8)-O(7)-N(7)-C(9)	-1.3(5)	-	-

TABLE-4
PERFORMANCES OF PHYSICO-CHEMISTRY AND DETONATION FOR COMPOUND 1 AND 2

	Nitrogen content (%)	Density (g cm ⁻³)	Decomposition temperature (°C)	Detonation velocity (m s ⁻¹)	Detonation pressure (Gpa)	Enthalpy of formation (kJ mol ⁻¹)
1	44.8	1.88	284.3	8545	33.5	644.52
2	41.9	1.96	288.7	8728	38.2	1282.0

Thermal behaviors: The DSC analysis of compound **1** revealed that it was thermally stable up to 288.7 °C. The DSC curve of compound **1** in Fig. 3 exhibited two thermal decomposition peaks at 288.7 and 338.7 °C, respectively. The TG-DTG curve of compound **1** in Fig. 4 showed two main mass loss stages. The first stage amounts to 49.44 % in the range of 247.6-273.5 °C, it is mainly attributed to the part of azepine. The second stage begins at 273.59 °C and ends at 290.22 °C, accompanied with 8.89 % mass loss, corresponding to the mass of residual furazan and furoxan.

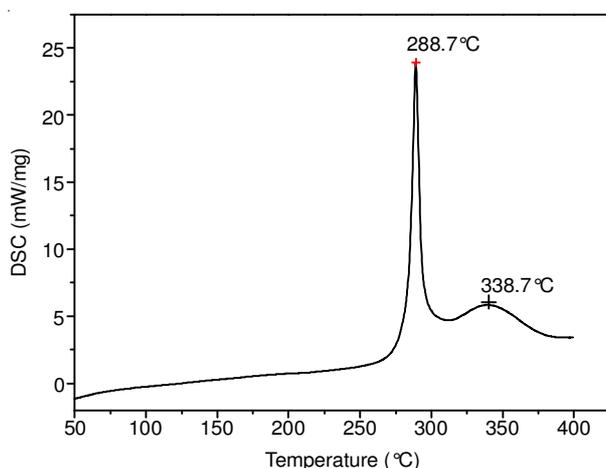


Fig. 3. DSC curve of compound 1

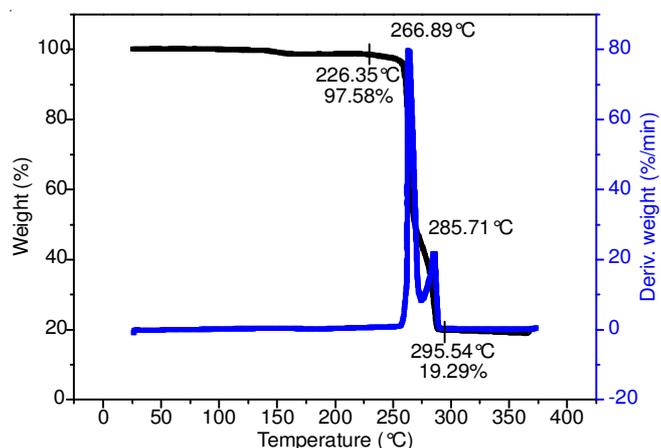


Fig. 4. TG-DTG curve of compound 1

The DSC curve of the title compound **2** in Fig. 5 exhibited a melting point, T_{max} , at 275.6 and one thermal decomposition peaks at 284.3 °C, according to the one obvious mass-loss stages in the TG-DTG curves in Fig. 6, which can be confirmed by the mass-loss stage in the temperature range of 241.35-321.02 °C with mass-loss of 65.61 and 11.26 % residue at 494.92 °C, which indicates that there are a few remains at the end of the decomposition.

The above-mentioned DSC and TGA results showed that their first decomposition temperatures were 288.7, 284.3 °C, respectively. The fact that their decomposition temperatures

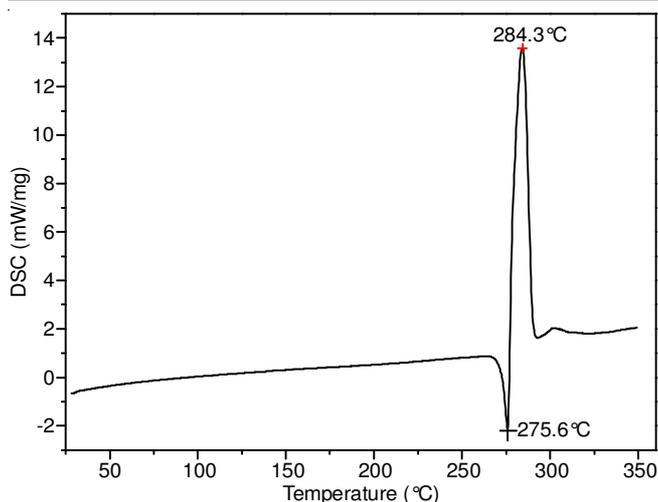


Fig. 5. DSC curve of the title compound 2

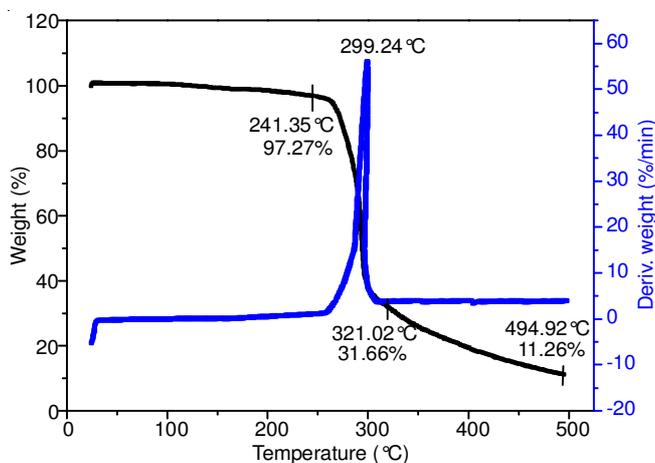


Fig. 6. TG-DTG curve of the title compound 2

were over 280 °C showed that they exhibited excellent thermal stability and they might be potentially useful as gas-forming agents or rocket propellants.

Conclusion

1,1'-Dioxide-7,7'-bis(terfurazan[3,4-b:3,4'-d:3'',4''-f]azepine) was synthesized with a total yield of 25.7 %. The X-ray single-crystal diffraction analysis of the title compound 2 shows that the title compound ($C_{18}H_{12}N_{14}O_{10}$, Mr = 584.42) crystallizes in trigonal system, P3(2) space group and constituted one 1,1'-dioxide-7,7'-bis(terfurazan[3,4-b:3,4'-d:3'',4''-f]azepine) and two acetone molecules. The performances of physico-chemistry and detonation, thermal

behaviors for the title compound 2 and its intermediate compound 1 were studied, their detonation velocities were found to be 8728, 8545 m s⁻¹ and their decomposition temperatures were 288.7, 284.3 °C, respectively. The fact that their detonation velocities were over 8000 m s⁻¹ and decomposition temperatures were over 280 °C showed that the two energetic compounds exhibit excellent thermal stability and detonation properties.

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