

Supporting information

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Experimental Section

N,N'-bis(4-azido-1,2,5-oxadiazol-3-yl)methanediamine (3):

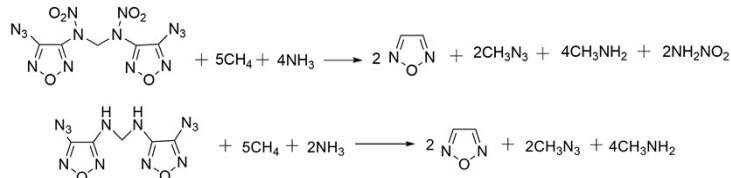
4-azido-1,2,5-oxadiazol-3-amine (1.26 g, 10 mmol) is dissolved in a minimum amount of water at 90 °C in a 100 mL round bottom flask equipped with a magnetic stirring bar. Aqueous formaldehyde (0.81 g, 10 mmol) is added. Six drops of concentrated hydrochloric acid are then added. The mixture is heated for one hour at reflux and then cooled, and the product is collected. The yield is 1.32 g (4.8 mmol, 96 %). T_d : 151.4 °C; ^1H NMR ([D6]DMSO, 500 MHz): δ =4.63 ppm (s, 2H, CH₂); δ =7.38 ppm (s, 1H, NH); ^{13}C NMR ([D6]DMSO, 500 MHz): δ =145.85, 150.11 ppm; IR (KBr): 3371, 3243, 3035, 2974, 2430, 2317, 2190, 2135, 1614, 1597, 1562, 1543, 1493, 1446, 1403, 1376, 1305, 1287, 1269, 1160, 1125, 1064, 1028, 997, 856, 810, 698, 635, 574, 549 cm^{-1} .

N,N'-methylenebis(N-(4-azido-1,2,5-oxadiazol-3-yl)nitramide)(4): N,N'-bis(4-azido-1,2,5-oxadiazol-3-yl)methanediamine (0.5 g, 1.89 mmol) is added slowly to the fuming nitric acid (2 ml) at -5 °C. Then the reaction solution is heated to room temperature for 2 hours. Then, the mixture is poured into ice water and extracted with ether. The combined organic extracts were washed with brine, dried with anhydrous MgSO₄ and concentrated under reduced pressure. The yield is 0.56 g (1.58mmol, 83.7%). T_d: 178 °C; ¹H NMR ([D₆]DMSO, 500 MHz): δ=4.95 ppm (s, 2H, CH₂). ¹³C NMR ([D₆]DMSO, 500 MHz): δ=148.11, 157.38 ppm; IR (KBr): 3049, 2284, 2151, 1616, 1585, 1557, 1530, 1407, 1368, 1310, 1277, 1190, 1168, 1116, 1061, 1032, 1011, 964, 906, 864, 825, 764, 751, 726, 654, 588, 581, 559 cm⁻¹.

Computational Details


Computations were performed by using the Gaussian09 suite of programs.¹ The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP)² functional with the 6-311++G** basis set.³ All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. Atomization energies were calculated by the CBS-4M.⁴ All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

The predictions of heats of formation (HOF) of compounds used the hybrid DFTB3LYP methods with the 6-311++G** basis set through designed isodesmic reactions. The isodesmic reaction processes, that is, the number of each kind of formal bond is conserved, were used with the application of the bond separation reaction (BSR) rules. The molecule was broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reaction used to derive the HOF of compound **3** and **4** is shown in Scheme S1.



Scheme S1. Isodesmic reaction for calculating heat of formation for **3** and **4**.

Table S1. Calculated zero-point energy (ZPE), thermal correction to enthalpy (HT), total energy (E0) and gas phase heats of formation (HOF)

Compound	ZPE ^a /au	H _T ^b /au	E ₀ ^c /au	HOF ^d /kJ mol ⁻¹
3	0.138648	0.017420	-1000.138326	963.46
4	0.141714	0.022532	-1409.076373	1045.3415
CH ₄	0.043894	0.003821	-40.52616	-74.6 ^e
NH ₃	0.033694	0.003825	-56.5671081	-45.9 ^e
CH ₃ N ₃	0.048824	0.004382	-204.0700453	304.8 ^f
CH ₃ NH ₂	0.062724	0.004419	-95.8719773	-23 ^e
NH ₂ NO ₂	0.037485	0.004404	-261.0368506	-6.11 ^e
	0.044784	0.004503	-262.0610572	196.75 ^e

^a Zero-point correction (Hartree/Particle), ^b Thermal correction to enthalpy (Hartree/Particle), ^c Total energy calculated by B3LYP/6-31++G** method (Hartree/Particle), ^d heat of formation, ^e data obtained from *Cryst. Growth Des.* 2019, 19, 839-844, ^f data obtained from *J. Phys. Chem. A* 2006, 110, 11890-11897.

The solid-state enthalpy of formation for neutral compound can be estimated by subtracting the heat of sublimation from gas-phase heat of formation. Based on the literature,⁶ the heat of sublimation can be estimated with Trouton's rule according to supplementary equation 1, where T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition:

$$\Delta H_{\text{sub}} = 188/\text{J mol}^{-1}\text{K}^{-1} \times T$$

Crystallographic data for **3**, **4**

Table S2. Crystallographic data of **3**, **4**.

Compd.	3	4
CCDC number	1939028	1937836
formula	C ₃ H ₄ N ₁₂ O ₂	C ₃ H ₂ N ₁₄ O ₆
Mw	264.20	354.21
crystal system	Monoclinic	Monoclinic
space group	<i>P</i> 2 ₁ /n	<i>P</i> 2 ₁ /n
a [Å]	13.252(2)	9.7238(9)

b [Å]	4.7966(8)	6.6508(6)
c [Å]	17.536(3)	20.1429(18)
α [°]	90	90
β [°]	105.273(5)	92.855(4)
γ [°]	90	90
V [Å ³]	1075.3(3)	1301.0(2)
Z	4	4
T [K]	296	173
λ [Å]	0.71073	0.71073
ρ_{calcd} [g cm ⁻³]	1.570	1.808
μ [mm ⁻¹]	0.134	0.162
F (000)	536	712
θ range [°]	3.19-26.73	3.226-25.020
Data/restraints/parameter	2481/0/167	3071/0/226
S	1.012	1.034
R ₁ [$I > 2\sigma(I)$]	0.0456	0.0480
wR ₂ [$I > 2\sigma(I)$]	0.1295	0.1121

Table S3. Selected bond lengths [Å] and angles [°] for compound **3**.

C(1)-N(1)	1.294(2)	N(1)-C(1)-N(3)	126.66(18)
C(1)-N(3)	1.396(2)	N(1)-C(1)-C(2)	110.92(16)
C(1)-C(2)	1.434(3)	N(3)-C(1)-C(2)	122.41(17)
C(2)-N(2)	1.303(2)	N(2)-C(2)-N(6)	125.08(16)
C(2)-N(6)	1.347(2)	N(2)-C(2)-C(1)	107.94(17)
C(3)-N(6)	1.434(2)	N(6)-C(2)-C(1)	126.97(15)
C(3)-N(7)	1.450(2)	N(6)-C(3)-N(7)	112.79(15)
C(3)-H(3A)	0.9700	N(6)-C(3)-H(3A)	109.0
C(3)-H(3B)	0.9700	N(7)-C(3)-H(3A)	109.0
C(4)-N(8)	1.298(2)	N(6)-C(3)-H(3B)	109.0
C(4)-N(7)	1.368(2)	N(7)-C(3)-H(3B)	109.0
C(4)-C(5)	1.416(3)	H(3A)-C(3)-H(3B)	107.8
C(5)-N(9)	1.297(2)	N(8)-C(4)-N(7)	124.79(17)
C(5)-N(10)	1.394(2)	N(8)-C(4)-C(5)	109.12(16)
N(1)-O(1)	1.384(2)	N(7)-C(4)-C(5)	126.08(16)
N(2)-O(1)	1.410(2)	N(9)-C(5)-N(10)	127.34(18)
N(3)-N(4)	1.246(3)	N(9)-C(5)-C(4)	110.46(16)
N(4)-N(5)	1.110(3)	N(10)-C(5)-C(4)	122.20(16)
N(6)-H(6)	0.8600	C(1)-N(1)-O(1)	104.91(16)
N(7)-H(7)	0.8600	C(2)-N(2)-O(1)	105.62(14)
N(8)-O(2)	1.400(2)	N(4)-N(3)-C(1)	114.37(17)
N(9)-O(2)	1.391(2)	N(5)-N(4)-N(3)	171.4(2)
N(10)-N(11)	1.252(2)	C(2)-N(6)-C(3)	121.14(15)
N(11)-N(12)	1.119(2)	C(2)-N(6)-H(6)	119.4
C(5)-N(9)-O(2)	104.68(15)	C(3)-N(6)-H(6)	119.4
N(11)-N(10)-C(5)	115.60(16)	C(4)-N(7)-C(3)	118.51(15)
N(12)-N(11)-N(10)	170.9(2)	C(4)-N(7)-H(7)	120.7

N(1)-O(1)-N(2)	110.61(13)	C(3)-N(7)-H(7)	120.7
N(9)-O(2)-N(8)	110.57(13)	C(4)-N(8)-O(2)	105.17(15)

Table S4. Selected bond lengths [Å] and angles [°] for compound 4.

C(1)-N(8)	1.447(3)	N(1)-N(2)	1.404(3)
C(1)-N(1)	1.458(3)	N(2)-O(1)	1.205(3)
C(1)-H(1A)	0.9900	N(2)-O(2)	1.210(3)
C(1)-H(1B)	0.9900	N(3)-O(3)	1.391(3)
C(2)-N(3)	1.296(4)	N(4)-O(3)	1.373(3)
C(2)-N(5)	1.390(4)	N(5)-N(6)	1.258(4)
C(2)-C(3)	1.428(4)	N(6)-N(7)	1.117(4)
C(3)-N(4)	1.306(4)	N(8)-N(9)	1.377(3)
C(3)-N(1)	1.397(4)	N(9)-O(4)	1.216(3)
C(4)-N(10)	1.300(4)	N(9)-O(5)	1.223(3)
C(4)-N(12)	1.379(4)	N(10)-O(6)	1.399(3)
C(4)-C(5)	1.421(4)	N(11)-O(6)	1.376(3)
C(5)-N(11)	1.288(4)	N(12)-N(13)	1.255(3)
C(5)-N(8)	1.399(3)	N(13)-N(14)	1.118(4)
N(8)-C(1)-N(1)	112.7(2)	C(5)-N(8)-C(1)	123.5(2)
N(2)-N(1)-C(1)	114.3(2)	N(1)-C(3)-C(2)	130.6(3)
N(3)-C(2)-N(5)	124.8(3)	O(4)-N(9)-O(5)	127.0(2)
N(6)-N(5)-C(2)	112.6(3)	N(10)-C(4)-N(12)	128.1(3)
N(3)-C(2)-N(3)	109.5(3)	O(4)-N(9)-N(8)	116.7(2)
N(7)-N(6)-N(5)	171.3(3)	N(10)-C(4)-C(5)	109.2(3)
N(5)-C(2)-C(3)	125.6(3)	O(5)-N(9)-N(8)	116.2(2)
N(9)-N(8)-C(5)	118.1(2)	N(12)-C(4)-C(5)	122.7(2)
N(4)-C(3)-N(1)	120.3(3)	C(4)-N(10)-O(6)	104.4(2)
N(9)-N(8)-C(1)	118.4(2)	N(11)-C(5)-N(8)	121.6(3)
N(4)-C(3)-C(2)	108.8(3)	C(5)-N(11)-O(6)	105.0(2)
N(14)-N(13)-N(12)	170.5(4)	N(11)-C(5)-C(4)	110.1(2)
C(3)-N(1)-N(2)	116.7(2)	N(13)-N(12)-C(4)	115.4(3)
N(4)-O(3)-N(3)	111.4(2)	N(8)-C(5)-C(4)	127.9(3)
C(3)-N(1)-C(1)	120.9(2)	N(11)-O(6)-N(10)	111.3(2)

Table S5. Hydrogen bonds present in compound 3.

D-H...A	D-H/Å	H...A/Å	D...A/Å	D-H...A/°
N(6)-H(6)...N(9)	0.86	2.29	3.122(2)	163.8
N(6)-H(6)...O(2)	0.86	2.58	3.260(2)	136.8
N(7)-H(7)...N(2)	0.86	2.47	3.041(2)	124.9

Table S6. Hydrogen bonds present in compound 4.

D-H...A	D-H/Å	H...A/Å	D...A/Å	D-H...A/°
C1-H1b...O4	0.991	2.532	3.370	142.264
C1-H1a...N7	0.990	2.526	3.240	128.836
C1-H1a...O5	0.990	2.531	3.200	124.632

Spectrogram

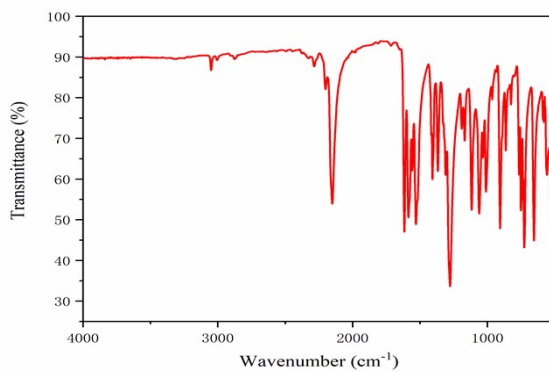


Figure S1. IR spectra for 4.

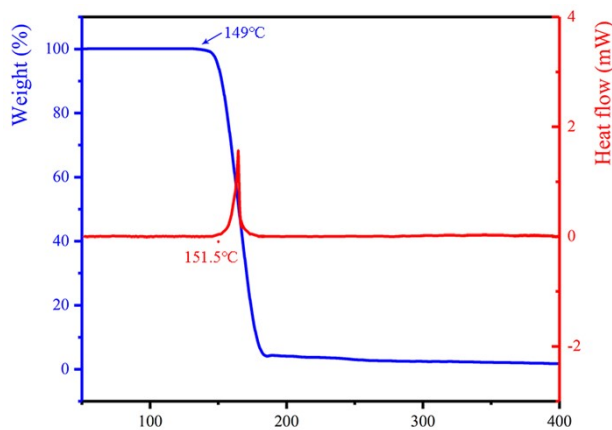


Figure S2. The DSC-TG curves of compound 4 measured at a heating rate of 5 °C min⁻¹.

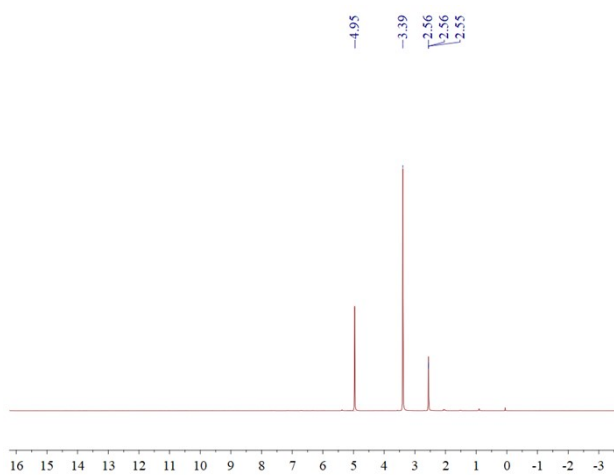


Figure S3. ¹H NMR spectra in DMSO-*d*₆ for 4.

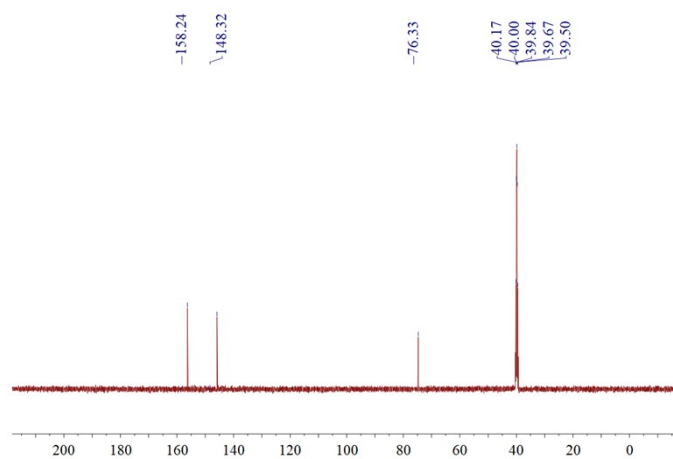


Figure S4. ^{13}C NMR spectra in $\text{DMSO-}d_6$ for **4**.

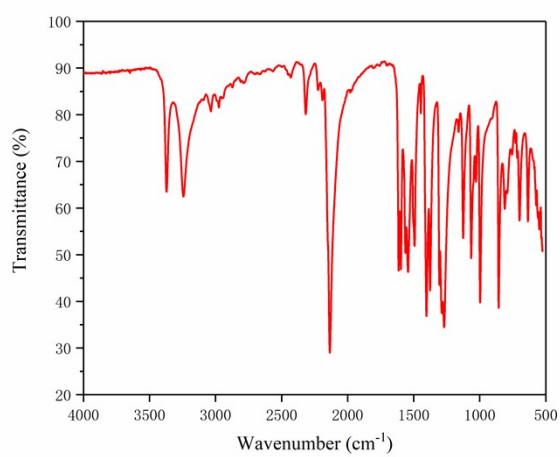


Figure S5. IR spectra for **3**.

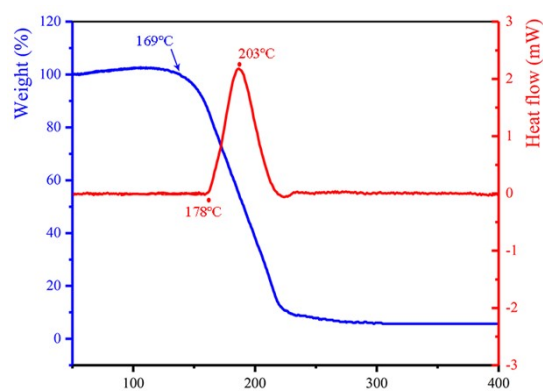


Figure S6. The DSC-TG curves of compound **3** measured at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$.

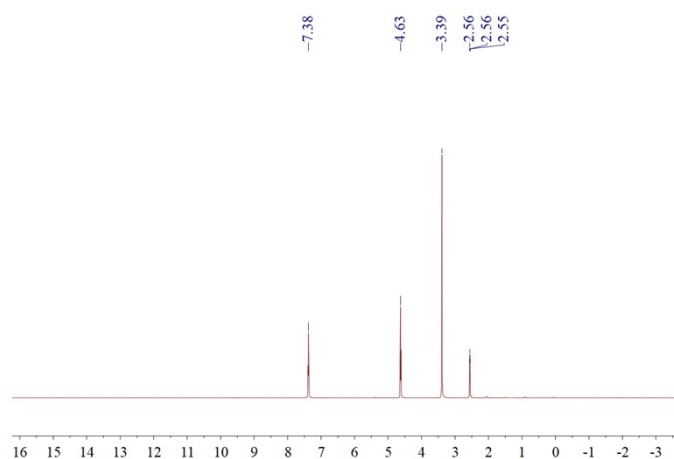


Figure S7. ^1H NMR spectra in $\text{DMSO-}d_6$ for **3**.

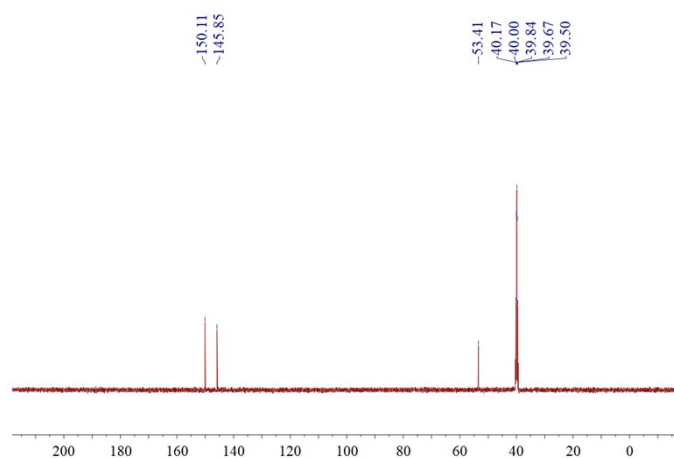


Figure S8. ^{13}C NMR spectra in $\text{DMSO-}d_6$ for **3**.

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