Supplementary Information (SI) for New Journal of Chemistry.

Supporting Information

4,4'-dimethyl-1,1'-bi(1,2,3-triazole): Exploring new insensitive energy sources Materials

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Experimental Section

Caution!

Although we have not experienced any safety incidents during the experimental operation, several compounds in this work present a potential explosion risk. Therefore, for the safety of researchers, necessary protective measures must be taken, such as lab coats, goggles and gloves, which are essential in experiments. In addition, experimental safety training is required before the experiment, and small-scale experiments are recommended during the initial exploration phase of the experiment.

Materials and Equipment

All reagents and solvents used in this work were used as received if not otherwise specified. 1H, and 13C spectra were recorded on a 500 MHz (Bruker AVANCE III 500 MHz) nuclear magnetic resonance spectrometer operating at 500 and 126 MHz, respectively. d_6-DMSO was used as solvent and locking solvent. Chemical shifts in the 1H and 13C spectra are reported relative to Me_4Si. IR spectra were recorded using KBr pellets with a FTIR spectrometer (Thermo Nicolet AVATAR 370). The materials prepared in this work are energetic with potential sensitivity to various stimuli. While no issues were encountered in the handling of these compounds, proper protective measures (face shield, Kevlar gloves, and earthened equipment) are recommended. Single-crystal X-ray diffraction measurements were conducted on a Bruker Smart Apex II diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) with a graphite monochromator at 170 K. An Oxford Cobra low temperature device was used to maintain the low temperature. DSC plots were acquired on a differential scanning calorimeter (NETZSCH DSC 204 F1 Phoenix) at a scan rate of 5 °C min-1 in perforated Al containers under a nitrogen flow of 60 mL min-1. TGA were also performed at a heating rate of 5 °C min-1 on a Mettler Toledo TGA/SDTA851e instrument. IR spectra were recorded on a Thermo Nicolet iS10 spectrometer equipped with a Thermo Scientific Smart iTR diamond ATR accessory. Elemental analyses were carried out on a vario EL III CHNOS elemental analyzer. Densities were measured at 25 °C with a Micromeritics AccuPyc II 1345 gas pycnometer. Impact and friction sensitivity measurements were made using a standard BAM Fallhammer and a BAM friction tester.

Synthesis of compound 1 and 2

(1E)-propane-1,2-diylidenebis(hydrazine) (1): Add solution of hydrazine hydrate (85%, 14.67 mL) to methanol (7.25 mL) and stir the solution while maintaining the temperature at 5°C. Then, slowly add pyruvaldehyde (40%, 18.16 g) dropwise while controlling the temperature between 0 and 10°C. After the addition of pyruvaldehyde, continue stirring at 5°C for 3 h. Finally, the reaction solution is extracted with EA to obtain an organic phase, which is dried and concentrated to obtain a light yellow solid. Acetonitrile recrystallized to obtain pure product (3.02 g, 0.03 mol). Yield: 30%. ^{1}H NMR (500 MHz, DMSO-d6) δ 7.28 (s, 1H), 6.42 (s, 2H), 6.24 (s, 2H), 1.75 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 144.55, 142.54, 9.46. Elemental analysis for $C_3H_8N_4$ (100.13): calcd C 35.99, N 55.96, H 8.05 %. Found: C 34.77, N 56.03, H 9.20 %.

4,4'-dimethyl-1,1'-bi(1,2,3-triazole) (2): In a 50 mL round-bottom flask equipped with an over-head stirrer, (1.0 g, 10 mmol) of compound 1 was dispersed in 10 mL CCl_4 at 18 °C. Active MnO_2 (1.74 g, 20 mmol) was added portion-wise over a few minutes to the vigorously stirred solution. The reaction was stirred for 1 h while additional manganese dioxide (0.87 g, 10 mmol) was added. The reaction was monitored by TLC (thin layer chromatography) analysis. After the reaction completed, the mixture was filtered and washed with ethyl acetate. Subsequently, the solution was concentrated under reduced pressure and separated by column chromatography (PE: EA = 1:1), yielding 0.43 g (51%) of 4,4 '-dimethylbitriazole. Tm = 172.66 °C, Td = 196.9 °C (DSC, 5 K/min); ^{1}H NMR (500 MHz, DMSO-d6) δ 8.67 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d6) δ 142.46, 123.29, 10.61. IR (KBr): 3148, 3145, 2929, 1480, 1405, 1370, 1279,1013, 939, 805, 602 cm^{-1}. Elemental analysis for $C_6H_8N_6$ (164.17): calcd C 43.90, N 51.19, H 4.91 %. Found: C 42.78, N 53.15, H 4.07 %.

Crystallographic data for 2

Table S1. Crystallographic data of 2

Compound	2
CCDC number	2417346
formula	$C_6H_8N_6$
Mw	164.18
crystal system	Orthorhombic
space group	Fdd2
a [Å]	16.877(5)
b [Å]	23.183(7)
c [Å]	4.0775(12)
α [°]	90
β [°]	90
γ [°]	90
V [Å^3]	1595.4(8)
Z	8
T [K]	296(2)
λ [Å]	0.71073
ρ_{calcd} [g cm^{-3}]	1.367
μ [mm^{-1}]	0.096
F (000)	688.0
θ range [°]	3.515 - 27.611
Data/restraints/parameter	924/1/60
S	1.045
R_1 [$I > 2\sigma(I)$]	0.0376
wR_2 [$I > 2\sigma(I)$]	0.0917

Table S2. Selected bond lengths [Å] and angles [°] for compound 2

C(1)-C(2)	1.355(3)	N(1)-C(2)-C(1)	103.9(2)
C(1)-N(3)	1.357(3)	N(1)-C(2)-H(2)	123.2(13)
C(1)-C(3)	1.490(2)	C(1)-C(2)-H(2)	132.9(13)
C(2)-N(1)	1.345(2)	C(1)-C(3)-H(3A)	109.5
C(2)-H(2)	0.90(3)	C(1)-C(3)-H(3B)	109.5
C(3)-H(3A)	0.9600	H(3A)-C(3)-H(3B)	109.5
C(3)-H(3B)	0.9600	C(1)-C(3)-H(3C)	109.5
C(3)-H(3C)	0.9600	H(3A)-C(3)-H(3C)	109.5
N(1)-N(2)	1.342(2)	H(3B)-C(3)-H(3C)	109.5
N(1)-N(1)#1	1.374(3)	N(2)-N(1)-C(2)	112.57(15)
N(2)-N(3)	1.310(2)	N(2)-N(1)-N(1)#1	119.19(15)
C(2)-C(1)-N(3)	108.40(17)	C(2)-N(1)-N(1)#1	128.10(17)
C(2)-C(1)-C(3)	129.6(2)	N(3)-N(2)-N(1)	105.07(14)
N(3)-C(1)-C(3)	122.02(19)	N(2)-N(3)-C(1)	110.09(15)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,z

Table S3. Torsion angles [°] for 2.

N(3)-C(1)-C(2)-N(1)	0.1(2)	N(1)#1-N(1)-N(2)-N(3)	176.90(15)
C(3)-C(1)-C(2)-N(1)	-179.9(2)	N(1)-N(2)-N(3)-C(1)	-0.8(2)
C(1)-C(2)-N(1)-N(2)	-0.7(2)	C(2)-C(1)-N(3)-N(2)	0.4(2)
C(1)-C(2)-N(1)-N(1)#1	-176.19(14)	C(3)-C(1)-N(3)-N(2)	-179.5(2)
C(2)-N(1)-N(2)-N(3)	0.9(2)	N(1)#1-N(1)-N(2)-N(3)	176.90(15)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,z

Calculation of heats of formation

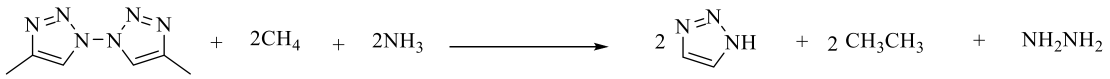
Computations were performed by using the Gaussian 09 suite of programs.[1] The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-YanParr (B3LYP)[2-3] functional with the 6-311++G** basis set.[4]All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. Atomization energies were calculated by the CBS-4M.[5] 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 DFT-B3LYP 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 2 is shown in Scheme S1. The solid phase of heat of formation can be calculated according to the equation 1.

$$\boldsymbol{\Delta H_{\mathrm{solid}} = \Delta H_{\mathrm{gas}} - \Delta H_{\mathrm{sub}}} \qquad \textbf{(1)}$$

Here, the heat of sublimation (ΔH_{sub}) was calculated by using an equation (2) proposed by Edward F. C. Byrd, et al.

$$\boldsymbol{\Delta H_{\mathrm{sub}} = aA^2 + \mathrm{b}(v\sigma_{\mathrm{tot}}^2)^{1/2} + \mathrm{c}} \qquad \textbf{(2)}$$



Scheme S1. Isodesmic reaction for calculating heat of formation for 2.

Spectrums

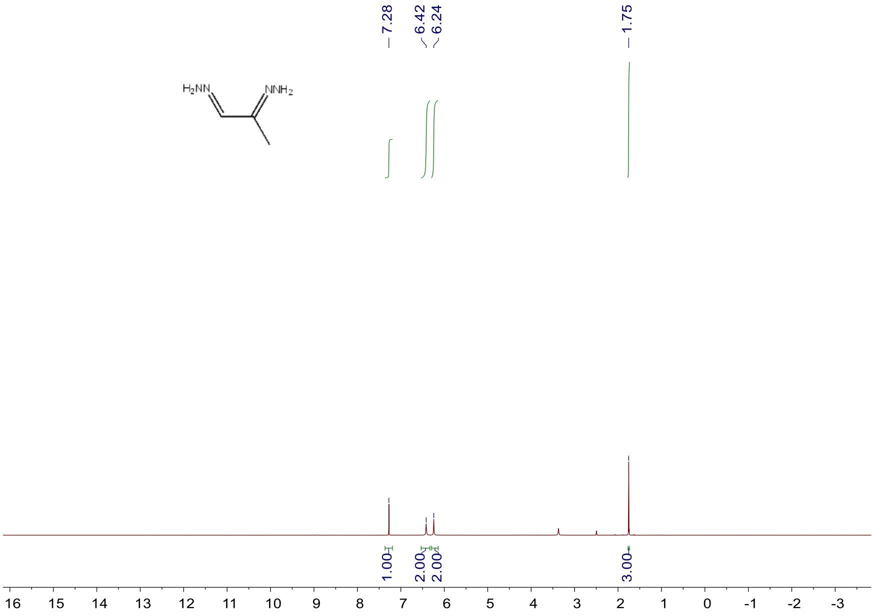


Figure S1. ^{1}H NMR spectrum of (1E)-propane-1,2-diylidenebis(hydrazine).

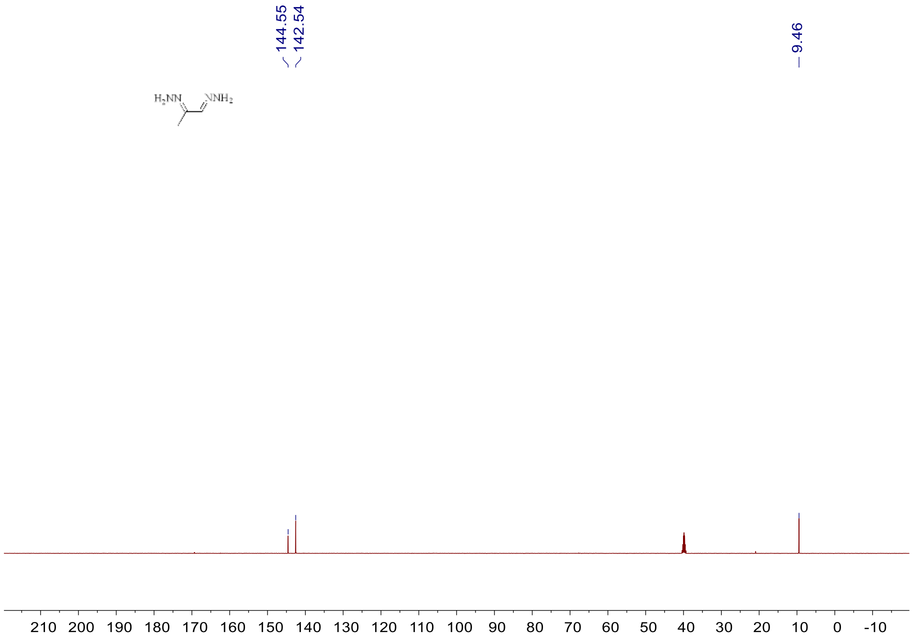


Figure S2. ^{13}C NMR spectrum of (1E)-propane-1,2-diylidenebis(hydrazine).

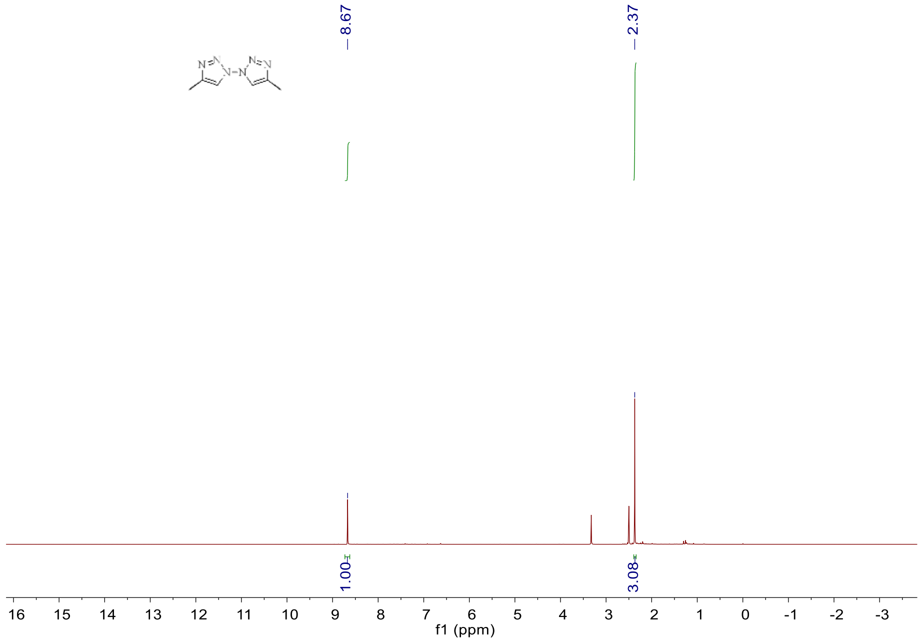


Figure S3. ^{1}H NMR spectrum of 4,4 '-dimethylbitriazole.

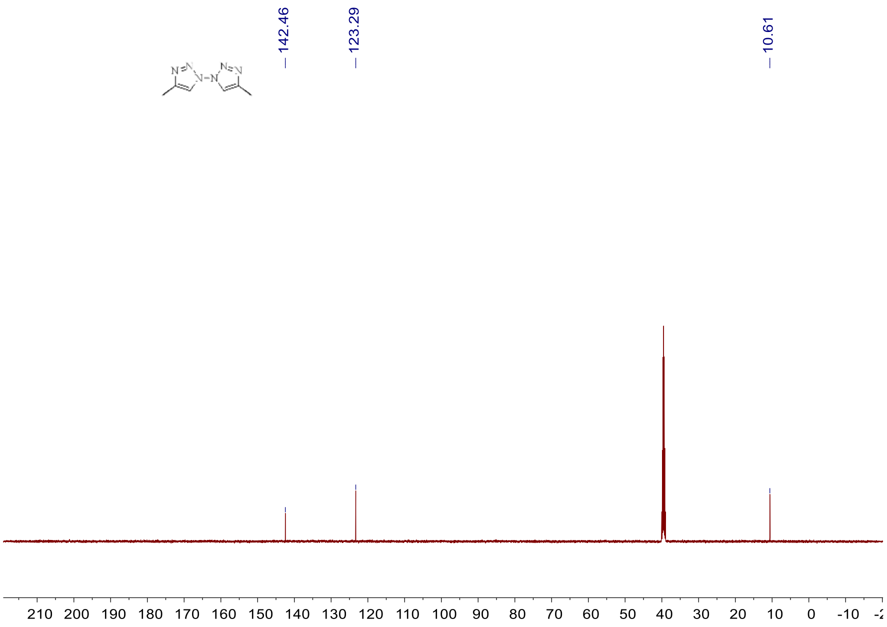


Figure S4. ^{13}C NMR spectrum of 4,4 '-dimethylbitriazole.

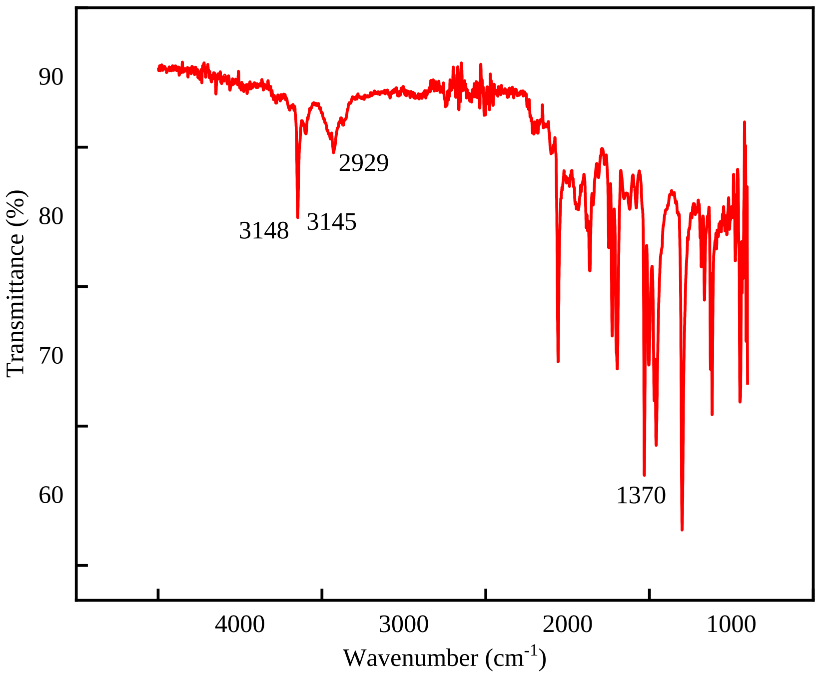


Figure S5. The IR spectrum of 4,4 '-dimethylbitriazole.

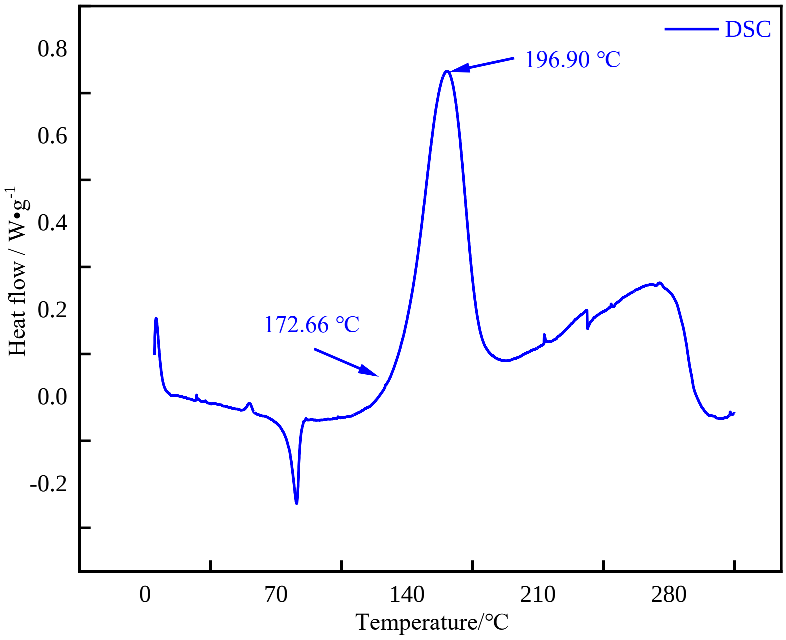


Figure S6. DSC curves of 4,4 '-dimethylbitriazole.

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