Searching for high performance asymmetrically substituted teterazine energetic materials based on 3-hydrazino-6-(1H-1,2,3,4-tetrazol-5-ylimino)-s-tetrazine

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**Table of Contents**

1. Materials and methods.

2. Crystallographic data and crystal structures.

3. DSC curves.

4. Computational details.

5. NMR spectra.

6. References.

**1. Materials and methods**

All of the reagents were purchased from commercial sources and used without further purification. IR were performed on Shimadzu IRAﬃnity-1S FTIR spectrophotometer (KBr pellets). Elemental analyses were recorded on a VarioEL III elemental analyzer (Elementar Co., Germany). 1H (500 MHz) and 13C (125 MHz) NMR spectra were performed on BRUKER AVANCE III HD. Single-crystal X-ray diﬀraction were performed on a Bruker D8 Venture diﬀractometer outfitted with a PHOTON-100 CMOS detector with highly oriented graphite crystal monochromated Mo-Kα radiation (λ =0.071073 nm). All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined using a riding model.

**2. Crystallographic data and crystal structures**

**Table S1** Crystallographic data for **6·CH3OH**, **7·2H2O**, **9·4/3DMF**, **12·5/2H2O**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Compound | **6·CH3OH** | **7·2H2O** | **9·4/3DMF** | **12·5/2H2O** |
| Empirical formula | C4H9N11O | C3H10N12O5 | C24H40N40O4 | C10H28N30O5 |
| Temperature/K | 296(2) | 173 | 296(2) | 296(2) |
| Crystal system | monoclinic | monoclinic | triclinic | triclinic |
| Space group | *P2*1*/c* | *P*21/*n* | *P*-1 | *P-*1 |
| *α*/° | 90 | 90 | 92.329(5) | 74.715(9) |
| *β*/° | 84.897(12) | 90.861(10) | 94.879(5) | 83.332(8) |
| *γ*/° | 90 | 90 | 96.746(5) | 86.715(8) |
| *a*/Å | 4.793(3) | 4.7674(15) | 7.4873(19) | 7.752(4) |
| *b*/Å | 11.213(7) | 11.521(4) | 11.912(3) | 12.315(6) |
| *c*/Å | 18.222(11) | 20.980(6) | 24.315(6) | 14.879(7) |
| Volume/Å3 | 975.5(10) | 1152.3(6) | 2143.1(9) | 1360.5(11) |
| *Z* | 4 | 4 | 2 | 2 |
| *μ*/mm‑1 | 0.123 | 0.152 | 0.113 | 0.13 |
| *F*(000) | 472 | 608 | 992 | 676 |
| Density/g·cm-3 | 1.547 | 1.696 | 1.477 | 1.583 |
| 2θ range/° | 4.27 to 50.054 | 3.884 to 50.052 | 3.366 to 50.052 | 3.852 to 50.194 |
| Data/restraints/parameters | 1732/18/169 | 2030/1/196 | 7448/0/614 | 4768/0/421 |
| Reflections collected | 4800 | 7957 | 10737 | 6713 |
| Independent reflections | 1732 | 2030 | 7448 | 4768 |
| GOOF | 0.897 | 1.024 | 0.988 | 0.918 |
| Final *R* indexes [I>=2*σ*(*I*)] | *R*1 = 0.0582, *wR*2 = 0.0983 | *R*1 = 0.0565, *wR*2 = 0.1212 | *R*1 = 0.0664, *wR*2 = 0.1551 | *R*1 = 0.0561, *wR*2 = 0.1076 |
| Final *R* indexes [all data] | *R*1 = 0.1934, *wR*2 = 0.1425 | *R*1 = 0.1045, *wR*2 = 0.1436 | *R*1 = 0.1252, *wR*2 = 0.1891 | *R*1 = 0.1168, *wR*2 = 0.1323 |
| Recrystallization solvent | methanol | water | DMF | water |
| CCDC | 1827108 | 2128375 | 1556002 | 2128377 |

**Table S2** Crystallographic data for **13·3/2H2O**, **Na2·14H2O** and **18·2DMSO·CH3OH**

|  |  |  |  |
| --- | --- | --- | --- |
| Compound | **13·3/2H2O** | **Na2·14·4H2O** | **18·2DMSO·2CH3OH** |
| Empirical formula | C10H28N34O3 | C4H9N13O6Na2 | C14H24N24O4S2 |
| Temperature/K | 296(2) | 273(2) | 296(2) |
| Crystal system | triclinic | triclinic | triclinic |
| Space group | *P-*1 | *P-*1 | *P*-1 |
| *α*/° | 98.876(5) | 103.137(9) | 111.135(12) |
| *β*/° | 96.670(5) | 91.652(10) | 100.035(14) |
| *γ*/° | 93.770(5) | 111.827(9) | 96.405(14) |
| *a*/Å | 10.461(3) | 8.178(6) | 5.860(3) |
| *b*/Å | 10.594(3) | 9.423(7) | 10.563(4) |
| *c*/Å | 12.613(3) | 10.212(7) | 12.709(4) |
| Volume /Å3 | 1366.7(6) | 705.8(9) | 709.4(5) |
| *Z* | 2 | 2 | 1 |
| *μ*/mm‑1 | 0.131 | 0.208 | 0.259 |
| *F*(000) | 700 | 388 | 340 |
| 2θ range/° | 3.296 to 50.054 | 5.408 to 54.968 | 4.21 to 50.682 |
| Density/g·cm-3 | 1.635 | 1.794 | 1.537 |
| Data/restraints/parameters | 4805/0/437 | 3133/0/226 | 2535/0/204 |
| Reflections collected | 6909 | 6116 | 2535 |
| Independent reflections | 4805 | 3133 | 2535 |
| GOOF | 0.905 | 1.054 | 1.077 |
| Final *R* indexes [I>=2*σ*(*I*)] | *R*1 = 0.0714, *wR*2 = 0.1432 | *R*1 = 0.0483, *wR*2 = 0.1377 | *R*1 = 0.1043, *wR*2 = 0.3042 |
| Final *R* indexes [all data] | *R*1 = 0.2383, *wR*2 = 0.2152 | *R*1 = 0.0664, *wR*2 = 0.1531 | *R*1 = 0.1430, *wR*2 = 0.3272 |
| Recrystallization solvent | water | water | DMSO and methanol |
| CCDC | 2128381 | 2128382 | 2128383 |



**Fig. S1** The asymmetric unit of **8·1/2HClO4·7/2H2O**.



**Fig. S2** The packing diagram of **8·1/2HClO4·7/2H2O**.

**3. DSC curves**



**Fig. S3** The DSC curve of compound **6**.



**Fig. S4** The DSC curve of compound **7**.



**Fig. S5** The DSC curve of compound **8**.



**Fig. S6** The DSC curve of compound **9**.



**Fig. S7** The DSC curve of compound **10**.



**Fig. S8** The DSC curve of compound **12**.



**Fig. S9** The DSC curve of compound **13**.



**Fig. S10** The DSC curve of compound **14**.



**Fig. S11** The DSC curve of compound **15**.



**Fig. S12** The DSC curve of compound **16**.



**Fig. S13** The DSC curve of compound **17**.



**Fig. S14** The DSC curve of compound **18**.

**Table S3** The *T*e and *T*p at different heating rates.

|  |  |  |  |
| --- | --- | --- | --- |
| Compound | *β* (oC·min-1) | *T*e(oC) | *T*p(oC) |
| **6** | 5 | 179.02 | 183.98 |
| 10 | 183.68 | 187.68 |
| 15 | 186.16 | 190.34 |
| 20 | 189.18 | 191.89 |
| **12** | 5 | 279.07 | 280.11 |
| 10 | 284.24 | 285.41 |
| 15 | 288.65 | 289.36 |
| 20 | 291.87 | 292.95 |
| **13** | 5 | 221.14 | 222.35 |
| 10 | 225.81 | 229.84 |
| 15 | 232.38 | 234.10 |
| 20 | 234.35 | 236.46 |
| **15** | 5 | 166.75 | 182.34 |
| 10 | 173.60 | 188.71 |
| 15 | 179.02 | 191.47 |
| 20 | 182.23 | 192.89 |
| **16** | 5 | 207.12 | 236.71 |
| 10 | 212.28 | 241.97 |
| 15 | 218.60 | 247.73 |
| 20 | 220.60 | 249.24 |
| **17** | 5 | 178.90 | 195.54 |
| 10 | 184.77 | 200.03 |
| 15 | 186.99 | 205.19 |
| 20 | 191.21 | 207.15 |

**4. Computational details**

The theoretical calculations were carried out by using Gaussian 16 program (Revision C.01). Geometric optimization and frequency analyses of the structures were performed at the level of B3LYP/6-31+G\*\*. Besides, single-point energies were calculated at MP2/6-311++G\*\* level.1 Atomization energies were calculated by using G2 ab initio method based on atomization reaction and NIST WebBook.2,3 All of the optimized structures were determined to be true local energy minima without imaginary frequencies. The heat of formation (HOF) of all the compounds were obtained using isodesmic reactions (Scheme S1). The calculation results of the gas-phase species were list in Table S4.



**Scheme S1** The isodesmic reactions of obtained compounds.

**Table S4** Calculated HOF of the gas-phase species

|  |  |  |  |
| --- | --- | --- | --- |
| Compound | (kJ·mol-1) | Compound | (kJ·mol-1) |
| 1 | 1603.85 | 2 | 478.70 |
| 3 | 318.08 | 4 | 998.59 |
| 5 | 682.59 | 6 | 804.94 |
| 7 | 1011.01 | 8 | 980.59 |
| 9 | 2273.61 | CH4 | -74.87 |
| NH3 | -45.90 | CH3NH2 | -22.50 |
| NH2NO2 | -6.11 | NH2NH2+ | 770.00 |
| NH=NH | 200.40 | NHNO2- | -6.74 |

For neutral compounds, the solid-phase HOF can be calculated by subtracting the heat of sublimation () from the gas-phase HOF. Based on Trouton’s rule, the solid-phase HOF were calculated by equation 1, where *T* denotes either the melting point or the decomposition temperature when no melting occurs before the decomposition.4

(1)

For energetic salts, the solid-phase HOF can be obtained on the basis of Born-Haber energy cycle, which is shown in Scheme S2. The calculation equation is simplified by using equation 2.



**Scheme S2** Born-Haber energy cycle for the formation of energetic salts.

(2)

In equation 2, represents the lattice energy of the ionic salts which can be obtained by using equation 3 that suggested by Jenkins, et al.5

(3)

In equation 3, the values of and depend on the nature of the ions ( and ), which equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. represents the lattice potential energy that can be calculated from equation 4:

(4)

where equals to the density of the energetic salt and denotes the chemical formula mass of the compound. The values of coefficients and can be assigned according to the literature.5

Based on the measured densities and the calculated heats of formation, the detonation velocities and detonation pressures of all the compounds were evaluated using EXPLO5 v6.04,and the results are summarized in Table 3.

**5. NMR spectra**



**Fig. S5** 1H NMR spectrum of **7**.



**Fig. S6** 13C NMR spectrum of **7**.



**Fig. S7** 1H NMR spectrum of **8**.



**Fig. S8** 13C NMR spectrum of **8**.



**Fig. S9** 1H NMR spectrum of **9**.



**Fig. S10** 13C NMR spectrum of **9**.



**Fig. S11** 1H NMR spectrum of **10**.



**Fig. S12** 13C NMR spectrum of **10**.



**Fig. S13** 1H NMR spectrum of **12**.



**Fig. S14** 13C NMR spectrum of **12**.



**Fig. S15** 1H NMR spectrum of **13**.



**Fig. S16** 13C NMR spectrum of **13**.



**Fig. S17** 1H NMR spectrum of **14**.



**Fig. S18** 13C NMR spectrum of **14**.



**Fig. S19** 1H NMR spectrum of **15**.



**Fig. S20** 13C NMR spectrum of **15**.



**Fig. S21** 1H NMR spectrum of **16**.



**Fig. S22** 13C NMR spectrum of **16**.



**Fig. S23** 1H NMR spectrum of **17**.

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**Fig. S24** 13C NMR spectrum of **17**.



**Fig. S25** 1H NMR spectrum of **18**.



**Fig. S26** 13C NMR spectrum of **18**.

**6. References.**

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