**Supporting Information**

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**Detailed Computational methods**

In this work, different kinds of pyrazolo[3,4-d][1,2,3] triazole based high energy materials with different bridges and energetic groups were theoretically designed. The optimization of the structures of the designed compounds were performed on Gaussian 16 program [1] by density functional theory (DFT) method (at B3LYP/6-311G(*d*,*p*) level). Firstly, the gas-phase heats of formation (Δ*Hf,gas*) of the designed compounds were calculated by isodesmic reactions [2-4] and Eq.(1)-(2).

 (1)

 (2)

where, ∆*H*f,p and ∆*H*f,R were presented as heats of formation of the products and reactants, and Δ*E*0, ΔZPE, Δ*H*T were presented energy changes between products and reactants, difference between the zero-point energy (ZPE) of products and reactants, thermal correction from 0 to 298 *K*, respectively. Besides, *n* was the number of the energetic groups, ∆(*PV*) equals to ∆*nRT*.

The isodesmic reactions were designed as follows:



**Scheme S1 The designed isodesmic reactions for the designed compounds**

In the isodesmic reactions, Δ*Hf,gas* of most of the small molecules can be obtained from <http://webbook.nist.gov>. However, the Δ*Hf,gas* of the other molecules were not available. Therefore, atomization reactions (CaHbNc→aC(g)+bH(g)+cN(g)) at CBS-Q level and isodesmic reactions were employed to calculated the Δ*Hf,gas* of pyrazolo[3,4-d][1,2,3] triazole, CH3CH(NO2)2 and CH3C(NO2)3).

CH3CH(NO2)2 +2CH4→CH3CH3+2CH3NO2

CH3C(NO2)3 +3CH4→CH3CH3+3CH3NO2

Data which were necessary to calculate the heats of formation of the designed compounds were summarized in Table S1.

**Table S1. Calculated total energies (*E*0), zero-point energies (ZPE), thermal corrections (*H*T) and heats of formation (HOFs) of the reference compounds**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Compound. | *E*0 (a.u.)a | ZPE (kJ mol-1)a | *H*T (kJ mol-1)a | Δ*H*f,gas (kJ mol-1) |
| NH3 | -56.576035 | 90.1 | 10.0 | -45.9b |
| CH4 | -40.533748 | 117.0 | 10.0 | -74.6b |
| CH3NHNH2 | -151.217035 | 213.0 | 14.3 | 94.5b |
| CH3NH2 | -95.888444 | 167.6 | 11.4 | -23.5b |
| CH3NHNO2 | -300.434462 | 176.5 | 16.0 | -8.5c |
| CH3NO2 | -245.081687 | 130.6 | 13.9 | -81.0b |
| CH3CN | -132.793330 | 118.7 | 11.9 | 74.0b |
| CH3N3 | -204.148401 | 131.7 | 14.2 | 289.9c |
| NH2CH2CH2NH2 | -190.576020 | 289.4 | 17.2 | -17.0b |
| NH2CH=CHNH2 | -189.352947 | 225.9 | 16.3 | 95.8c |
| NH2NHNHNH2 | -222.581433 | 231.1 | 15.8 | 304.2c |
| NH2N=NNH2 | -221.395185 | 165.5 | 14.4 | 301.2c |
| NH2CH2NHNH2 | -206.587775 | 260.3 | 16.5 | 123.9c |
| NH2CH=NNH2 | -205.386542 | 195.7 | 15.7 | 165.6c |
| CH3CH(NO2)2 | -488.950712 | 212.3 | 22.8 | 81.8d |
| CH3C(NO2)3 | -693.479196 | 215.6 | 29.3 | 105.1d |
| NH2CN | -148.829415 | 89.5 | 11.9 | 140.8c |
| NH2N3 | -220.158873 | 101.8 | 14.0 | 416.3c |
| NH2NH2 | -111.901535 | 139.9 | 11.1 | 95.4b |
| NH2NHNH2 | -167.241789 | 184.7 | 13.4 | 206.8c |
| NH2NO2 | -261.110946 | 100.1 | 11.7 | -6.4c |
| NH2NHNO2 | -316.445860 | 146.7 | 15.5 | 119.1c |
| NH2CH(NO2)2 | -504.995416 | 182.9 | 22.8 | -73.7d |
| NH2C(NO2)3 | -709.522642 | 185.2 | 29.4 | -34.5d |
|  | -389.883008 | 199.6 | 16.8 | 510.6c |

a, calculated at B3LYP/ 6-311G (d,p) level; b, obtained from http://webbook.nist.gov; c, calculated values were calculated at the CBS-Q level; d, obtained by isodesmic reaction.

Accurate values of solid-phase HOFs (Δ*Hf,solid*) of the designed compounds were calculated Hess's law [6] :

 (3)

In which Δ*H*sub stands for the heat of sublimation and can be calculated by Multiwfn program.[7]

Detonation velocities (D) and detonation pressures (P) were calculated by Kamlet-Jacobs equations (Eq.(4)-(5)) [8]:

 (4)

 (5)

In those equations, N presented the moles of detonation gases per gram of explosive (mol·g-1), on behalf of the average molecular weight of these gases (g·mol-1) and Q presented heat of detonation (cal·g-1), respectively. Moreover, ρ was the density, and the accurate values of *ρ* can been modified by Multiwfn program.

Impact sensitivity (*h*50) was calculated according to equation 6 since it can reflect the security of an energetic material during the storage or handling process.

h50=aσ+2+b+c (6)

where *a*, *b* and *c* were constants; σ+2 was indicator of the strengths and variabilities of the positive surface potentials, σ-2 was indicator of the strengths and variabilities of the negative surface potentials.

**Reference**

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; et al, Gaussian 16, Gaussian Inc, Pittsburgh, PA, **2016**.
2. Chen, J. F.; Yu, Y.; Zhang, S J.; Li, Y. C.; Pang, S. P.; Energetic materials with fluorinated four-membered heterocyclic ring: 3, 3′-difluoroazetidine (DFAZ) salts[J]. *New J. Chem.*, **2019**, *43*, 15115-15119.
3. Ghule, V. D.; Sarangapani, R.; Jadhav, P. M.; Tewari, S. P. Theoretical Studies on Nitrogen Rich Energetic Azoles*. J. Mol. Model.* **2011**, *17*, 1507-1515.
4. Tan, B. S; Li, H. Z.; Huang, H.; Han, Y.; Li, J. M.; Li, M.; Long, X. P.; Large π-π separation energies of some energetic compounds[J]. Chem. Phys., **2019**, *520*, 81-87.
5. Zhu, W. H.; Zhang, C. C.; Wei, T.; Xiao, H. M. Theoretical Studies of Furoxan-based Energetic Nitrogen-rich Compounds. *Struct. Chem.* **2011**, *22*, 149-159.
6. P. W. Atkins, Physical chemistry, 2nd edn. Oxford University Press: Oxford, **1982**.
7. Lu, T.; Chen, F. Multiwfn: A Multifunctional Wavefunction Analyzer. *J. Comput. Chem.* **2012**, *33*, 580-592.
8. Kamlet, M. J.; Jacobs, S. J. Chemistry of Detonations. I. A Simple Method for Calculating Detonation Properties of CHNO Explosives. *J. Chem. Phys.* **1968**, *48*, 1968, 23-25.