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Design and Properties of a New Family of Bridged Bis(nitraminotetrazoles) as Promising Energetic Materials

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1. Selected optimized parameters

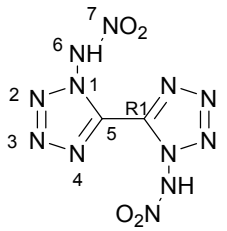

Figure S1 New bridged bis(nitraminotetrazoles)

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Table S1 Selected optimized parameters of bridged bis(nitraminotetrazoles)

Bond length/angle[a]	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
N1-N2	1.349	1.374	1.365	1.352	1.372	1.377	1.381	1.347
N2-N3	1.280	1.268	1.272	1.281	1.268	1.267	1.267	1.288
N3-N4	1.362	1.382	1.371	1.361	1.376	1.373	1.373	1.355
N1-N6	1.366	1.352	1.361	1.362	1.358	1.354	1.354	1.362
N6-N7	1.478	1.463	1.480	1.481	1.467	1.493	1.484	1.479
C5-N1	1.367	1.361	1.355	1.358	1.358	1.361	1.354	1.360
C5-N4	1.308	1.298	1.306	1.310	1.300	1.305	1.308	1.312
C5-R1	1.458	1.321	1.493	1.484	1.381	1.365	1.368	1.388
N1-N2-N3	106.6	106.0	105.8	106.4	106.3	105.6	105.6	106.0
N1-C5-N4	108.0	109.4	107.6	107.9	109.3	108.5	108.7	108.0
N1-N6-N7	113.2	114.9	113.4	113.1	114.1	113.5	113.7	113.2
N4-C5-R1	126.4	130.1	127.7	126.9	125.2	130.7	127.0	132.4
N1-N2-N3-N4	-0.2	0.5	-1.1	-0.1	0.4	0.7	-0.9	-1.3
N2-N1-N6-N7	83.2	74.5	-81.6	-82.4	78.8	76.2	-75.9	-81.5
N3-N4-C5-R1	177.9	-179.7	-178.9	-175.9	-177.0	-179.9	-176.7	178.76

a Bond length (Å), Bond angle (º), Dihedral angle (º). R1denates the atom directly connected to C1 atom.

2. HOMO-LUMO and energy gap

Table S2 HOMO-LUMO and energy gap of bridged bis(nitraminotetrazoles) (eV)

Energy	LUMO	HOMO	$\Delta E_{LUMO-HOMO}$
1	-4.85	-8.41	3.55
2	-2.74	-8.46	5.72
3	-3.10	-8.57	5.47
4	-4.02	-8.93	4.91
5	-3.11	-8.12	5.01
6	-3.08	-7.96	4.88
7	-2.83	-8.00	5.17
8	-4.61	-8.34	3.73

3. Thermodynamic parameters

Table S3 Thermodynamic parameters of bridged bis(nitraminotetrazoles)

Energy	ZPE (kcal/mol)	*U* (kcal/mol)	*H* (kcal/mol)	*G* (kcal/mol)	*S* (kcal/(mol·K))	C_v (kcal/(mol·K))
1	88.84	100.60	101.19	56.24	150.76	66.79
2	111.13	123.16	123.76	77.45	155.32	66.86
3	87.55	97.37	97.96	57.93	134.29	55.07
4	75.34	85.53	86.12	45.51	136.24	56.98
5	96.36	107.99	108.58	64.15	149.01	65.82
6	80.28	90.00	90.59	51.31	131.77	55.09
7	90.84	101.41	102.01	60.11	140.52	59.65
8	75.05	85.23	85.82	44.96	137.04	56.83

4. Calculations description

Density and heat of formation (HOF) are important parameters of an energetic material. The density was predicted by using an improved equation proposed by Politzer[1] referring to intermolecular interactions within the crystal as follows:

$$\rho = \alpha\left(\frac{M}{V(0.001)}\right) + \beta\left(\upsilon\sigma_{Tot}^2\right) + \gamma \quad (1)$$

Where M is molecular mass in g/molecule; $V(0.001)$ is volume in cm^3/molecule, which is average value of calculated molecular volumes by using a Monte Carlo integration embedded in Gaussian program[2]; The $\upsilon\sigma^2_{Tot}$ is derived from the molecular electrostatic potential calculation, which is performed by using the Multiwfn program[3]; α, β and γ are coefficients from the reference (0.9183, 0.0028, 0.0443). [1]

The heat of formation was determined by deducting the enthalpy of sublimation either vaporization[4, 5] based on the Hess' law[6].

$$\Delta H(Solid) = \Delta H(Gas) - \Delta H(Sublimation) \quad (2)$$

$$\Delta H(Liquid) = \Delta H(Gas) - \Delta H(Vaporization) \quad (3)$$

$$\Delta H(Sublimation) = a(SA)^2 + b\sqrt{\sigma_{Tot}^2\upsilon} + c \quad (4)$$

$$\Delta H(Vaporization) = a\sqrt{(SA)} + b\sqrt{\sigma_{Tot}^2 v} + c \quad (5)$$

Where (SA) is the molecular surface area for this structure, σ^2_{Tot} is described as an indicator of the variability of the electrostatic potential on the molecular surface, and υ is the degree of balance between the positive and negative potentials on the molecular surface. And where a, b, and c are fitting parameters (sublimation: 0.00042343, 2.5793785, -6.7335407; vaporization: 1.818689, 1.3321583, -16.14246).

And the heat of formation of gas-phase was calculated *via* atomization energies method[7] as follows:

$$\Delta H_f(A_x B_y, 0K) = x\Delta H^0(A, 0K) + y\Delta H^0(B, 0K) - \sum D_0 \quad (6)$$

Where ΔH^0 is the heat of formation of isolated atoms; D_0 is calculated atomization energies.

The detonation velocity and detonation pressure are the key parameters to assess the potential of an energetic material and were predicted by Empirical Kamlet-Jacobs equations[8]:

$$V_D = 1.01\left(N\bar{M}^{\frac{1}{2}}Q^{\frac{1}{2}}\right)^{\frac{1}{2}}(1 + 1.30\rho) \quad (7)$$

$$P_D = 1.558\rho^2 N\bar{M}^{\frac{1}{2}}Q^{\frac{1}{2}} \quad (8)$$

Where V_D is detonation velocity (km/s); P_D is detonation pressure (GPa); N is moles of detonation gases per gram explosive; $\bar{M}$ is average molecular weight of these gases; Q is heat of detonation (cal/g); and ρ is the theoretical density (g/cm^3) here.

In order to investigate the sensitivity of explosives, the property-structure relation method "generalized interaction property function" (GIPF) was used to estimate the impact sensitivity $h_{50\%}$. Here we give four introduced methods summarized below[9]:

Method 1: $h_{50\%} = 9.2 + 8.03 \times 10^2 \times exp[-(0.0875\ mol/kJ \times |\bar{V}^+ - |\bar{V}^-||)]$ (9)

Method 2: $h_{50\%} = 29.3 + 1.386 \times 10^{-3} \times exp[48.84 \cdot v]$ (10)

Method 3: $h_{50\%} = 27.8 + 0.1135 \times exp[-(2.6479\ g/kJ \times [Q_d - 6.9496\ kJ/g])]$ (11)

Method 4: $h_{50\%} = 1.341 \times exp[8.1389 \cdot v - 1.6234\ g/kJ \times (Q_d - 6.166\ kJ/g)]$ (12)

$|V^+ - |V^-||$ is the difference between magnitudes of average values of the positive and negative electrostatic potential; ν is balance parameter, and Q_d is heat of detonation.

5. References

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