Supporting Information

Polynitro-substituted Bispyrazoles: A New Family of High-Performance Energetic Materials

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Theoretical study: Calculations were performed using the Gaussian 03 (Revision E.01) suite of programs.[1] The geometric optimization of the structures and frequency analyses were conducted using the B3LYP functional with the 6–31+G** basis set,[2] and single-point energies were calculated at the MP2(full)/6–311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

Based on the Born-Haber energy cycle (Fig. 1), the heat of formation of a salt can be simplified according to Equation. (1),

where ΔH_L is the lattice energy of the salt.

$$\Delta H_f^o(\text{ionic salt, 298K}) = \Delta H_f^o(\text{cation, 298K}) + \Delta H_f^o(\text{anion, 298K}) - \Delta H_L \quad (1)$$

The ΔH_L value could be predicted by the formula suggested by Jenkins et al. [Eq. 2],[2] in which U_{POT} is the lattice potential energy and n_M and n_X depend on the nature of the ions M_p^+ and X_q^-, respectively, and are equal to three for monatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions.

$$\Delta H_L = U_{POT} + [p(n_M/2-2) + q(n_X/2-2)]RT \quad (2)$$

The equation for the lattice potential energy, U_{POT}, takes the form of Equation (3), where ρ_m is the density (g cm^{-3}), M_m is the chemical formula mass of the ionic material (g), and the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.[3]

$$U_{POT}\ (\text{kJ mol}^{-1}) = \gamma\,(\rho_m/M_m)^{1/3} + \delta \quad (3)$$

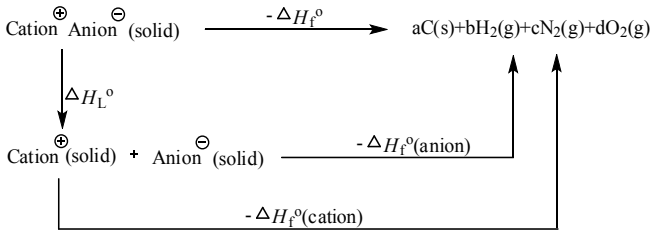
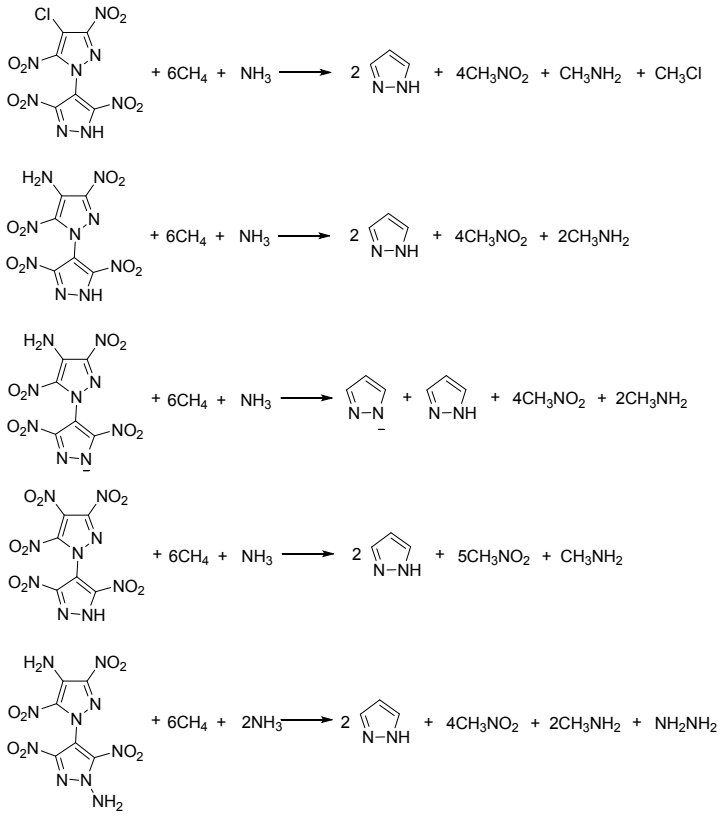


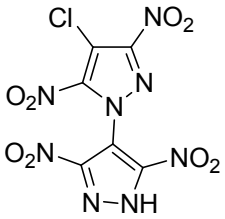
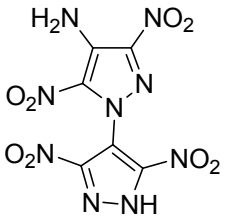
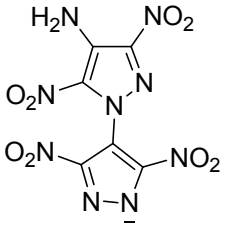
Figure S1 Born-Haber cycle for the formation for energetic salts.

The remaining task was the determination of the heats of formation of the compound, which were computed by using the method of isodesmic reactions (Scheme 1). The enthalpy of an isodesmic reaction (ΔH_f^o298) was obtained by combining the MP2(full)/6–311++G** energy difference for the reaction, the scaled zero-point energies (B3LYP/6–31+G**). The heats of formation of the cations and anions being investigated could then be extracted readily.



Scheme 1 Isodesmic reactions for the calculations of heats of formation.

Table S1 Calculated (B3LYP/6-31+G**//MP2/6-311++G**) Total Energy (E0), Zero Point Energy (ZPE), Values of Thermal correction (HT), and Heats of Formation (HOF) [kJ/mol] of the compounds.

	E_0	ZPE	H_T	HOF
	-1725.9665266	0.121797	0.020098	185.4
	-1322.12714	0.148726	0.019990	388.1
	-1321.6409448	0.134750	0.019912	105.4

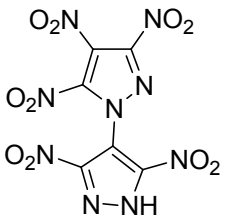
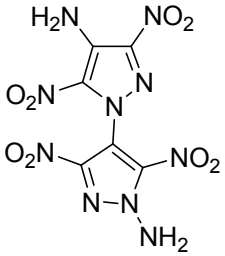
	-1470.7062961	0.130974	0.021289	824.2
	-1377.338097	0.164974	0.021443	477.9
	-225.7180621	0.071265	0.004690	179.4
	-225.1444688	0.056627	0.004552	124.2
CH_4	-40.39849	0.044791	0.003812	-74.6
NH_3	-56.43462	0.034377	0.003818	-45.9
CH_3Cl	-259.936099	0.026168	0.030444	-6.7
CH_3NH_2	-95.6318759	0.064032	0.004369	-23.0
NH_2NH_2	-111.63188	0.053399	0.004202	95.4
CH_3NO_2	-244.5543604	0.049857	0.005272	-74.3

Table S2. Selected bond lengths (Å) for compound **3, 6, 9, 12**

compound **3**			
N1-N2	1.338(2)	N1-C1	1.344(2)
N2-C3	1.341(2)	N3-N4	1.3418(19)
N3-C2	1.4182(19)	N3-C4	1.380(2)
N4-C6	1.327(2)		
compound **6**			
N1-N2	1.339(2)	N1-C1	1.384(2)
N1-C5	1.398(2)	N2-C3	1.325(3)
N4-N5	1.316(3)	N4-C4	1.318(3)
N5-C6	1.363(3)	N5-N6	1.384(3)
compound **9**			
N1-N2	1.3309(18)	N1-C1	1.3316(18)
N2-C3	1.3864(18)	N2-C5	1.4151(19)
N4-C4	1.3391(18)	N4-N5	1.3482(19)
N5-C6	1.339(2)		
compound **12**			
N7-C3	1.3384(16)	N7-N8	1.3507(14)
N8-C5	1.3408(16)	N9-N10	1.3310(14)
N9-C8	1.3790(16)	N9-C4	1.4111(15)
N10-C6	1.3304(17)		

References:

[1] Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, J. T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

[2] R. G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules,* Oxford University Press, New York, **1989**.

[3] H. D. B. Jenkins, D. Tudeal, L. Glasser, *Inorg. Chem.* **2002**, *41*, 2364–2367.