Asymmetrically substituted 5,5'-Bistriazoles – Nitrogen-Rich materials with various energetic functionalities

Supporting Information

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Heats of Formation

In bomb calorimetric measurements nitrogen-rich highly energetic compounds tend to burn incompletely due to the trend of explosion. Oftentimes wrong heats of combustion ($\Delta_c H$) and finally wrong heats of formation ($\Delta_f H°$) are obtained. Therefore the heats of formation of **5–7** have been calculated on the same level for better comparison. All calculations were carried out using the Gaussian 09 (revision C.01) program package.[1] The enthalpies (H) were calculated using the complete basis set (CBS) method described by Petersson and coworkers in order to obtain very accurate values. In this study we applied the modified CBS-4M method (M referring to the use of minimal population localization) which is a re-parameterized version of the original CBS-4 method and also includes some additional empirical corrections.[2]

The enthalpies of the gas-phase species M were calculated by the atomization energy method according to Equation 1,[3] using literature values for atomic $\Delta_f H°_{(g,A)}$.[4]

$$\Delta_f H°_{(g,M)} = H^{298}_{(g,M)} - \sum H^{298}_{(g,A)} + \sum \Delta_f H°_{(g,A)} \tag{1}$$

The solid-state enthalpy of formation for neutral compounds can be estimated with Trouton's rule according to Equation 2,[5] where T is either the melting point or the decomposition temperature (in K) if no melting occurs prior to decomposition.

$$\Delta_f H°_{(s)} = \Delta_f H°_{(g)} - \Delta_{sub} H = \Delta_f H°_{(g)} - (188 / \text{J mol}^{-1} \text{ K}^{-1} \times T) \tag{2}$$

Finally, the solid-state molar enthalpies of formation ($\Delta_f H°$) were used to calculate the solid-state energies of formation ($\Delta_f U°$) according to Equation 3, with Δn being the change of moles of gaseous components.

$$\Delta U = \Delta H - \Delta n R T \tag{3}$$

Table S1:   CBS-4M calculation results.

M	PG [a]	$-H$ / a.u. [b]	$\Delta_f H°_{(g)}$ / kJ mol^{-1} [c]	$-\Delta n$ [d]
1	C_1	833.286389	587.7	7.5
2	C_1	778.023249	526.3	6.5
3	C_1	737.128110	862.2	6.5
NNBT^{2-}, C$_4$HN$_9$O$_4$$^{2-}$	C_1	945.400176	229.1	−
NH$_4$O$^+$	C_s	131.863249	164.1	−
G$^+$, CH$_6$N$_3$$^+$	C_1	205.453192	137.1	−
TAG$^+$, CH$_9$N$_6$$^+$	C_3	371.197775	208.8	−
4a	−	−	915.5	13.0
4b	−	−	800.3	16.0
4c	−	−	1102.1	22.0
RDX	C_1	896.346781	174.2	9.0

[a] Point group, [b] CBS-4M calculated enthalpy, [c] gas-phase enthalpy of formation, [d] change of moles of gaseous components.

Table S2.   Literature values for atomic $\Delta H°_f^{298}$ / kcal mol^{-1}

	NIST [4]
H	52.1
C	171.3
N	113.0
O	59.6

Table S3:   Molecular volumes, lattice energies and lattice enthalpies.

	V_M /nm^3	U_L /kJ mol^{-1}	ΔH_L / kJ mol^{-1}
4a	0.271	1353.8	1358.8
4b	0.345	1235.3	1242.8
4c	0.431	1134.2	1141.6

References

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09 Revision C.01*, Gaussian, Inc., Wallingford, CT, USA, **2010**.

[2] a) J. W. Ochterski, G. A. Petersson, J. A. Montgomery, *J. Chem. Phys.* **1996**, *104*, 2598–2619; b) J. A. Montgomery, M. J. Frisch, J. W. Ochterski, G. A. Petersson, *J. Chem. Phys.* **2000**, *112*, 6532–6542.

[3] a) B. M. Rice, S. V. Pai, J. Hare, *Combust. Flame* **1999**, *118*, 445–458; b) B. M. Rice, J. J. Hare, *J. Phys. Chem. A* **2002**, *106*, 1770–1783; c) E. F. C. Byrd, B. M. Rice, *J. Phys. Chem. A* **2006**, *110*, 1005–1013.

[4] a) P. J. Linstrom, W. G. Mallard (Editors), *NIST Standard Reference Database Number 69*, http://webbook.nist.gov/chemistry (accessed December 31, 2012); b) J. D. Cox, D. D. Wagman, V. A. Medvedev, *CODATA Key Values for Thermodynamics*, Hemisphere Publishing Corp., New York, **1984**.

[5] a) F. Trouton, *Philos. Mag.* **1884**, *18*, 54–57; b) M. S. Westwell, M. S. Searle, D. J. Wales, D. H. Williams, *J. Am. Chem. Soc.* **1995**, *117*, 5013–5015.