

Boron-Based High Explosives

Ernst-Christian Koch^{*,[a]} and Thomas M. Klapötke^[b]

Abstract: The detonation velocity, detonation pressure, and cylinder expansion energy of a series of boron compounds including nitroalkylborates, and mixed amino-nitrosobstituted borazines, borazenes, iminoboranes, and azaboridines were calculated with Cheetah 2.0. The detonation velocity

of the boron compounds is always superior to the all-carbon analogues at the corresponding densities. Nitro-substituted boron compounds bearing amino groups instead of hydrogen display even higher performance.

Keywords: Borazine · Borazene · Iminoborane · Cheetah 2.0 · Detonation

1 Introduction

Boron is an important high energy fuel used in pyrotechnic delays and igniters [1], decoy flares [2], green burning pyrotechnic flares [3–5], and a key ingredient in gas generators for air-breathing propulsion systems [6]. Typical high explosives however are constituted from carbon, nitrogen, hydrogen, and oxygen exclusively [7]. The performance of high explosives is related to their density and their energy content. Classical explosives like TNT, HMX, and PETN derive their detonation energy exclusively from the oxidation of the hydrocarbon backbone. More recently developed explosive molecules derive their performance either from strong cage strain and high density – such as CL-20 [8] or octanitrocubane [9] – or extended nitrogen structures that lead to high positive heats of formation – such as DAAF [10]. Current research on new HEDM is focused on high nitrogen compounds and such elusive target molecules like e.g. pentazole, N₅H [11], its derivatives, N₁₀ and homologues such as N₆₀ [12].

The elements next to carbon in the periodic system of elements, boron and nitrogen, as a group “BN” give (3 + 5 = 8) electrons and thus are isoelectronic with a CC unit. Thus the CC group in organic molecules can be formally replaced by a BN unit. It is hence reasonable to consider a series of BN analogous aromatic and olefinic explosives molecules.

The interest in boron based homogeneous explosives stems from the low atomic weight of boron (10.811 g mol⁻¹), its high molar and gravimetric enthalpy of combustion (627 kJ mol⁻¹, 58 kJ g⁻¹) and its high affinity to both oxygen and nitrogen. Thus opposed to particulate boron, whose combustion is hampered due to coating with glassy boron oxide, molecular boron compounds could prove to oxidize smoothly if accessible.

Zwicky in 1957 inter alia proposed to use boron based energetic materials in propellant applications to circumvent the “carbon dilemma”, which is the competing formation of

CO and CO₂ and its interaction with the water gas equilibrium affecting the specific impulse of propellants [13]. Shortly after this, in 1959 Mader considered B-trinitroborazine (I) (see Figure 1) for the first time as an explosive molecule [14]. He calculated the detonation performance of this and other boron containing explosive molecules based on the

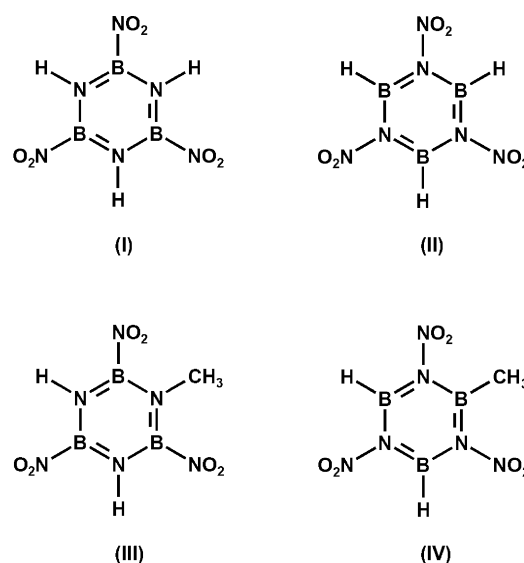


Figure 1. Trinitroborazines investigated by Zhou [27] and Ball [28].

[a] E.-C. Koch
NATO Munitions Safety Information Analysis Center (MSIAC),
Boulevard Leopold III, 1110 Bruxelles, Belgium
*e-mail: e-c.koch@msiac.nato.int

[b] T. M. Klapötke
Department of Chemistry, Energetic Materials Research, Ludwig-
Maximilians-University Munich, Butenandtstraße 5–13 (D), 81377
Munich, Germany

Table 1. Detonation parameters of selected boron based explosives.

System	Density/g cm ⁻³	P _{CJ} /GPa		T _{CJ} /K	V _{det} /m s ⁻¹		Ref.
		calcd.	exp.		calcd.	exp.	
14.7 % B ₁₀ H ₁₃ C ₂ H ₅ + 85.3 % C(NO ₂) ₄	1.40	19.1	17.2	4900	6890	6740	[14] ^{a)}
16.9 % B ₁₀ H ₁₃ C ₂ H ₅ + 83.1 % C(NO ₂) ₄	1.43	14.3		4951	6858		
		19.0	16.7	4810	6850	6820	[14] ^{a)}
B ₃ N ₆ H ₃ O ₆ (I)	1.70	14.6		5143	6850		
		20.7		6530	6530		[14] ^{a)} ^{b)}
4 % B ₃ N ₃ H ₆ + 96 % C(NO ₂) ₄	1.58	21.3		4766	8552		
		14.7		3229	6519	6700	[21] ^{a)}
8 % B ₃ N ₃ H ₆ + 92 % C(NO ₂) ₄	1.53	15.1		3697	6664		
		14.8		4134	6696	6600	[21] ^{a)}
12.5 % B ₃ N ₃ H ₆ + 87.5 % C(NO ₂) ₄	1.47	14.8		4696	6547		[21] ^{a)}
20 % B ₃ N ₃ H ₆ + 80 % C(NO ₂) ₄	1.37	13.3				6500	
		12.8				6300	[21]
30 % B ₃ N ₃ H ₆ + 70 % C(NO ₂) ₄	1.28	12.0		4690	6130	6357	[36] ^{a)}

a) This work. b) Obtained with thermodynamic data used in reference [14], $\Delta_f H = -485$ kJ mol⁻¹.

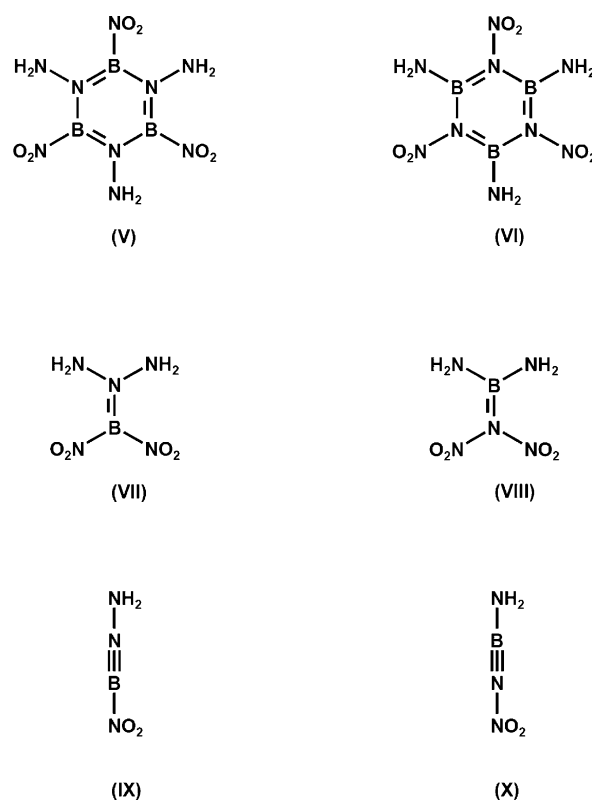
BKW equation. As compound I was not accessible he also carried out experiments with mixtures based on ethyldeca-borane, B₁₀C₂H₁₈, and tetranitromethane, C(NO₂)₄ code-named ET (see results in Table 1). Kury et al. continued the investigations on ET in 1960 and found that the predictions using Chapman–Jouguet–Gamma equations underestimated the actual performance of boron based explosives [15]. However they did not continue their work, as they had announced and thus Mader is believed to have sealed the fate of boron based explosives with his statement in 1961 [16]. Therein he assessed the experimental and theoretical results of boron based materials were largely disappointing and came to the conclusion that despite the large detonation enthalpy of boron based materials the volume-change term though positive is much smaller than in conventional explosives. This was explained due to fewer but larger molecules with heavier molecular weight. Thus he considered the improvements over conventional explosives were only marginal. A disclosure from 1968 on explosives mixtures based on tetranitromethane and various carboranes mentions plate dent values [17] in the order of TNT or 20% above thus in part confirming Mader's resume [18].

The low detonation velocity (LVD) of low density-mixtures of TNT [19] can be increased with admixtures of colloidal boron (90/10) [20].

In 1972 Akimova et al. however unaware of then partly classified results of Mader's work investigated the performance of a series of mixtures based on PETN and boron as well as tetranitromethane and borazine, B₃N₃H₆ [21]. The results are listed as well in Table 1.

Despite Mader's statement attempts – though unsuccessful – to synthesize nitroborazines have been reported ten years later in 1971 by Hirata [22,23]. B-Nitroborazine has been considered in a number of theoretical studies by

Pietro et al. [24], Jayasuriya [25], and Portalone et al. [26]. Quantum chemical studies on both B-/N-trinitroborazines derivatives have been carried out by Zhu et al. [27] and by Ball et al. [28]. The latter looked at a variety of potentially useful molecules analogous to trinitrobenzene and TNT

**Figure 2.** New B–N compounds considered in this report.

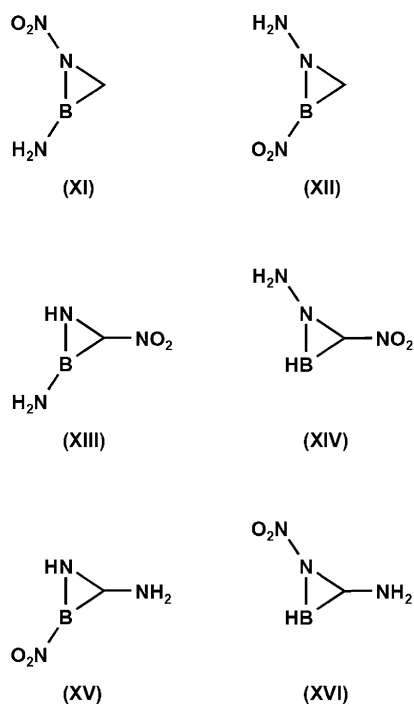


Figure 3. New B–N compounds considered in this report.

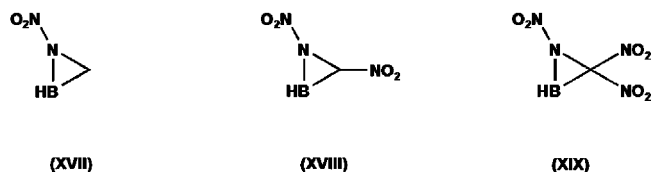


Figure 4. B–N compounds considered by Srivastava et al. [35].



Figure 5. Nitroalkyl borates XX and XXI considered by Klapötke et al. [34].

(see Figure 1). Boron, aluminium boron alloy and carbaboranes have been considered as ingredients in thermobaric explosive formulations recently [29–32]. Klapötke et al. have characterized the highly energetic tetraazidoborate anion [33], recently synthesized nitro substituted ethyl borates, $\text{B}[\text{OCH}_2\text{CH}_2\text{NO}_2]_3$ and $\text{B}[\text{OCH}_2\text{C}(\text{NO}_2)_3]_3$ [34]. Srivastava et al. recently investigated the potential of nitro-substituted azaboriridines based on Kamlet–Jacobs method [35].

So far since the early work of Mader and Akimova no information about the detonation performance of boron based explosives is available.

In view of the predictive capabilities with Cheetah 2.0 code and the current demand for powerful but also less sensitive explosive molecules, it was considered to screen the theoretical performance of a number of nitro substitut-

ed borazene, borazine, and iminoboranes type compounds and explore the effect of mixed amino- and nitro substitution. The structures of the compounds investigated are displayed in Figures 1–5. The names, formulas enthalpy of formation and oxygen balance of the investigated compounds in comparison to some all-carbon analogues are presented in Table 2.

2 Methodology

The enthalpy of formation of compounds I, II, III, and IV was taken from reference [28]. The enthalpies of formation of compounds V–XVI were calculated using the atomization method based on CBS-4 M enthalpies described recently in detail in the literature [37a,b].

$$\Delta_f H^\circ_{(g,M,298)} = H_{(Molecule,298)} - \sum H^\circ_{(Atoms,298)} + \sum \Delta_f H^\circ_{(Atoms,298)}$$

All quantum chemical calculations were performed with the Gaussian09 software [37b]. The enthalpy of formation of compounds XVII–XIX was taken from reference [35].

The detonation performance was calculated with Cheetah 2.0 program package [38]. To check the suitability of Cheetah 2.0 code to calculate boron based explosives the experimental results from references [14,21] were repeated. They give very good agreement with the detonation velocities ($\pm 2\%$) but seem to underestimate the detonation pressures (-25%). With Cheetah 2.0 however the detonation velocity of B-trinitroborazine I is predicted to be 30% higher than with BKW code used in 1959. Zaug et al. had calculated tetranitromethane/borazine (75/25) with more advanced Cheetah 5.0 and obtained a reasonably close result as with Cheetah 2.0 [36].

As density prediction of the boron containing molecules is currently not possible a range of densities was considered from 1.3–2.0 g cm^{-3} except for compounds XVII–XIX. Their density was obtained with an undisclosed method. In general comparison of borazine and benzene shows that densities are quite similar ($\rho_{(\text{Borazine})} = 0.8419 \text{ g cm}^{-3}$ vs. $\rho_{(\text{Benzene})} = 0.8788 \text{ g cm}^{-3}$). Hence comparison with all carbon type molecule densities is reasonable.

3 Results and Discussion

The enthalpy of formation for the B-nitro compounds I and III is more negative than with the analogous N-nitro compounds II and IV. However with the mixed amino-nitro compounds the trend is reverse showing that N-nitro-B-amino compounds VI, VIII, X, and XI display a lower negative enthalpy of formation than the B-nitro-N-amino compounds V, VII, IX, and XII. Correspondingly the compounds II, IV, V, VII, IX, and XII display higher detonation performance than the opposite substituted ones.

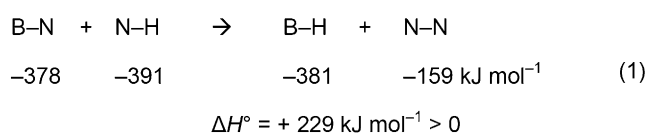
Table 2. Enthalpy of formation and oxygen balance of the investigated compounds and their all carbon counterparts.

Compounds	Formula	$\Delta_f H^\circ / \text{kJ mol}^{-1}$	$\Omega / \%$	Compounds	$\Delta_f H^\circ / \text{kJ mol}^{-1}$	$\Omega / \%$
B-Trinitroborazine (I)	$(\text{B}_3\text{N}_3)\text{H}_3(\text{NO}_2)_3$	-721	0	1,3,5-Trinitrobenzene	-37	-56
N-Trinitroborazine (II)	$(\text{B}_3\text{N}_3)\text{H}_3(\text{NO}_2)_3$	-196	0	-	-	-
N-Methyl-B-trinitroborazine (III)	$(\text{B}_3\text{N}_3)\text{H}_2(\text{CH}_3)(\text{NO}_2)_3$	-680	-21	2,4,6-Trinitrotoluene	-63	-74
B-Methyl-N-trinitroborazine (IV)	$(\text{B}_3\text{N}_3)\text{H}_2(\text{CH}_3)(\text{NO}_2)_3$	-246	-21	-	-	-
N-Triamino-B-trinitroborazine (V)	$(\text{B}_3\text{N}_3)(\text{NH}_2)_3(\text{NO}_2)_3$	-357	-9	1,3,5-Triamino-2,4,6-trinitrobenzene	-75	-56
B-Triamino-N-trinitroborazine (VI)	$(\text{B}_3\text{N}_3)(\text{NH}_2)_3(\text{NO}_2)_3$	-662	-9	-	-	-
N-Diamino-B-dinitroborazene (VII)	$\text{BN}(\text{NO}_2)_2(\text{NH}_2)_2$	-4	+5	1,1-Diamino-2,2-dinitroethylene	-130	-22
B-Diamino-N-dinitroborazene (VIII)	$\text{BN}(\text{NO}_2)_2(\text{NH}_2)_2$	-162	+5	-	-	-
N-Amino-B-nitroiminoborane (IX)	$\text{NO}_2\text{-BN-NH}_2$	159	-9	1-Amino-2-nitroethyne	-	-
B-Amino-N-nitroiminoborane (X)	$\text{NH}_2\text{-BN-NO}_2$	43	-9	-	-	-
1-Amino-2-nitro-1,2-azaboridine (XI)	$\text{BCH}_2\text{N}(\text{NO}_2)(\text{NH}_2)$	41	-56	1-Amino-2-nitrocyclopropane	-	-
2-Amino-1-nitro-1,2-azaboridine (XII)	$\text{BCH}_2\text{N}(\text{NO}_2)(\text{NH}_2)$	185	-56	-	-	-
1-Amino-3-nitro-1,2-azaboridine (XIII)	$\text{BCH}_2\text{N}(\text{NO}_2)(\text{NH}_2)$	-55	-56	-	-	-
2-Amino-3-nitro-1,2-azaboridine (XIV)	$\text{BCH}_2\text{N}(\text{NO}_2)(\text{NH}_2)$	193	-56	-	-	-
3-Amino-1-nitro-1,2-azaboridine (XV)	$\text{BCH}_2\text{N}(\text{NO}_2)(\text{NH}_2)$	67	-56	-	-	-
3-Amino-2-nitro-1,2-azaboridine (XVI)	$\text{BCH}_2\text{N}(\text{NO}_2)(\text{NH}_2)$	204	-56	-	-	-
1-Nitro-1,2-azaboridine (XVII)	$\text{BCH}_3\text{N}(\text{NO}_2)$	187	-56	Nitrocyclopropane	-	-119
1,3-Dinitro-1,2-azaboridine (XVIII)	$\text{BCH}_2\text{N}(\text{NO}_2)_2$	151	-6	1,2-Dinitrocyclopropane	-	-49
1,3,3-Trinitro-1,2-azaboridine (XIX)	$\text{BCHN}(\text{NO}_2)_3$	168	+18	1,2,2-Trinitrocyclopropane	-	-14
Tris(2-nitroethyl) borate (XX)	$\text{B}[\text{O}-\text{C}_2\text{H}_4\text{NO}_2]_3$	-1161	-60	-	-	-
Tris(2,2,2-trinitroethyl)borate (XXI)	$\text{B}[\text{O}-\text{C}_2\text{H}_2(\text{NO}_2)_3]_3$	-931	+13	-	-	-

Table 3. Performance of compounds I and II on comparison to 1,3,5-trinitrobenzene, TNB at $\rho = 1.668 \text{ g cm}^{-3}$.

Density	Detonation velocity/ km s^{-1}		Detonation pressure/GPa		Cylinder expansion $V/V_0 = 2.20/\text{kJ cm}^{-3}$	
	I	II	I	II	I	II
1.3	5.577	6.000	8.63	10.22	-2.25	-2.65
1.4	6.137	6.581	10.62	12.52	-2.56	-3.05
1.5	6.769	7.236	13.07	14.32	-2.94	-3.53
1.6	7.485	7.978	16.09	18.74	-3.39	-4.08
1.668	8.027	8.540	18.53	21.52	-3.37	-4.49
1.7	8.300	8.822	19.81	22.97	-3.91	-4.70
1.8	9.233	9.787	24.45	28.20	-4.52	-5.42
1.9	10.304	10.894	30.24	34.72	-5.21	-6.24
2.0	11.542	12.172	37.52	42.90	-6.02	-7.19
TNB	7.290		22.70		-4.80	

The fact that compounds I and III are more stable (lower detonation velocities) than compounds II and IV can be rationalized by the fact that the N–H (391 kJ mol^{-1}) and B–H (381 kJ mol^{-1}) [40] bond energies are almost equal, whereas the B–N “single” bond (-378 kJ mol^{-1} [41]) is apparently more stable than the particularly weak N–N single bond (159 kJ mol^{-1}) [40]:



Although the above calculation may very well over-estimate the strength of a B–N single bond, it can definitely be assumed that the B–N single bond is significantly more stable than a N–N single bond.

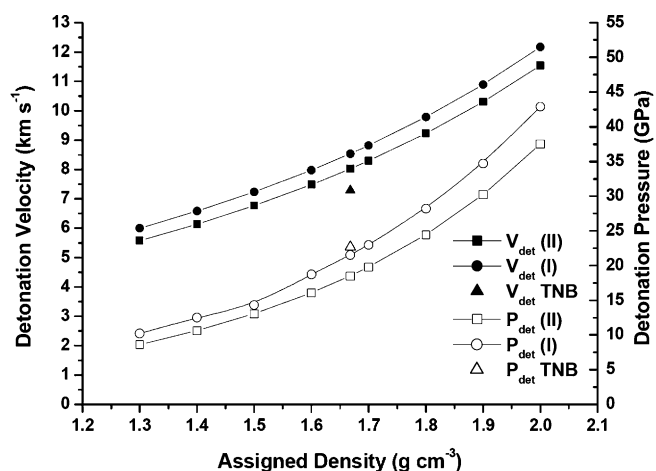
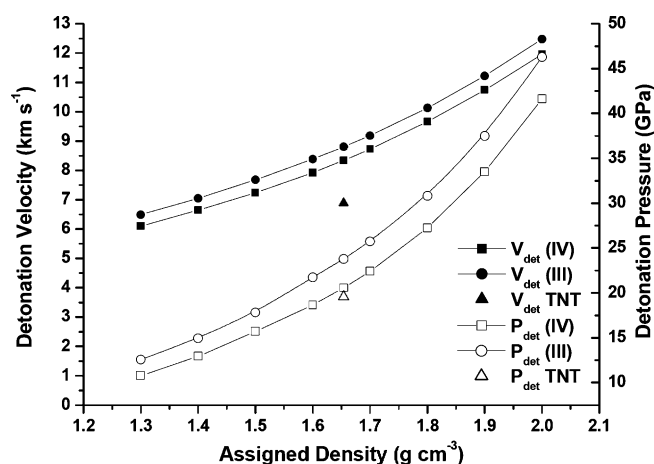
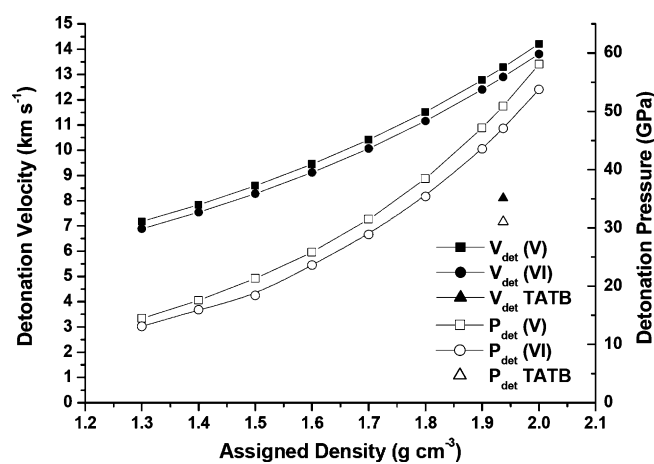
**Figure 6.** Performance of borazines I and II relative to TNB at TMD.

Table 4. Performance of compounds III and IV on comparison to 2,4,6-trinitrotoluene, TNT at $\rho = 1.654 \text{ g cm}^{-3}$.

Density	Detonation velocity/ km s^{-1}		Detonation pressure/GPa		Cylinder expansion $V/V_0 = 2.20/\text{kJ cm}^{-3}$	
	III	IV	III	IV	III	IV
1.3	6.099	6.941	10.77	12.57	-2.82	-3.41
1.4	6.646	7.046	12.93	14.94	-3.22	-3.89
1.5	7.238	7.682	15.71	17.83	-3.67	-4.41
1.6	7.923	8.389	18.66	21.75	-4.17	-4.99
1.654	8.341	8.805	20.56	23.78	-4.46	-5.34
1.7	8.726	9.188	22.40	25.73	-4.71	-5.64
1.8	9.661	10.128	27.24	30.82	-5.33	-6.36
1.9	10.737	11.221	33.52	37.50	-6.03	-7.17
2.0	11.963	12.474	41.62	46.29	-6.83	-8.09
TNT	6.886		19.57		-4.14	


Figure 7. Performance of borazines III and IV relative to TNT at TMD.

Figure 8. Performance of borazines V and VI relative to TATB at TMD.

For the group of amino ($-\text{NH}_2$)/nitro ($-\text{NO}_2$) substituted compounds V vs. VI, the $[\text{H}_2\text{NB}-\text{NNO}_2]_3$ isomers are more stable than the $[\text{H}_2\text{NN}-\text{BNO}_2]_3$ derivatives. This can be explained that in borazines the resonance structure with three lone pairs of electrons located at the three nitrogen atoms has a higher weight than the two Kekulé-type structures [42] and the lone pair localized at the nitrogen atom

favors the $\text{N}=\text{NO}_2$ resonance structure with two formally negatively charged oxygen atoms.

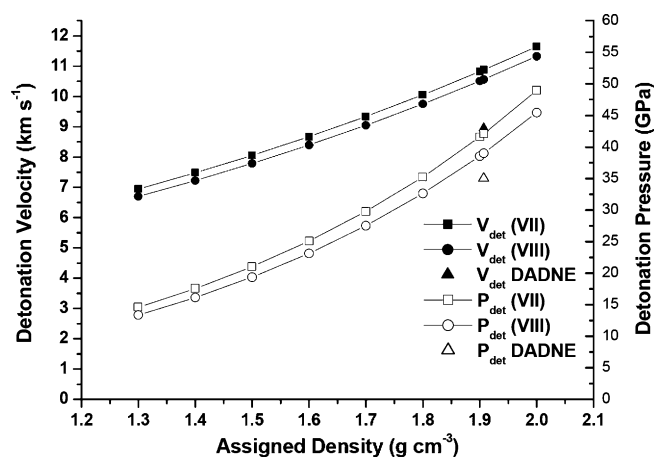
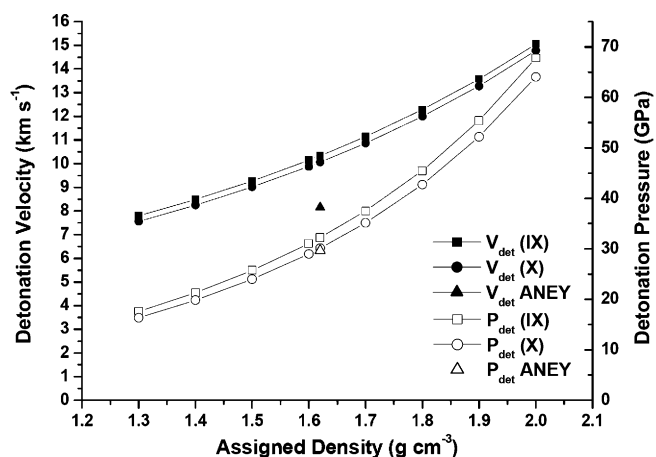
The enthalpy of formation of the mixed amino-nitro azaboridines XIII–XVI however seems to follow a different trend with substituents being placed on the C–N moiety yield definitely higher energy content ($193\text{--}204 \text{ kJ mol}^{-1}$)

Table 5. Performance of compounds V and VI on comparison to 1,3,5-triamino-2,4,6-trinitrobenzene, TATB at $\rho = 1.937 \text{ g cm}^{-3}$.

Density	Detonation velocity/ km s^{-1}		Detonation pressure/GPa		Cylinder expansion $V/V_0 = 2.20/\text{kJ cm}^{-3}$	
	V	VI	V	VI	V	VI
1.3	7.176	6.889	14.44	13.10	-3.39	-3.02
1.4	7.842	7.542	17.57	15.96	-3.95	-3.52
1.5	8.592	8.279	21.31	19.42	-4.56	-4.07
1.6	9.444	9.116	25.85	23.64	-5.35	-4.68
1.7	10.413	10.070	31.46	28.87	-6.03	-5.36
1.8	11.518	11.158	38.44	35.40	-6.87	-6.12
1.9	12.777	12.397	47.17	43.56	-7.83	-6.97
1.937	13.286	12.898	50.92	47.07	-8.21	-7.31
2.0	14.212	13.810	58.07	53.76	-8.90	-7.92
TATB	8.108		31.07		-5.48	

Table 6. Performance of compounds VII and VIII on comparison to 1,1-diamino-2,2-dinitroethylene, DADNE at $\rho = 1.907 \text{ g cm}^{-3}$.

Density	Detonation velocity/ km s^{-1}		Detonation pressure/GPa		Cylinder expansion $V/V_0 = 2.20/\text{kJ cm}^{-3}$	
	VII	VIII	VII	VIII	VII	VIII
1.3	6.944	6.697	14.58	13.38	-3.60	-3.25
1.4	7.482	7.225	17.55	16.14	-4.14	-3.74
1.5	8.059	7.791	21.02	19.36	-4.75	-4.29
1.6	8.677	8.399	25.07	23.13	-5.41	-4.89
1.7	9.341	9.052	29.77	27.52	-6.14	-5.56
1.8	10.054	9.754	35.24	32.63	-6.94	-6.28
1.9	10.822	10.510	41.59	38.56	-7.82	-7.07
1.907	10.878	10.565	42.07	39.01	-7.88	-7.13
2.0	11.648	11.325	48.96	45.46	-8.77	-7.93
DADNE	8.956		35.01		-6.46	

**Figure 9.** Performance of borazines VII and VIII relative to DADNE at TMD.**Figure 10.** Performance of borazines IX and X relative to 1-amino-2-nitroethyne, ANEY at TMD.

opposed to substitution pattern placed along B–C, where enthalpy of formation is quite low (-55 to -67 kJ mol^{-1}).

1,3,5-Trinitrobenzene (A) is the parent compound of borazines I and II. At the theoretical maximum density of A ($\rho = 1.668 \text{ g cm}^{-3}$), the borazines show higher detonation velocity (10–17%), but lower CJ pressure (19–6%) and lower cylinder expansion energy (23–7%) than TNB. Com-

ound I being slightly more powerful due to the more positive enthalpy of formation (Table 3, Figure 6).

The detonation performance of the TNT (B) analogous molecules III and IV is superior to TNT itself at the maximum density of TNT (1.654 g cm^{-3}). III and IV both exceed the detonation velocity by 21 and 27%, and the detonation

Table 7. Performance of compounds IX and X in comparison to 1-amino-2-nitroethyne, ANEY at $\rho = 1.907 \text{ g cm}^{-3}$.

Density	Detonation velocity / km s^{-1}		Detonation pressure/GPa		Cylinder expansion $V/V_0 = 2.20/\text{kJ cm}^{-3}$	
	IX	X	IX	X	IX	X
1.3	7.795	7.560	17.60	16.36	-4.28	-3.93
1.4	8.490	8.244	21.33	19.85	-4.98	-4.57
1.5	9.268	9.012	25.74	24.00	-5.76	-5.29
1.6	10.146	9.880	31.04	29.01	-6.63	-6.08
1.62	10.336	10.068	32.23	30.13	-6.81	-6.25
1.7	11.144	10.868	37.50	35.14	-7.59	-6.97
1.8	12.280	11.993	45.49	42.74	-8.67	-7.96
1.9	13.575	13.276	55.42	52.21	-9.88	-9.07
2.0	15.052	14.783	67.81	64.05	-11.24	-10.32
ANEY	8.155		29.69		-6.79	

Table 8. Performance of compounds **XI** and **XII**.

Density	Detonation velocity/km s ⁻¹		Detonation pressure/GPa		Cylinder expansion $V/V_0=2.20$ /kJ cm ⁻³	
	XI	XII	XI	XII	XI	XII
1.3	7.431	7.721	15.72	17.26	-4.01	-4.53
1.4	8.109	8.408	18.91	20.67	-4.57	-5.16
1.5	8.881	9.191	22.87	24.91	-5.21	-5.85
1.6	9.753	10.076	27.85	30.23	-5.91	-6.63
1.7	10.732	11.068	34.05	36.84	-6.72	-7.51
1.8	11.826	12.178	41.68	44.98	-7.63	-8.50
1.9	13.048	13.418	51.04	54.94	-8.66	-9.63
2.0	14.365	14.779	65.41	71.73	-9.86	-10.92

Table 9. Performance of compounds **XIII** and **XIV**.

Density	Detonation velocity/km s ⁻¹		Detonation pressure/GPa		Cylinder expansion $V/V_0=2.20$ /kJ cm ⁻³	
	XIII	XIV	XIII	XIV	XIII	XIV
1.3	7.218	7.736	14.65	17.34	-3.65	-4.56
1.4	7.887	8.423	17.68	20.76	-4.17	-5.19
1.5	8.649	9.207	21.44	25.02	-4.76	-5.89
1.6	9.510	10.092	26.15	30.35	-5.42	-6.67
1.7	10.477	11.086	32.03	36.99	-6.18	-7.55
1.8	11.558	12.196	39.29	45.16	-7.03	-8.55
1.9	12.764	13.436	48.41	55.15	-8.00	-9.68
2.0	14.057	14.801	61.41	72.10	-9.11	-10.98

Table 10. Performance of compounds **XV** and **XVI**.

Density	Detonation velocity/km s ⁻¹		Detonation pressure/GPa		Cylinder expansion $V/V_0=2.20$ /kJ cm ⁻³	
	XV	XVI	XV	XVI	XV	XVI
1.3	7.486	7.757	16.00	17.45	-4.10	-4.60
1.4	8.166	8.445	19.23	20.89	-4.68	-5.24
1.5	8.940	9.229	23.25	25.17	-5.32	-5.94
1.6	9.815	10.115	28.29	30.53	-6.05	-6.72
1.7	10.796	11.109	34.57	37.19	-6.86	-7.61
1.8	11.894	12.221	42.30	45.39	-7.79	-8.61
1.9	13.119	13.462	51.77	55.43	-8.84	-9.75
2.0	14.444	14.836	66.51	72.61	-10.05	-11.05

pressure by 5 and 21% respectively. In addition the cylinder expansion energy is 7 and 29% higher (Table 4, Figure 7).

The TATB analogous molecules **V** and **VI** outperform TATB and the considered materials but **IX** and **X** at the maximum density of TATB (1.937 g cm⁻³). Both detonation velocity and pressure even exceed and approach the known limits reported for CL-20 with a calculated detonation velocity of 13.298 and 12.987 km s⁻¹, and CJ pressures of 51.04 and 47.93 GPa. The cylinder expansion energies are little below the theoretical maximum values reported for CL-20 (-9.04 kJ cm⁻³), 8.24 and 7.51 kJ cm⁻³, respectively (Table 5, Figure 8).

The molecules analogous to the most powerful insensitive explosive 1,1-diamino-2,2-dinitroethylene (DADNE) **VII** and **VIII** display also higher performance than DADNE itself

when considered at the maximum density of DADNE (1.907 g cm⁻³). The detonation velocity is 21–17% higher than with DADNE, the detonation pressure is 20–10% higher and the cylinder expansion energy is 23–10% higher at the maximum density of DADNE (Table 6, Figure 9)

The iminoboranes **IX** and **X** display superior detonation velocity (+27, +24%) but comparable detonation pressure and cylinder expansion energy compared to the all carbon analogue 1-amino-2-nitroethylene (ANEY) that has been theoretically investigated recently [39] (Table 7, Figure 10).

The all-carbon counterpart of the azaboridine **XII–XVI** have neither been described nor reported about so far. The high positive heats of formation of these compounds facilitate high detonation velocity. Realistic densities possibly

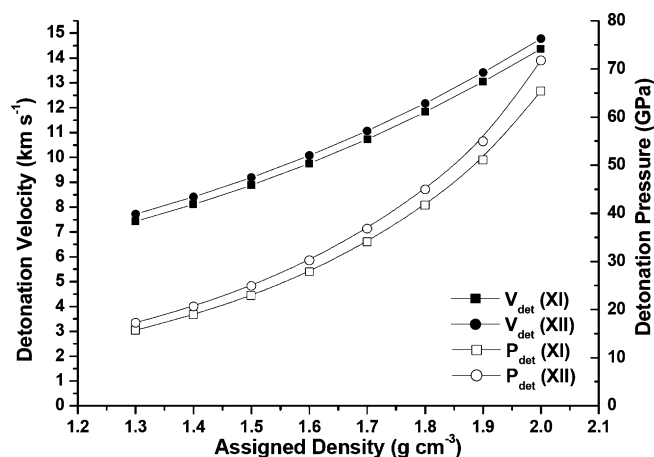


Figure 11. Performance of borazines XI and XII.

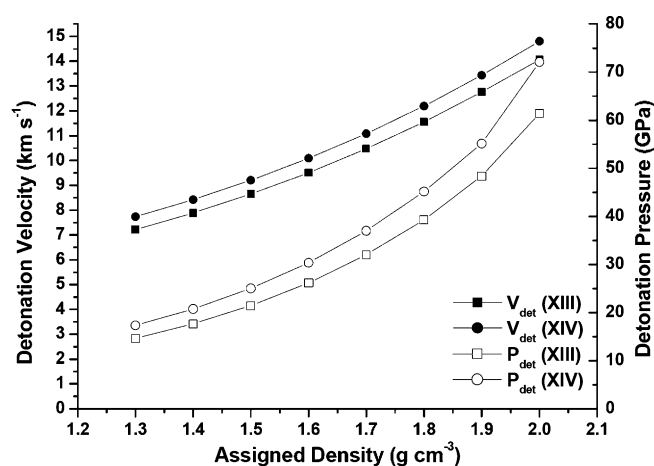


Figure 12. Performance of borazines XIII and XIV.

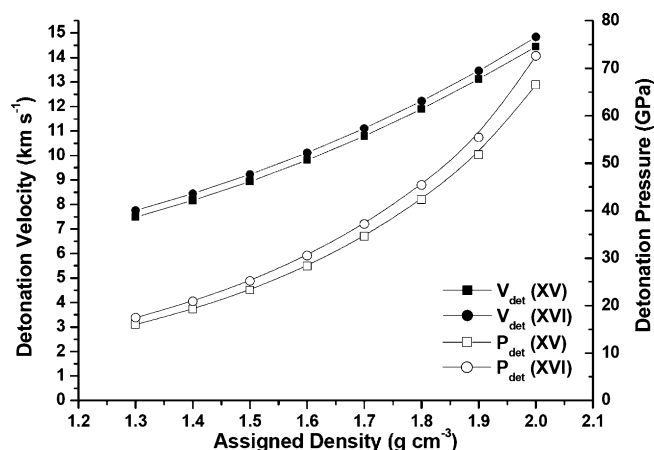


Figure 13. Performance of borazines XV and XVI.

range around 1.6 g cm^{-3} . They can be compared with nitro substituted compounds XVII–XIX considered recently. Compounds XII–XVI outperform XVII–XIX in terms of detona-

Table 11. Performance of compounds XVII–XXI.

Compound	Density	Detonation velocity/ km s^{-1}	Detonation pressure/GPa	Cylinder expansion $V/V_0=2.20/\text{kJ cm}^{-3}$
XVII	1.637	9642	28.80	−6.69
XVIII	1.639	8952	27.39	−6.07
XIX	1.905	9579	34.69	−6.95
XX	1.524	6157	12.92	−2.89
XXI	1.885	8523	28.80	−5.72

tion velocity but show similar detonation pressures and cylinder expansion energies (Table 8, Table 9, Table 10, Figure 11, Figure 12, Figure 13).

The nitroalkyl borate XXI at its TMD = 1.885 g cm^{-3} shows a promising high detonation velocity 8523 km s^{-1} (Table 11).

An important shortfall the authors are aware of is that Cheatah 2.0 applied in the present work is using the BKWC library. This library, which was originally developed by Fried and Souers [43], is based on purely empirical equation of state only and it contains only one single boron compound, $\text{B}_2\text{O}_{3(l)}$. Hence it is likely that more advanced codes treating also important species such as HBO_2 [36], BN , B_2O_2 , BO , B will yield significantly different and probably more realistic results, although the overall trend of improved detonation performance compared with the CC analogues may be preserved.

4 Conclusions

Nitro substituted borazene, borazine, iminoborane and azaboridine display much higher detonation velocity, CJ pressure and cylinder expansion energy than comparable all-carbon based materials at corresponding densities. Mixed amino-nitro substitution yields even higher performance, with the substitution pattern $\text{H}_2\text{N-N/B-NO}_2$ yielding the highest performance in all investigated structures.

Symbols and Abbreviations:

Ω	Oxygen balance/%
V_{det}	Detonation velocity/ km s^{-1}
P_{det}	Detonation pressure/GPa
$V/V_0=2$	Cylinder expansion energy/ kJ cm^{-3}

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