



Thermochemical and Performance Properties of NO₂-Substituted Borazines as New Energetic Compounds with High Thermodynamic Stability

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Abstract: The structural isomers of nitroborazines were optimized at M06-2X/6-311++G** level of theory. The effects of the NO₂ group on the molecular volume, molecular surface area, crystal density, positive, negative and total average potentials, variances, average deviation and electrostatic balance parameter on the molecular surface were considered. In addition, some important thermodynamic properties of these compounds, such as gas phase and condensed phase enthalpies of formation ($\Delta_f H^\circ(g)$ and $\Delta_f H^\circ(c)$), and the enthalpy of sublimation (ΔH_{sub}°), were calculated. It was found that the crystal densities (ρ) are in the range 1.447-1.902 g/cm³. These values are slightly smaller than the corresponding values of their carbon analogues (except for the mononitro compounds). Meanwhile, the values of ρ for B-substituted, di- and trinitroborazines are larger than the related N-substituted compounds. The calculated values of ΔH_{sub}° are in the range 20.1-30.4 kcal/mol. The calculated values of $\Delta_f H^\circ(g)$ and $\Delta_f H^\circ(c)$ for the B-substituted nitroborazines are more negative than those for the N-substituted ones. The stability sequence of the hydrogen bonded network structures of nitroborazines in the condensed phase is: dinitroborazine > mononitroborazine > trinitroborazine. The detonation pressure and velocity of these compounds were also calculated. Nitroborazines can be introduced as energetic compounds with high thermodynamic stability and relatively low detonation performance.

Keywords: electrostatic potential, enthalpy of sublimation, enthalpy of formation, density

List of Symbols

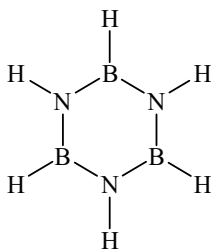
- $\Delta_f H^\circ(g)$ Enthalpy of formation in the gas phase
 $\Delta_f H^\circ(c)$ Enthalpy of formation in the condensed phase

$\Delta H_{\text{sub}}^{\circ}$	Enthalpy of sublimation
ρ	Crystal density
\overline{V}_S^+	Positive potential
\overline{V}_S^-	Negative potential
\overline{V}_S	Overall potential
$V_S(r)$	Electrostatic potential on the surface
v	Electrostatic balance parameter
σ_+^2	Positive variance on the molecular surface
σ_-^2	Negative variance on the molecular surface
σ_{tot}^2	Total variance on the molecular surface
A_s	Molecular surface area
M	Molecular weight
V_m	Molecular volume
Π	Average deviation of $V_S(r)$

1 Introduction

Before synthesizing energetic materials, it is important to predict their performance, sensitivity, and physical and thermodynamic properties. Moreover, determining measured data of a new energetic compound is dangerous, expensive and time consuming or sometimes even impossible. However, it is desirable to improve the methods used for predicting the different properties of energetic materials from a given molecular structure, so that energetic molecules of interest can be recognized. Thus, the calculated properties can help us to decide whether it is worthwhile to attempt a new and complex synthesis of novel energetic materials.

It is well known that organic compounds containing nitro (NO_2) substituents have a high energy content and are useful as explosive materials. However there is insufficient information about inorganic ones. The different properties of borazine **1** in comparison to its organic analogue (benzene) have provided an interesting chemical topic. It has been reported that borazine, with a gas phase enthalpy of formation of -121.9 kcal/mol, is thermodynamically very stable [1]. The aromaticity of borazine has been a subject of great controversy. For example, valence bond theory indicates that borazine has substantial aromatic character, similar to benzene [2]. But, nucleus-independent chemical shifts (NICS) and atom in molecule (AIM) studies predict rather poor aromatic character for this compound [3].



1

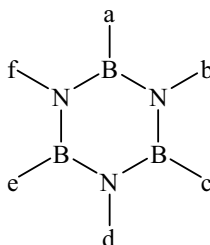
The structure, infrared spectra, gas phase enthalpy of formation and enthalpy of combustion of some nitroborazines have been theoretically investigated for the first time by Janning and Ball using the B3LYP/6-311+G** level of theory [4]. The detonation velocities of some boron-based high explosives have been calculated by using the calculated gas phase heat of formation at the corresponding densities of the carbon analogues [5].

Since most of the dispersion uncorrected GGA and hybrid density functional methods are unable to describe correlation effects and dispersion forces [6-9], it is very important to calculate the thermochemical properties of these compounds using the more accurate DFT methods. The M06-2X meta hybrid density functional is one of the recommended DFT methods for applications involving main-group thermochemistry [10], and has been used for the results described in this article.

For explosives, the accurate estimation of the condensed phase enthalpy of formation is one of the key factors in the calculation of their performance. It appears as the input in different computer codes, such as CHEETAH [11], NASA-CEC-71 [12], EXPLO5 [13] and ICT [14], in order to investigate the detonation characteristics of explosives and to evaluate the performance of propellants. In order to determine the solid phase heat of formation at 298.15 K, using the predicted gas phase enthalpy of formation ($\Delta_f H^\circ$ (g)) and enthalpy of sublimation ($\Delta H^\circ_{\text{sub}}$), Hess's law can be used. Various approaches, such as group additivity, molecular mechanics, semi-empirical, empirical and quantum chemical methods, have been developed to predict $\Delta_f H^\circ$ (g) for some classes of organic compounds [15-19]. In order to estimate $\Delta H^\circ_{\text{sub}}$, the electrostatic potential method developed by Politzer *et al.* [20-24], can be used. In this method, the $\Delta H^\circ_{\text{sub}}$ of solid compounds can be estimated on the basis of the molecular surface properties, including the molecular surface area, the total variance of the electrostatic potential on the molecular surface and the electrostatic balance parameter. This method was used by many research groups for calculating the phase transformation properties of various energetic materials [25-32]. For some

classes of energetic compounds, reliable correlations have also been developed to predict the thermochemical and phase transformation properties, which include $\Delta H_{\text{sub}}^{\circ}$ [33-35], $\Delta_f H^{\circ}(\text{g})$ [36, 37], the condensed phase enthalpy of formation ($\Delta_f H^{\circ}(\text{c})$) [38-41], the enthalpy of fusion [42-45] and the entropy of fusion [46, 47].

For chemists concerned with the synthesis of a new high explosive, the prediction of the detonation performance without using experimental values of $\Delta_f H^{\circ}(\text{c})$ and the crystal density (ρ) is very important. For many years the detonation pressure and velocity have been the two important detonation parameters, and these can be used to show the performance of an energetic material. If $\Delta_f H^{\circ}(\text{c})$ and ρ of an energetic compound are measured or estimated, the detonation pressure and velocity can be calculated using a suitable computer code or empirical method [48-51]. The purpose of the present work is to introduce NO_2 -substituted borazines **2-20** as new energetic compounds, having high thermodynamic stability. Suitable pathways were selected to calculate $\Delta H_{\text{sub}}^{\circ}$ and $\Delta_f H^{\circ}(\text{g})$ for these compounds. The values of $\Delta_f H^{\circ}(\text{c})$ and ρ have also been calculated in order to estimate the detonation performance of various nitroborazines by using an appropriate computer code.

*Mononitro:*

a = NO_2 , b-f = H **2**
 b = NO_2 , a, c-f = H **3**

Dinitro:

a, b = NO_2 , c-f = H **4**
 a, c = NO_2 , b, d-f = H **5**
 b, d = NO_2 , a, c, e, f = H **6**
 a, d = NO_2 , b, c, e, f = H **7**

Trinitro:

a, c, e = NO_2 , b, d, f = H **8**
 b, d, f = NO_2 , a, c, e = H **9**
 a, b, f = NO_2 , c, d, e = H **10**
 a-c = NO_2 , d-f = H **11**
 a, b, d = NO_2 , c, e, f = H **12**
 a, b, e = NO_2 , c, d, f = H **13**

Tetranitro:

a-d = NO_2 , e, f = H **14**
 a, b, c, e = NO_2 , d, f = H **15**
 a, b, d, e = NO_2 , c, f = H **16**
 a, b, d, f = NO_2 , c, e = H **17**

Pentanitro:

a-e = NO_2 , f = H **18**
 a-d, f = NO_2 , e = H **19**

Hexanitro:

a-f = NO_2 **20**

2 Computational details

All of the quantum chemical calculations in this work were done using the Gaussian-09 software package [52]. Geometry optimization and frequency calculations of compounds **1-20** were performed at M06-2X/6-311++G** level of theory. There are no imaginary frequencies for all of the optimized structures. The electrostatic potential analysis (ESP) was done at the 0.001 e/Bohr³ isosurface of electron density and the ESP maps were plotted by M06-2X/6-311++G** and B3LYP/6-311++G** methods. The positive, negative and overall potentials on the surface (\bar{V}_s^+ , \bar{V}_s^- and \bar{V}_s) were defined by Equations (1)-(3), where $V_s(r)$ is an electrostatic potential on the surface:

$$\bar{V}_s^+ = \frac{1}{n} \sum_{i=1}^n V_s^+(r) \quad (1)$$

$$\bar{V}_s^- = \frac{1}{m} \sum_{i=1}^m V_s^-(r) \quad (2)$$

$$\bar{V}_s = \frac{1}{m+n} \left[\sum_{i=1}^n V_s^+(r) + \sum_{i=1}^m V_s^-(r) \right] \quad (3)$$

The positive, negative and total variances on the molecular surface (σ_+^2 , σ_-^2 and σ_{tot}^2), which reveal the range and variability of $V_s(r)$, were calculated by Equation (4):

$$\sigma_{\text{tot}}^2 = \sigma_+^2 + \sigma_-^2 = \frac{1}{n} \sum_{i=1}^n [V_s^+(r) - \bar{V}_s^+]^2 + \frac{1}{m} \sum_{i=1}^m [V_s^-(r) - \bar{V}_s^-]^2 \quad (4)$$

The average deviation (Π) of $V_s(r)$ and the electrostatic balance parameter (ν) were expressed by Equations (5) and (6):

$$\Pi = \frac{1}{m+n} \sum_{i=1}^{m+n} |V_s(r) - \bar{V}_s| \quad (5)$$

$$\nu = \frac{\sigma_+^2 \sigma_-^2}{[\sigma_{\text{tot}}^2]^2} \quad (6)$$

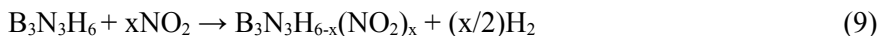
These molecular surface properties, along with the molecular surface area (A_s), were used for estimating the $\Delta H_{\text{sub}}^\circ$ of NO₂-substituted borazines via Equation (7) [27]:

$$\Delta H_{\text{sub}}^\circ = 0.000267(A_s)^2 + 1.650087(\nu \sigma_{\text{tot}}^2)^{0.5} + 2.966078 \quad (7)$$

Equation (8) was used to calculate the crystal density (ρ) of compounds **2-20**, where M and V_m are the molecular mass in g/molecule and the molecular volume in $\text{cm}^3/\text{molecule}$, respectively [53].

$$\rho = 0.9183\left(\frac{M}{V_m}\right) + 0.0028(v\sigma_{\text{tot}}^2) + 0.0443 \quad (8)$$

The following isodesmic reaction (Equation (9)) was used to calculate the $\Delta_f H^\circ$ (g) of the nitroborazines. Two stages have been followed to determine the values of $\Delta_f H^\circ$ (g): (1) the standard enthalpy of reaction was calculated; then (2) the calculated value, along with the benchmark $\Delta_f H^\circ$ (g) of $\text{B}_3\text{N}_3\text{H}_6$ (-121.9 kcal/mol) and NO_2 (7.9 kcal/mol), were used for estimating $\Delta_f H^\circ$ (g) of these compounds. The experimental $\Delta_f H^\circ$ (g) of borazine and NO_2 were taken from the National Institute of Standards and Technology (NIST) [54].



Equation (10) was used to calculate the values of $\Delta_f H^\circ$ (c) for compounds **2-20**.

$$\Delta_f H^\circ (\text{c}) = \Delta_f H^\circ (\text{g}) - \Delta H_{\text{sub}}^\circ \quad (10)$$

The Becker-Kistiakowsky-Wilson equation of state (BKW-EOS) is a semi-empirical equation of state, which is based upon a repulsive potential applied to the virial equation of state. The BKW computer code uses BKW-EOS to compute the Chapman-Jouguet (C-J) equilibrium detonation product composition, the C-J pressure, detonation velocity, temperature, the single shock Hugoniot and the isentrope. If the elemental composition, ρ and $\Delta_f H^\circ$ (c) of an energetic compound are known, the BKW computer code can calculate its detonation performance [48]. For the NO_2 -substituted borazines **2-20**, the calculated detonation velocity and pressure, on the basis of the cyclotrimethylene trinitramine (RDX) parameter set, were also calculated.

3 Results and Discussion

For some of the most important compounds in the group of nitroborazines **1-20**, the calculated electrostatic potential maps using the M06-2X method are shown in Figure 1. The light and dark positions indicate the most negative and the most positive electrostatic potentials, respectively. Table 1 lists the effects of the NO_2

groups on V_m , A_s , ρ and Π , as well as the values of \bar{V}_s^+ , \bar{V}_s^- , \bar{V}_s , σ_{+}^2 , σ_{-}^2 , σ_{tot}^2 and v on the molecular surface of compounds **1-20**.

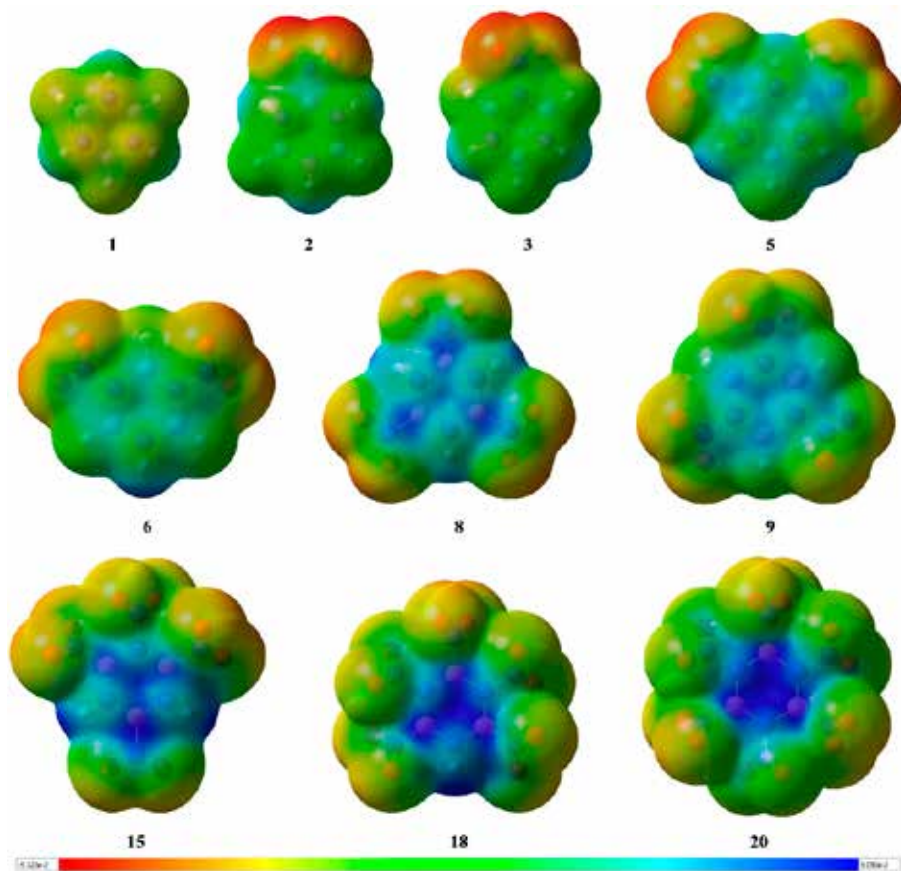


Figure 1. The calculated ESP maps at 0.001 e/Bohr³ isosurface of electron density for some NO₂-substituted borazines via M06-2X/6-311++G** level of theory. The legend for the range of the ESPs is -0.05 (left) to +0.09 (right).

It was found for the mono-, di-, tri-, tetra-, penta- and hexanitroborazines, that the value of A_s is enhanced by increasing the number of NO₂ groups (Figure 2). Of compounds **1-20**, borazine **1** has the lowest value of A_s (129.8 Å²) on the basis of the M06-2X calculations. The corresponding value predicted by B3LYP is 130.4 Å². For the mono-, di-, tri-, tetra-, penta- and hexanitroborazines, the values of A_s are in the ranges 155.3-275.1 (M06-2X) and 156-276.2 Å² (B3LYP).

Table 1. Theoretical estimation of the molecular surface properties, density, enthalpy of sublimation, gas phase heat of formation, condensed phase heat of formation, detonation velocity and detonation pressure of NO₂-substituted borazines calculated by M06-2X and B3LYP (in parenthesis) levels of theory. The results of the B3PWP1 method for density are also shown underlined.

Com- pounds	V _m [Å ³]	A _s [Å ²]	ρ [g/cm ³]	\bar{V}_s [kcal/ mol]	\bar{V}_s^+ [kcal/ mol]	\bar{V}_s^- [kcal/ mol]	σ _{ot} ² [kcal/ mol] ²	σ ₊ ² [kcal/ mol] ²	σ ₋ ² [kcal/ mol] ²	v	vσ _{ot} ² [kcal/ mol] ²	Π [kcal/ mol]	ΔH _{sub} ^o [kcal/ mol]	ΔH ^o (gas) [kcal/ mol]	ΔH ^o (solid) [kcal/ mol]	Detona- tion pressure [kbar]	Detona- tion velocity [m/s]
1	119.7 (120.7)	129.8 (130.4)	1.089 (<u>1.075</u> , <u>1.124</u>)	1.7 (2.0)	11.8 (11.6)	-4.1 (-4.0)	103.4 (98.9)	96.1 (94.0)	7.3 (5.0)	0.066 (0.048)	6.8 (4.7)	7.5 (7.5)	11.8 (11.1)	-121.9 ^a	-133.7	-	-
2	148.7 (149.9)	156.3 (157.0)	1.447 (<u>1.432</u> , <u>1.499</u>)	3.9 (4.1)	12.6 (12.4)	-20.1 (-19.4)	165.3 (159.2)	77.6 (75.5)	87.7 (83.7)	0.249 (0.249)	41.2 (39.7)	12.9 (12.4)	20.1 (19.9)	-149.6 (-141.8) ^b	-169.7	-	-
3	148.8 (149.8)	155.3 (156.0)	1.452 (<u>1.441</u> , <u>1.503</u>)	3.0 (3.2)	12.8 (12.9)	-18.2 (-17.4)	173.9 (170.2)	91.0 (88.6)	82.9 (81.6)	0.249 (0.249)	43.4 (42.5)	13.5 (13.4)	20.3 (20.2)	-107.7 (-100.0) ^b	-128.0	-	-
4	178.3 (179.6)	181.1 (181.8)	1.615 (<u>1.598</u> , <u>1.663</u>)	4.0 (4.2)	20.9 (20.4)	-18.3 (-17.4)	173.6 (166.1)	111.4 (108.6)	62.2 (57.5)	0.230 (0.226)	39.9 (37.6)	19.4 (18.6)	22.1 (21.9)	-126.0	-148.1	224	7464
5	178.2 (179.4)	183.4 (184.1)	1.607 (<u>1.593</u> , <u>1.662</u>)	6.4 (6.5)	21.1 (20.6)	-16.0 (-15.6)	153.5 (146.8)	91.5 (87.4)	62.1 (59.4)	0.241 (0.241)	37.0 (35.4)	18.1 (17.6)	22.0 (21.8)	-173.7 (-161.7) ^b	-195.7	203	7249
6	178.1 (179.2)	181.2 (181.9)	1.589 (<u>1.577</u> , <u>1.632</u>)	5.0 (5.1)	18.9 (18.8)	-13.9 (-13.5)	151.0 (148.7)	109.6 (108.7)	41.3 (40.0)	0.199 (0.197)	30.0 (29.2)	16.3 (16.1)	20.8 (20.7)	-89.7 (-78.0) ^b	-110.5	230	7511
7	178.1 (179.2)	182.2 (182.8)	1.597 (<u>1.585</u> , <u>1.647</u>)	6.1 (6.1)	19.8 (19.5)	-14.5 (-14.1)	150.3 (146.5)	101.2 (99.7)	49.1 (46.9)	0.220 (0.218)	33.0 (31.9)	16.8 (16.4)	21.3 (21.2)	-132.3	-153.6	216	7371
8	207.9 (209.3)	211.0 (211.6)	1.721 (<u>1.707</u> , <u>1.784</u>)	9.0 (8.9)	25.9 (25.3)	-12.4 (-12.2)	225.5 (212.6)	183.6 (171.9)	41.9 (40.7)	0.151 (0.155)	34.1 (32.9)	19.8 (19.3)	24.5 (24.4)	-194.3 (-172.1) ^b	-218.8	-	-
9	207.8 (208.9)	207.6 (208.2)	1.678 (<u>1.668</u> , <u>1.724</u>)	7.1 (7.1)	20.5 (20.2)	-9.5 (-9.3)	171.5 (171.9)	150.2 (151.7)	21.3 (20.2)	0.109 (0.104)	18.6 (17.9)	15.5 (15.3)	21.6 (21.5)	-68.4 (-46.7) ^b	-90.0	216	6941

Compounds	V _m [Å ³]	A _s [Å ²]	ρ [g/cm ³]	\bar{V}_s [kcal/mol]	\bar{V}_s^- [kcal/mol]	\bar{V}_s^+ [kcal/mol]	σ_s^2 [kcal/mol] ²	σ_s^{int} [kcal/mol] ²	σ_s^- [kcal/mol] ²	σ_s^+ [kcal/mol] ²	v	vσ _s ^{int} [kcal/mol] ²	Π [kcal/mol]	ΔH _{sub} ⁰ [kcal/mol]	ΔH ⁰ (gas) [kcal/mol]	ΔH ⁰ (solid) [kcal/mol]	Detonation pressure [kbar]	Detonation velocity [m/s]
10	207.4 (208.6)	203.7 (204.5)	1.743 (1.723, 1.787)	4.6 (4.7)	24.6 (23.8)	-15.0 (-14.2)	160.2 (153.2)	215.0 (201.7)	54.7 (48.5)	0.190 (0.183)	40.8 (36.8)	20.0 (19.2)	24.6 (24.1)	-101.9	-126.5	224	7001	
11	207.8 (209.2)	206.1 (207.0)	1.725 (1.708, 1.778)	5.5 (5.6)	26.5 (25.4)	-14.4 (-13.7)	174.0 (166.7)	218.1 (208.0)	44.1 (41.3)	0.161 (0.159)	35.2 (33.1)	20.7 (19.9)	24.1 (23.9)	-142.1	-166.2	207	6810	
12	207.9 (209.2)	207.2 (207.9)	1.713 (1.696, 1.739)	6.5 (6.6)	23.5 (22.9)	-12.0 (-11.5)	174.2 (169.9)	212.5 (204.8)	38.3 (34.9)	0.148 (0.141)	31.4 (28.9)	18.2 (17.6)	23.7 (23.4)	-105.7	-129.4	214	6901	
13	208.0 (209.3)	208.4 (209.1)	1.723 (1.707, 1.777)	7.2 (7.2)	25.3 (24.6)	-13.0 (-12.5)	174.2 (165.7)	218.1 (206.6)	43.9 (40.9)	0.161 (0.159)	35.1 (32.8)	19.6 (19.0)	24.3 (24.1)	-147.7	-172.0	205	6784	
14	237.1 (238.5)	229.1 (230.0)	1.808 (1.792, 1.862)	6.5 (6.6)	26.2 (25.2)	-10.9 (-10.3)	265.1 (246.0)	300.7 (279.1)	35.6 (33.1)	0.104 (0.104)	31.4 (29.2)	19.0 (18.3)	26.2 (26.0)	-116.0	-142.2	214	6865	
15	237.7 (239.2)	233.9 (234.7)	1.791 (1.777, 1.856)	8.7 (8.7)	26.6 (25.8)	-10.0 (-9.7)	301.3 (280.4)	330.6 (308.4)	29.3 (27.9)	0.081 (0.082)	26.7 (25.4)	19.4 (18.8)	26.1 (26.0)	-160.9	-187.0	-	-	
16	237.9 (239.3)	233.4 (234.2)	1.791 (1.775, 1.847)	8.3 (8.3)	24.6 (23.9)	-9.4 (-9.0)	271.1 (257.6)	301.6 (285.5)	30.5 (28.0)	0.091 (0.088)	27.4 (25.2)	18.1 (17.5)	26.1 (25.9)	-119.1	-145.2	208	6803	
17	237.2 (238.5)	230.1 (230.9)	1.807 (1.788, 1.853)	7.2 (7.2)	22.8 (22.2)	-9.6 (-9.0)	217.2 (208.1)	253.8 (240.2)	36.6 (32.0)	0.123 (0.116)	31.3 (27.8)	17.0 (16.4)	26.3 (25.9)	-78.9	-105.2	224	6971	
18	267.1 (268.6)	254.9 (255.9)	1.852 (1.839, 1.917)	8.5 (8.4)	23.5 (22.6)	-7.6 (-7.4)	368.8 (339.6)	392.7 (362.2)	23.9 (22.7)	0.057 (0.059)	22.4 (21.3)	17.1 (16.6)	28.1 (28.1)	-128.0	-156.1	-	-	
19	266.8 (268.2)	252.7 (253.6)	1.866 (1.851, 1.922)	7.6 (7.6)	21.9 (21.0)	-7.9 (-7.4)	302.8 (281.3)	332.4 (308.4)	29.6 (27.1)	0.081 (0.080)	26.9 (24.7)	16.2 (15.6)	28.6 (28.3)	-87.9	-116.5	217	6895	
20	296.4 (297.9)	275.1 (276.2)	1.902 (1.889, 1.967)	8.2 (8.1)	17.6 (17.0)	-6.4 (-6.2)	316.6 (287.7)	337.1 (306.8)	20.5 (19.1)	0.057 (0.058)	19.3 (17.9)	13.9 (13.4)	30.4 (30.3)	-95.7	-126.1	224	6826	

^a Ref. [54]

^b Ref. [4]

A similar trend was found for the V_m data of these compounds (Table 1).

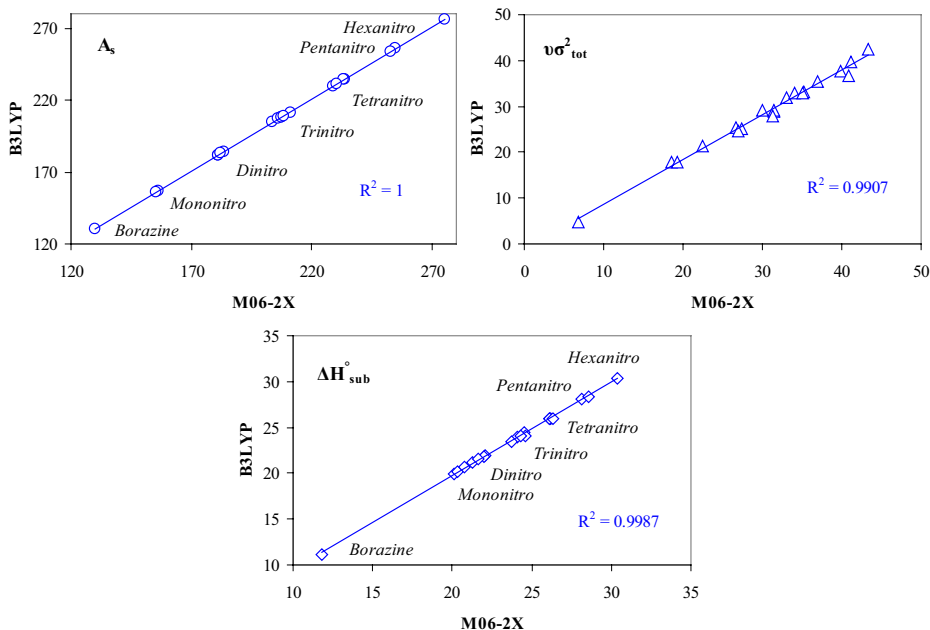


Figure 2. Relationship between the M06-2X and B3LYP methods for predicting the molecular surface properties (A_s and $v\sigma_{tot}^2$) and enthalpy of sublimation (ΔH_{sub}°) of compounds **1-20** using Equation 7.

The overall average values of \bar{V}_s for the nitroborazines **2-20** are in the range 3-9 kcal/mol. The maximum difference between the values of \bar{V}_s and \bar{V}_s^+ was calculated for the trinitro compound **11**, *i.e.* -14.4 to 26.5 kcal/mol, respectively. The maximum value of Π , which is a measure of local polarity or internal charge separation, is also observed for this compound (20.7 kcal/mol). According to the results of Table 1, the values of σ_+^2 for compounds **9** and **11-20** are 4-15 times larger than σ_-^2 . Therefore, the value of v in these compounds is quite small, in the range 0.057-0.161. The maximum possible value of v is 0.250, which is attained when $\sigma_+^2 = \sigma_-^2$. The closeness of v to 0.250 is related to a greater tendency of the molecule for interaction to a similar extent through both its positive and negative surface potentials. Of the nitroborazines **2-20**, the mononitro compounds **2** and **3** have the highest v values (0.249). These results show that the degree of balance between the positive and negative regions is reduced by increasing the number of NO_2 groups. It has been reported that σ_{tot}^2 is a measure of a molecule's tendency for non-covalent interactions [20]. The

minimum and maximum values of σ_{tot}^2 were calculated for compounds **7** and **18**, as 150.3 and 392.7 kcal²/mol², respectively. The product $v\sigma_{\text{tot}}^2$ is important for describing properties that are related to the interactions of a molecule with others of its own kind. This value is also important for the estimation of the crystal density and enthalpy of sublimation using Equations (8) and (7), respectively. The minimum and maximum values of $v\sigma_{\text{tot}}^2$ were also calculated for compounds **9** and **3**, as 18.6 and 43.4 kcal²/mol², respectively.

The values of A_s and $v\sigma_{\text{tot}}^2$ given in Table 1 were utilized for the estimation of the enthalpy of sublimation using Equation (7). This equation is parameterized for C, H, N, O compounds at the B3LYP level [27]. Here we used this equation for B, H, N, O molecules, because experimental data for $\Delta H_{\text{sub}}^\circ$ of boron containing compounds are not available. For the nitroborazines **2-20**, the calculated values of $\Delta H_{\text{sub}}^\circ$ by the B3LYP method are in the range 19.9-30.3 kcal/mol. Of the various nitroborazines, B-nitroborazine **2** and the hexanitro compound **20** have the lowest and the highest values of $\Delta H_{\text{sub}}^\circ$, respectively. The M06-2X method predicts similar values, *i.e.* 20.1-30.4 kcal/mol. Due to the very good agreement of the data presented in Table 1 and Figure 2 for the molecular surface properties calculated by the M06-2X and B3LYP methods, Equation (7) is also reliable for the M06-2X level of theory.

Although the standard enthalpies of phase change are well estimated by B3LYP [27], the rather poor performance of B3LYP, as well as the significant improvements with M06-2X, have been reported for calculating the standard enthalpies of formation [55]. The M06-2X method predicts values of $\Delta_f H^\circ$ (g) for the nitroborazines **2, 3, 5, 6, 8** and **9**, respectively. A comparison between these values and the B3LYP data reported in Ref. [4] (-141.8, -100.0, -161.7, -78.0, -172.1 and -46.7 kcal/mol, respectively) shows that M06-2X improves on the B3LYP results, from -7.8 (for mononitroborazine) to -22.2 kcal/mol (for trinitroborazine) (Table 1).

The calculated values of $\Delta H_{\text{sub}}^\circ$ and $\Delta_f H^\circ$ (g) by the M06-2X method were used for the estimation of $\Delta_f H^\circ$ (c) via Equation (10) for compounds **1-20**, and are given in Table 1. The values of $\Delta_f H^\circ$ (g) and $\Delta_f H^\circ$ (c) for B-substituted nitroborazines are more negative than the corresponding N-substituted ones. For example, B-nitroborazine **2** is more stable than N-nitroborazine **3**, by about 41.9 kcal/mol in the gas phase. The energy differences between B- and N-substitution increase to 84.0 and 125.9 kcal/mol for di- and trinitroborazines, respectively. The stability of these species dramatically decreases when the number of NO₂ groups is more than three (Figure 3).

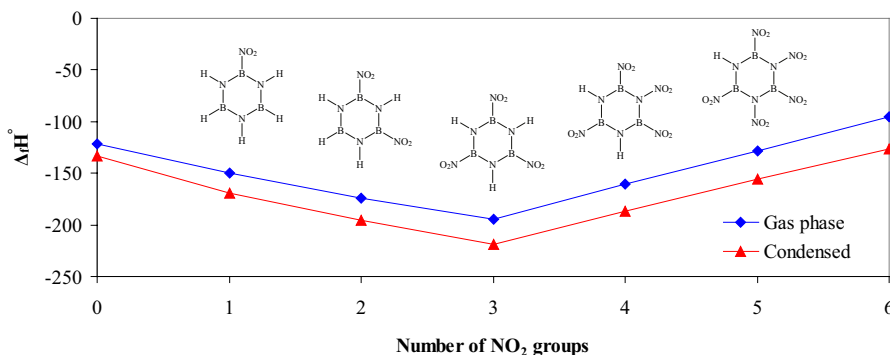


Figure 3. Influence of the number of NO₂ groups on the $\Delta_f H^\circ$ (g) and $\Delta_f H^\circ$ (c) data for the more stable isomers of nitroborazines.

Equation 8, used to predict densities, was parameterized for B3PW91/6-31G** level of theory [53]. According to the results in Table 1, the predicted values of ρ by this method for mono-, di-, tri-, tetra-, penta- and hexanitroborazines are in the range 1.499-1.967 g/cm³. No improvement in densities over those calculated by B3PW91 was obtained with B3LYP (1.432-1.889 g/cm³) or M06-2X (1.447-1.902 g/cm³) functionals (Figure 4). The crystal density of nitroborazines is raised by increasing the number of NO₂ groups. Except for the mononitro compounds **2** and **3**, these values are slightly smaller than the corresponding values of their carbon analogues. The measured and calculated crystal densities of nitrobenzenes through B3LYP are in the ranges 1.34-2.01 and 1.39-1.93 g/cm³, respectively [56]. In contrast to the mononitroborazines, the values of ρ for the B-substituted di- and trinitroborazines are larger than their N-substituted isomers.

Schematic pictures of the intermolecular interactions for mono-, di- and tri-nitro compounds **2**, **5** and **8** are shown in Figure 5. The calculated basis set superposition error (BSSE), corrected interaction energy (ΔE_{int}), between two molecules of mononitroborazine **2** at M06-2X/6-311++G** level of theory is -6.6 kcal/mol. Due to the repulsion between NO₂ groups, the corresponding value for the trinitroborazine **8** dimer is less negative (-4.5 kcal/mol). The interaction energy in the dinitroborazine **5** dimer is more negative, *i.e.* -7.4 kcal/mol, representing a higher stability of the hydrogen bonded network structure of compound **5** in the condensed phase.

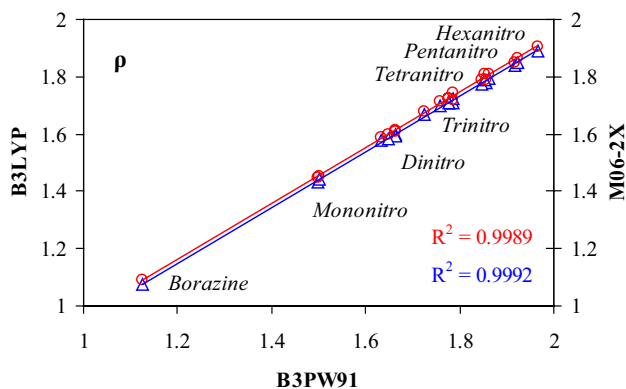


Figure 4. Relationship between the B3PW91, B3LYP (Δ) and M06-2X (\circ) methods for predicting the crystal density (ρ) of compounds **1-20** using Equation 8.

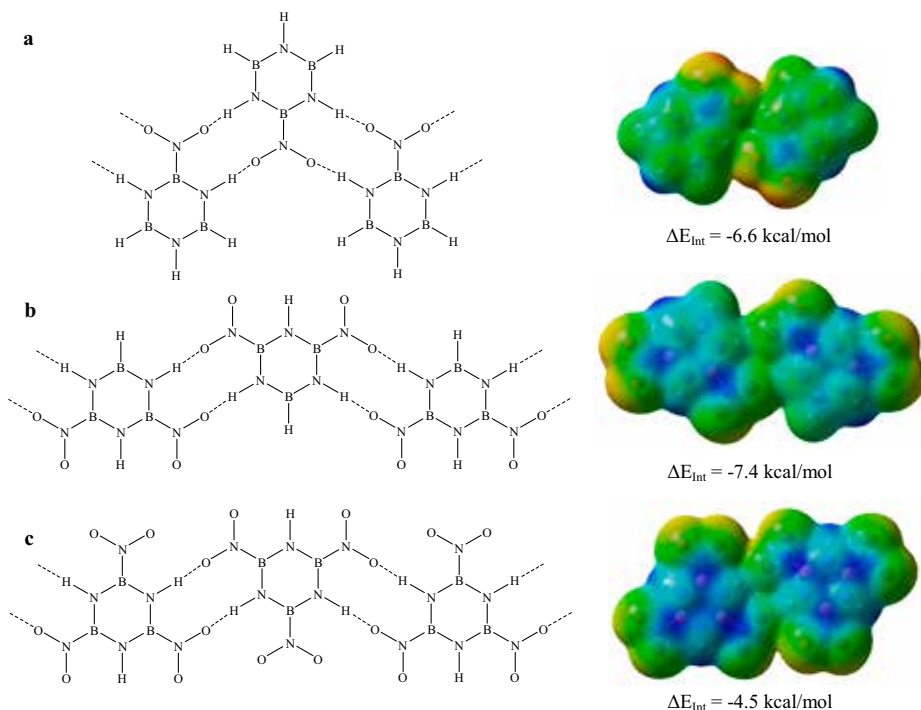


Figure 5. Schematic pictures and ESP maps of the intermolecular interactions of B-substituted mononitro- (a) dinitro- (b) and trinitroborazines (c) in the condensed phase.

Since the detonation reactions of energetic materials are usually complicated and violent, they have characteristics such as high reaction rates, high temperatures, complex product compositions, and so on. It can be inferred that a high detonation performance is promoted by the formation of light gaseous products and a high positive heat of formation. The first factor produces a greater number of moles of gaseous products per unit weight of explosives. The second factor leads to a greater release of heat of detonation and a higher detonation temperature. Moreover, experiments for determining the performance of explosives reveal that the C-J pressure and detonation velocity are roughly proportional to the square and linear functions of the loading density, respectively [48].

Koch and Klapötke have reported overestimated detonation velocity values for trinitroborazines on the basis of the calculated gas phase heat of formation at the corresponding densities of 1,3,5-trinitrobenzene [5]. For explosives containing “exotic” elements such as boron, aluminum, or fluorine, the observed C-J pressures and detonation velocities are not as high as those of the superior C, H, N, O explosives at the same densities [48]. The heat of detonation may be increased in nitroborazines, as compared to the corresponding isomers of nitrobenzenes, because boron is an “exotic” element. For C, H, N, O explosives, higher values of the detonation velocity and pressure can be expected for explosives with greater densities as compared to B, H, N, O explosives. As an example, HMX with density 1.9 g/cm^3 , has relatively large values of detonation velocity and pressure, *i.e.* 9100 m/s and 393 kbar, respectively [48]. Whilst the measured values of the detonation velocity and pressure for trinitrotoluene (TNT) are 6950 m/s and 190 kbar, respectively, at $\rho=1.64 \text{ g/cm}^3$ [48]. As indicated in Table 1, the calculated detonation velocity and pressure are relatively low for nitroborazines. Several factors can account for the low performance of nitroborazines: (1) they have large negative values of $\Delta_r H^\circ$ (c), which may classify them as thermodynamically very stable energetic compounds; (2) although increasing the number of nitro groups can improve the density, the number of moles of gaseous products will be diminished; and (3) it was confirmed that the poor C-J performance of the boron explosives relative to the C, H, N, O explosives, results from formation of complex detonation product molecules such as B_2O_3 .

4 Conclusions

The effects of NO_2 groups on the molecular surface area, crystal density, the positive, negative and total average potentials, variances, average deviation, the

electrostatic balance parameter on the molecular surface, gas phase enthalpy of formation, condensed phase enthalpy of formation, enthalpy of sublimation and detonation properties of nitroborazines have been investigated theoretically.

The efficiency of new M06-2X meta hybrid density functional for predicting the standard enthalpies of phase changes and crystal densities was considered. M06-2X performs comparably to B3LYP for predicting molecular surface properties and enthalpies of sublimation. However this method significantly improves the enthalpies of formation. No improvement in densities over those calculated by B3PW91 was obtained with the B3LYP and M06-2X methods.

The crystal densities of nitroborazines are slightly smaller than those of their corresponding carbon analogues, except for the mononitro compounds. In contrast to the mononitro compounds, the crystal densities of B-substituted di- and trinitroborazines are larger than the corresponding N-substituted ones. The calculated values of $\Delta H_{\text{sub}}^{\circ}$ are in the range 20.1-30.4 kcal/mol. The calculated values of $\Delta_f H^{\circ}$ (g) and $\Delta_f H^{\circ}$ (c) for the B-substituted nitroborazines are more negative than those for the N-substituted compounds. The stability of nitroborazines decreases dramatically when the number of NO₂ groups is greater than three. The stability sequence of the hydrogen bonded network structures of nitroborazines in the condensed phase is: dinitroborazine > mononitroborazine > trinitroborazine.

Nitroborazines have higher thermodynamic stability and lower detonation parameters compared to the corresponding nitrobenzenes. Presumably the problem with regard to the detonation properties is that the oxygen atoms in the molecules are used to form solid B₂O₃. While these compounds have large negative heats of formation, and thus release energy, the fact that B₂O₃ is a solid means that the number of moles of gaseous products is small. Since the number of moles of gaseous products is a key factor in determining the detonation pressure and velocity, the predicted values for these properties will be poor.

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5 References

- [1] Chase M.W. Jr., *NIST-JANAF Thermochemical Tables*, 4th ed., J. Phys. Chem. Ref. Data, Monograph No. 9, **1998**, 1-1951.
- [2] Benker D., Klapötke T.M., Kuhn G., Li J., Miller C., An Ab Initio Valence Bond

- (VB) Calculation of the π Delocalization Energy in Borazine, $B_3N_3H_6$, *Heteroatom Chem.*, **2005**, *16*, 311-315.
- [3] Shen W., Li M., Li Y., Wang S., Theoretical Study of Borazine and its Derivatives, *Inorganica Chimica Acta*, **2007**, *360*, 619-624.
- [4] Janning J.D., Ball D.W., Nitroborazines as Potential High Energy Materials: Density Functional Theoretical Calculations, *J. Mol. Model.*, **2010**, *16*, 857-862.
- [5] Koch E.-C., Klapötke T.M., Boron-based High Explosives, *Propellants Explos. Pyrotech.*, **2012**, *37*, 335-344.
- [6] Grimme S., Accurate Description of Van Der Waals Complexes by Density Functional Theory Including Empirical Corrections, *J. Comput. Chem.*, **2004**, *25*, 1463-1473.
- [7] Grimme S., GGA-Type Density Functional Constructed with a Long-range Dispersion Correction, *J. Comput. Chem.*, **2006**, *27*, 1787-1799.
- [8] Grimme S., Anthony J., Ehrlich S., Krieg H., A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu, *J. Chem. Phys.*, **2010**, *132*, 154104.
- [9] Grimme S., Density Functional Theory with London Dispersion Corrections, *WIREs Comput. Mol. Sci.*, **2011**, *1*, 211-228.
- [10] Zhao Y., Truhlar D.G., The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-class Functionals and 12 Other Functionals, *Theor. Chem. Account*, **2008**, *120*, 215-241.
- [11] Lu J.P., *Evaluation of the Thermochemical Code – CHEETAH 2.0 for Modeling Explosives Performance*, DSTO-DR-1199, Defence Science and Technology Organization (Australian Government), Edinburgh, **2001**.
- [12] Sanford G., McBride B.J., *Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications. I. Analysis*, Vol. 1331, NASA Reference Publication, Washington D.C., **1994**.
- [13] Sućeska M., *EXPLO5 Program, Version 5.04*, Zagreb, Croatia, **2010**.
- [14] *ICT Thermodynamic Code, Version 1.00*, Fraunhofer Institut Chemische Technologie, ICT **1998-2000**.
- [15] Poling B.E., Prausnitz J.M., O'Connell J.P., *The Properties of Gases and Liquids*, 5th ed., McGraw-Hill, New York, **2001**.
- [16] Politzer P., Lane P., Concha M.C., Computational Approaches to Heats of Formation, in: *Theoretical and Computational Chemistry*, (Politzer P., Murray J.S., Eds.), Vol. 12, Elsevier, Amsterdam, **2003**, pp. 247-277.
- [17] Keshavarz M.H., Research Progress on Heats of Formation and Detonation of Energetic Compounds, in: *Hazardous Materials: Types, Risks and Control*, (Brar S.K., Ed.), Nova Science Publishers, Inc., New York, **2011**, pp. 339-359.
- [18] Watts J.D., Chemical Reactions: Thermochemical Calculations, in: *Handbook of Computational Chemistry*, (Leszczynski J., Ed.), Springer, Berlin Heidelberg, **2012**, pp. 467-482.

- [19] Rogers D.W., Zavitsas A.A., Matsunaga N., Determination of Enthalpies ('Heats') of Formation, *WIRES Comput. Mol. Sci.*, **2013**, 3, 21-36.
- [20] Murray J.S., Brinck T., Politzer P., Relationships of Molecular Surface Electrostatic Potentials to Some Macroscopic Properties, *Chem. Phys.*, **1996**, 204, 289-299.
- [21] Politzer P., Murray J.S., Grice M.E., Desalvo M., Miller E., Calculation of Heats of Sublimation and Solid Phase Heats of Formation, *Mol. Phys.*, **1997**, 91, 923-928.
- [22] Murray J.S., Politzer P., Statistical Analysis of the Molecular Surface Electrostatic Potential: an Approach to Describing Noncovalent Interactions in Condensed Phases, *J. Mol. Struct. Theochem.*, **1998**, 425, 107-114.
- [23] Politzer P., Ma Y., Lane P., Concha M.C., Computational Prediction of Standard Gas, Liquid, and Solid-phase Heats of Formation and Heats of Vaporization and Sublimation, *Int. J. Quantum Chem.*, **2005**, 105, 341-347.
- [24] Bulat F.A., Toro-Labbé A., Brinck T., Murray J.S., Politzer P., Quantitative Analysis of Molecular Surfaces: Areas, Volumes, Electrostatic Potentials and Average Local Ionization Energies, *J. Mol. Model.*, **2010**, 16, 1679-1691.
- [25] Rice B.M., Pai S.V., Hare J., Predicting Heats of Formation of Energetic Materials using Quantum Mechanical Calculations, *Combust. Flame*, **1999**, 118, 445-458.
- [26] Rice B.M., Hare J.J., A Quantum Mechanical Investigation of the Relation between Impact Sensitivity and the Charge Distribution in Energetic Molecules, *J. Phys. Chem. A*, **2002**, 106, 1770-1783.
- [27] Byrd E.F.C., Rice B.M., Improved Prediction of Heats of Formation of Energetic Materials Using Quantum Mechanical Calculations, *J. Phys. Chem. A*, **2006**, 110, 1005-1013.
- [28] Shi L.-W., Zhou J.-H., Zhang T., Kang Q., Chen M.-B., Calculation of Heat of Formation for Tensile Cyclic Molecules in Condensed Phase using Electrostatic Potential and QSPR Schemes, *Chin. J. Chem.*, **2008**, 26, 1181-1190.
- [29] Jaidann M., Roy S., Abou-Rachid H., Lussier L.-S., A DFT Theoretical Study of Heats of Formation and Detonation Properties of Nitrogen-rich Explosives, *J. Hazard. Mater.*, **2010**, 176, 165-173.
- [30] Singh H., Mukherjee U., Saini R.S., Computational Studies on Nitro Derivatives of 1-Hydroxy-1,2,4-triazole, *J. Energ. Mater.*, **2012**, 30, 265-281.
- [31] Keshavarz M.H., Zamani M., Atabaki F., Hosseini Monjezi K., Theoretical Investigation of Phase Transformations and Molecular Surface Properties of Polycyclic Saturated Hydrocarbon Isomers of JP-10, *Comput. Theoret. Chem.*, **2013**, 1006, 105-112.
- [32] Keshavarz M.H., Zamani M., Atabaki F., Hosseini Monjezi K., Reliable Approach for Prediction of Heats of Formation of Polycyclic Saturated Hydrocarbons Using Recently Developed Density Functionals, *Comput. Theoret. Chem.*, **2013**, 1011, 30-36.
- [33] Keshavarz M.H., Prediction of Heats of Sublimation of Nitroaromatic Compounds via Their Molecular Structure, *J. Hazard. Mater.*, **2008**, 151, 499-506.
- [34] Keshavarz M.H., Yousefi M.H., Heats of Sublimation of Nitramines Based on Simple Parameters, *J. Hazard. Mater.*, **2008**, 152, 929-933.

- [35] Keshavarz M.H., Improved Prediction of Heats of Sublimation of Energetic Compounds using Their Molecular Structure, *J. Hazard. Mater.*, **2010**, *177*, 648-659.
- [36] Keshavarz M.H., New Pathway for Quick Estimation of Gas Phase Heat of Formation of Non-aromatic Energetic Compounds, *Indian J. Eng. Mater. Sci.*, **2006**, *13*, 542-548.
- [37] Keshavarz M.H., Kavosh Tehrani M., A New Method for Determining Gas Phase Heat of Formation of Aromatic Energetic Compounds, *Propellants Explos. Pyrotech.*, **2007**, *32*, 155-159.
- [38] Keshavarz M.H., Oftadeh M., New Method for Estimating the Heat of Formation of CHNO Explosives in Crystalline State, *High Temp. High Press.*, **2003**, *35*, 499-504.
- [39] Keshavarz M.H., Predicting Condensed Phase Heat of Formation of Nitroaromatic Compounds, *J. Hazard. Mater.*, **2009**, *169*, 890-900.
- [40] Keshavarz M.H., Sadeghi H., A New Approach to Predict the Condensed Phase Heat of Formation in Acyclic and Cyclic Nitramines, Nitrate Esters and Nitroaliphatic Energetic Compounds, *J. Hazard. Mater.*, **2009**, *171*, 140-146.
- [41] Keshavarz M.H., Prediction of the Condensed Phase Heat of Formation of Energetic Compounds, *J. Hazard. Mater.*, **2011**, *190*, 330-344.
- [42] Keshavarz M.H., Predicting Heats of Fusion of Nitramines, *Indian J. Eng. Mater. Sci.*, **2007**, *14*, 386-390.
- [43] Keshavarz M.H., A Simple Correlation for Predicting Heats of Fusion of Nitroaromatic Carbocyclic Energetic Compounds, *J. Hazard. Mater.*, **2008**, *150*, 387-393.
- [44] Semnani A., Keshavarz M.H., Using Molecular Structure for Reliable Predicting Enthalpy of Melting of Nitroaromatic Energetic Compounds, *J. Hazard. Mater.*, **2010**, *178*, 264-272.
- [45] Mosaei Oskoei Y., Keshavarz M.H., Improved Method for Reliable Predicting Enthalpy of Fusion of Energetic Compounds, *Fluid Phase Equilib.*, **2012**, *36*, 1-14.
- [46] Keshavarz M.H., Pouretedal H.R., A New Simple Approach to Predict Entropy of Fusion of Nitroaromatic Compounds, *Fluid Phase Equilib.*, **2010**, *298*, 24-32.
- [47] Keshavarz M.H., Zakinejad S., Esmailpour K., An Improved Simple Method for Prediction of Entropy of Fusion of Energetic Compounds, *Fluid Phase Equilib.*, **2013**, *340*, 52-62.
- [48] Mader C.L., *Numerical Modeling of Explosives and Propellants*, 3rd ed., CRC Press, Boca Raton, **2008**.
- [49] Agrawal J.P., *High Energy Materials, Propellants, Explosives and Pyrotechnics*, Wiley-VCH, Weinheim, **2010**.
- [50] Keshavarz M.H., Motamedoshariati H., Moghayadnia R., Nazari H.R., Azarniamehraban J., A New Computer Code to Evaluate Detonation Performance of High Explosives and Their Thermochemical Properties, Part I, *J. Hazard. Mater.*, **2009**, *172*, 1218-1228.
- [51] Keshavarz M.H., Motamedoshariati H., Moghayadnia R., Ghanbarzadeh M.,

- Azarniamehraban J., A New Computer Code for Assessment of Energetic Materials with Crystal Density, Condensed Phase Enthalpy of Formation, and Activation Energy of Thermolysis, *Propellants Explos. Pyrotech.*, **2013**, *38*, 95-102.
- [52] Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Montgomery J.A. Jr., Vreven T., Kudin K.N., Burant J.C., Millam J.M., Iyengar S.S., Tomasi J., Barone V., Mennucci B., Cossi M., Scalmani G., Rega N., Petersson G.A., Nakatsuji H., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Klene M., Li X., Knox J.E., Hratchian H.P., Cross J.B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R.E., Yazyev O., Austin A.J., Cammi R., Pomelli C., Ochterski J.W., Ayala P.Y., Morokuma K., Voth G.A., Salvador P., Dannenberg J.J., Zakrzewski V.G., Dapprich S., Daniels A.D., Strain M.C., Farkas O., Malick D.K., Rabuck A.D., Raghavachari K., Foresman J.B., Ortiz J.V., Cui Q., Baboul A.G., Clifford S., Cioslowski J., Stefanov B.B., Liu G., Liashenko A., Piskorz P., Komaromi I., Martin R.L., Fox D.J., Keith T., Al-Laham M.A., Peng C.Y., Nanayakkara A., Challacombe M., Gill P.M.W., Johnson B., Chen W., Wong M.W., Gonzalez C., Pople J.A., *Gaussian 09, Revision A.02*, Gaussian, Inc., Wallingford CT, **2009**.
- [53] Politzer P., Martinez J., Murray J.S., Concha M.C., Toro-Labbe A., An Electrostatic Interaction Correction for Improved Crystal Density Prediction, *Mol. Phys.*, **2009**, *107*, 2095-2101.
- [54] NIST Standard Reference Data Base Number 69, which can be accessed electronically through the NIST Chemistry Web Book (<http://webbook.nist.gov/chemistry/>); references for individual molecules are given therein.
- [55] Fabian W.M.F., Quantum Chemical Calculation of Tautomeric Equilibria, in: *Tautomerism: Methods and Theories*, (Antonov L., Ed.), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, **2014**, pp. 337-368.
- [56] Wang G., Gong X., Liu Y., Du H., Xiao H., Prediction of Crystalline Densities of Polynitro Arenes for Estimation of Their Detonation Performance based on Quantum Chemistry, *J. Mol. Struct. Theochem*, **2010**, *953*, 163-169.

