Proceedings Paper

A Facile Method for Assessing the Change in Detonation Properties during Chemical Functionalization: The Case of NH₂→NHNO₂ and NH₂→=N⁺=N⁻ Conversions †

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Abstract: A simple and fast procedure for estimation of the effect of chemical functionalization on the change in detonation properties of energetic materials is reported. The procedure consists of two levels. Computations at Level 1 can be performed with a pocket calculator. At Level 2, quantum-chemical calculations are needed, but these include only three computational tasks: vacuum-isolated molecule relaxation (PBE/DND) → crystal structure prediction (COMPASSII) → crystal cell relaxation (PBE/DND). Thus, we have analyzed transformation of both aromatic and aliphatic amines into the corresponding nitramines and diazo compounds. The calculations at Level 1 indicated that both crystal density (d_c) and solid-state enthalpy of formation (ΔH_f) are always positive and increase detonation properties, while the calculations at Level 2 revealed those amines, which are the most sensitive to such chemical transformation.

Keywords: nitrogen-rich compound; energetic material; density functional theory; nitramine; diazo compound

1. Introduction

Recently, we have proposed a convenient method for estimation of crystalline density (d_c) and solid-state enthalpy of formation (ΔH_f) on the basis of empirical formulas of C–H–N–O energetic materials, which were then applied for prediction of their detonation properties [1]. Using this method, we compiled a list of the predicted values of d_c, ΔH_f, detonation energy (Q), velocity (D) and pressure (P) for all compositions up to $C_{30}H_{30}N_{30}O_{30}$ [1]. This method appeared to be very useful for prediction of the influence of chemical transformation on the changes in detonation properties, since one only needs find the interested compound in the table and crudely estimate its potential as an energetic material or compare it potential with other molecule in the table. Thus, we have recently shown how this method performs for chemical transformation of energetic amines in the corresponding triazenes [2] and pentazoles [3].

At the same time, due to a recent trend in the synthesis of nitrogen-rich heterocyclic energetic materials [4–7], the number of interesting and promising energetic amines demonstrates a sustainable growth. Consequently, the area of its possible functionalization plays an increasingly important role. Apart of triazenes and pentazoles, it is interesting to estimate how the detonation properties changes upon transformation into the corresponding nitramines and diazo compounds. Both these families of compounds are energetic and these are well known as conventional explosives [8–10]. The specific chemical route leading to these classes of compounds is also known and can be schematically illustrated as follows [11–15]:
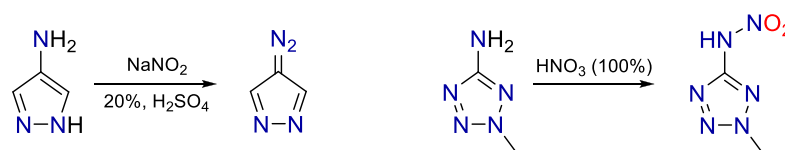
Scheme 1. Chemical routes from amines to diazo compounds (**left**) and nitramines (**right**).

Thus, in this work, we have applied the two-level scheme to estimate the potential of the afore-mentioned chemical reactions for enhancing detonation properties of a number of heterocyclic nitrogen-rich amines.

2. Computational Method

Quantum-chemical calculations in this work were performed using the Materials Studio 2017 suite of programs [16]. Crystal structure predictions were done using ab initio forcefield Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASSII) [17]. The predicted values were then corrected using the previously developed regression model [2,3]:

$$d_{theor} = 1.0144 \, d_{pred} - 0.0706, \tag{1}$$

where d_{pred} is the uncorrected value obtained using the COMPASSII calculations.

Geometry optimizations of vacuum-isolated molecules and crystals were carried out within all-electron approximation with pure GGA functional due to Perdew-Burke-Ernzerhof (PBE) [18] together with a double numerical basis set, DND, as implemented in the DMol³ code [19]. Enthalpies of formation were calculated using the following Equations (2) and (3):

$$\Delta H_{f,pred} = E_{C_iH_jN_kO_l} - (iE_C + jE_H + kE_N + lE_O), \tag{2}$$

where $E_{C_iH_jN_kO_l}$ is the total energy of the crystal geometry optimization and E_X are the corresponding atomic increments [2]. The $\Delta H_{f,pred}$ values were then corrected using the following regression model [2]:

$$\Delta H_{f,theor} = 1.1142 \, \Delta H_{f,pred} - 44.657, \tag{3}$$

Detonation properties were calculated using the Kamlet-Jacobs scheme [20].

3. Results and Discussion

3.1. Calculation at Level 1

The changes in empirical formulas for transformation into nitramines and diazo compounds are expressed in Equations (4) and (5). Taking into account the general method for estimation of ΔH_f [1], one can express the constant differences $\Delta\Delta H_f$, which are presented in Equations (6) and (7).

$$C_xH_yN_zO_w \rightarrow C_xH_{y-1}N_{z+1}O_{w+2} \tag{4}$$

$$C_xH_yN_zO_w \rightarrow C_xH_{y-3}N_{z+1}O_w \tag{5}$$
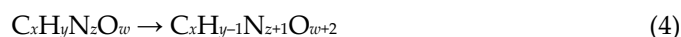
$$\Delta\Delta H_f = 1.2845(N + 2O - H) = 3.85 \text{ kJ/mol} \tag{6}$$

$$\Delta\Delta H_f = 1.2845(N - 3H) = 214.51 \text{ kJ/mol} \tag{7}$$

It is clear that the studied reactions always increase the heat of formation that lead to increase detonation properties. On the other hand, the more important property is crystal density. Taking into account the previously developed equation for d_c [1], the same difference Δd_c, can be expressed as in Equation (8) and Table 1:

$$\Delta d_c = -\frac{0.2965(a_1 x + a_2 y + a_3 z + a_4 w)}{\left(\sum V_M(\text{atoms})\right)\left(b + \sum V_M(\text{atoms})\right)} , \tag{8}$$

where V_M(atoms) are the previously estimated atomic volumes [1].

Table 1. Coefficients for nitramines and diazo compounds used in Equation (8).

Compounds	a_1	a_2	a_3	a_4	b
Nitramines	−3885	−1925	−2065	70	40
Diazo compounds	−1939	−553	−1659	1302	−2

As it follows from Equation (8) and Table 1, the expected Δd_c are about 0.2 g/cm³ for compositions of typical energetic materials and are always positive too. Thus, fast calculations at Level 1, which can be performed without involvement of quantum-chemical methods, endorse transformation of amines in nitramines and diazo compounds.

3.2. Calculations at Level 2

On the basis of calculations at Level 2, we have identified those chemical compositions, which are sensitive to the studied transformations and select the corresponding experimentally available energetic amines from the literature. Chemical structures of the potential products of the amine transformations into nitramines (**1–15**) and diazo compounds (**16–30**) are illustrated in Figure 1 and the calculated absolute values of detonation properties and their changes caused upon the transformation are listed in Table 2. As one can see in Table 2, the calculations at both levels demonstrate increase in detonation properties. At Level 1, the mean absolute and relative differences in *Q*, *D* and *P* values under the formation of nitramines are: 166 cal/g (13.8%), 680 m/s (8.7%) and 6.0 GPa (23.2%), respectively. For diazo compounds these differences for *Q*, *D* and *P* are the following: 266 cal/g (26.2%), 459 m/s (6.5%) and 3.9 GPa (18.7%), respectively. The differences obtained at Level 2 are generally comparable. For example, in the case of the nitramine formation, the *Q*, *D* and *P* values are the following: 323 cal/g (47.9%), 1191 m/s (15.5%) and 10.6 GPa (39.2%), respectively. Finally, for diazo compounds, these differences are the following: 597 cal/g (225.1%), 1041 m/s (20.1%) and 5.1 GPa (46.2%) for *Q*, *D* and *P*, respectively.
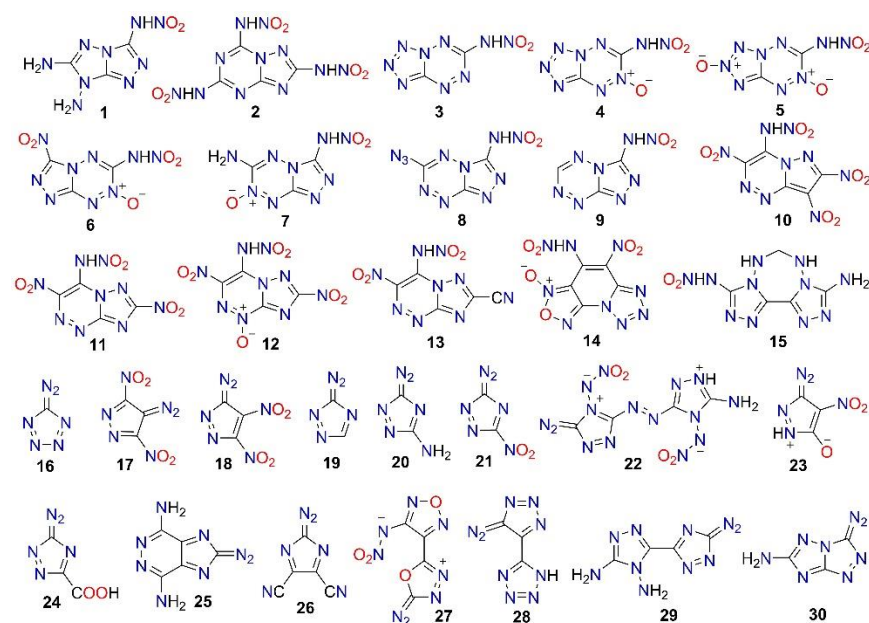
Figure 1. Chemical structures of the potential nitramines (**1–15**) and diazo compounds (**16–30**).

Table 2. The calculated detonation properties (*Q* in cal/g, *D* in m/s and *P* in GPa) obtained at Levels 1 and 2 and the corresponding absolute differences with ones calculated for the amine precursors.

Entry	Ref.	Level 1						Level 2					
		Q	*D*	*P*	Δ*Q*	Δ*D*	Δ*P*	*Q*	*D*	*P*	Δ*Q*	Δ*D*	Δ*P*
1	[21]	1345.4	7961	26.8	363.2	713	5.9	1115.5	8154	30.2	555.3	1164	8.8
2	[21]	1535.1	8806	34.8	80.0	537	5.0	1376.6	9371	42.3	341.4	1009	9.3
3	[21]	1495.7	8668	33.4	239.3	800	7.4	1534.7	9309	40.3	472.9	1096	9.7
4	[21]	1525.4	8949	36.1	136.0	851	7.9	1574.3	9900	47.5	364.0	1495	15.2
5	[21]	1550.6	9198	38.7	116.5	741	7.3	1769.0	10,208	50.2	414.5	1580	16.6
6	[21]	1535.1	8996	36.9	103.6	672	6.3	1580.5	9955	48.6	236.1	1371	14.8
7	[21]	1446.7	8344	30.4	209.7	716	6.2	1227.5	8779	36.3	341.8	1358	12.2
8	[21]	1516.4	8431	31.3	180.4	644	5.8	1419.5	8429	31.7	908.0	2028	13.8
9	[21]	1393.5	8008	27.8	313.9	864	7.0	1366.1	8754	36.0	505.3	1402	12.2
10	[21]	1530.6	8882	36.3	76.7	517	4.9	1597.5	9373	41.8	209.8	432	3.6
11	[21]	1522.7	8834	35.6	93.1	615	5.7	1476.9	9209	40.2	239.6	604	5.2
12	[21]	1541.8	9028	37.5	83.5	556	5.3	1545.5	9298	40.7	207.0	815	7.8
13	[21]	1445.5	8050	28.7	119.1	769	6.1	1404.4	8162	30.0	333.5	763	5.2
14	[21]	1492.8	8503	32.7	94.1	624	5.5	1638.3	9526	44.0	304.5	1252	12.4
15	[21]	1288.5	7589	23.8	281.1	575	4.4	995.1	8142	30.8	455.6	1489	11.5
16	[22]	1301.2	8096	28.6	434.6	633	5.9	1476.0	7948	26.4	1036.3	1520	9.3
17	[23]	1434.1	8600	33.8	111.9	422	4.3	1604.0	8524	32.2	411.9	133	−0.3
18	[23]	1434.1	8600	33.8	111.9	422	4.3	1670.1	8765	34.6	330.5	−16	−1.4
19	[23]	1046.7	7031	20.6	473.0	879	5.9	1192.8	6741	18.2	1016.0	2069	9.6
20	[23]	1079.7	7358	22.4	397.7	728	5.3	945.5	6561	16.4	870.0	2638	10.3
21	[24]	1388.5	8425	32.0	153.8	573	5.5	1460.0	8085	28.1	522.3	506	2.7
22	[25]	1574.3	8666	33.1	56.7	227	2.3	1628.7	8818	34.6	251.6	270	2.0
23	[26]	1316.9	8002	28.5	143.2	517	4.6	1276.1	7672	25.4	479.9	620	3.5
24	[27]	1253.9	7555	24.9	166.6	585	4.7	916.2	6814	19.8	688.8	1873	9.2
25	[28]	1061.7	6695	18.0	239.9	366	2.5	693.0	6023	14.6	540.8	1674	6.9
26	[28]	1140.1	6019	15.0	291.1	267	2.0	1156.4	5523	11.5	646.7	522	1.8
27	[29]	1465.6	8366	31.6	89.2	334	3.3	1613.4	8370	31.0	406.2	607	4.6
28	[29]	1340.4	7621	24.6	240.3	264	2.6	1228.6	7548	24.8	608.9	891	6.0
29	[30]	1206.5	7408	22.5	209.9	294	2.5	849.1	7102	21.6	480.0	1199	7.0
30	[31]	1221.3	7414	22.9	272.1	372	3.2	1042.3	7127	21.2	660.2	1107	5.8

The absolute predicted values of *D* and *P*, indicate that transformation into the nitramines is the most effective for precursor of compound **8** (Figure 1). In this case, one can expect an increase in detonation properties up to 2028 m/s and 13.8 GPa (Table 2). At the same time, for the diazo compounds, significant gain in detonation properties observed only for precursors with very low detonation profile, namely, compounds **19**, **20**, **24** and **25** (Table 2). The transformation of amines into diazo compounds can even slightly reduce detonation properties, like in the case of compounds **17** and **18** (Table 2). This is mainly caused be the lower crystal density of the resulting diazo compounds, due to the vanishing of intermolecular hydrogen bonds (Figure 1). The only compound, which demonstrates a significant rise in detonation properties and has high absolute values is compound **16** (Table 2).

4. Conclusions

Thus, in this article, we presented an example of using our two-level scheme to evaluate the effectiveness of changes in the detonation properties of energetic amines undergone two types of chemical functionalization. Since, this family of nitrogen-rich energetic compounds demonstrate intensive growth, it is of current interest to study possible routs for enhancement of their detonation profiles by means of a simple

functionalization. Thus, in this work, we have found that transformation of amines into the corresponding nitramines increases their detonation properties up to 15 and 40% for *D* and *P*, as an average. At the same time, transformation into diazo compounds, generally has a little effect on highly energetic amines. A significant enhancement is observed only for low-energy density precursors. Nevertheless, in this work we have revealed those energetic amines, whose detonation properties can be easily enhanced via a simple one-pot functionalization. These are the amine precursors of the compounds **8** and **16**.

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