Structure enhancement of energetic materials: A theoretical study of the arylamines to arylpentazoles transformation

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ABSTRACT

A theoretical study of the effect of amines-to-pentazoles transformation on the detonation performance is reported in this paper. A quantitative description of the latter is performed for the general case according to our recently developed compositional criterion evaluation algorithm. It is shown that increments of crystal density and enthalpy of formation are both positive meaning a higher detonation performance of the resulting pentazoles. Since the known arylpentazoles are thermally unstable compounds, a simple descriptor of the thermal stability was revealed ($R^2 = 0.98$), which allowed modeling of new pentazoles with expected thermal stability up to 77 °C. Five the most thermally stable structures were then analyzed using high-level first-principles calculations, which provided negative values of the detonation energy for all ionic compounds; this may allow proposing them as safe gas-forming agents. Meanwhile, the relative gain in detonation energy caused by the studied reaction is always positive and can reach 600%. Thus, we have shown that amines-to-pentazoles transformation is an effective tool for enhancing detonation properties when the resulting compound satisfies the thermal stability criterion. Also, we have demonstrated that aromatic/heterocyclic pentazoles may be considered as self-sufficient materials without further modifications by detachment of the aromatic ring.

1. Introduction

Recent trends in computational design of energetic materials are based on various strategies to improve detonation performance due to high-throughput quantitative structure-property relationship screening [1,2], regulating of molecular configuration [3], introducing of atoms [4] or modeling of chemical transformations [5]. The latter method assumes an existing chemical route from starting precursor to a desired product, which allows estimation of the effectiveness/cost compromise. Increase in the nitrogen content is one of the most promising methods for improvement of the detonation properties of high-energy density materials (HEDM), which provides the latter with outstanding performance [6–9]. On the other hand, there is a known problem of a delicate balance between high performance and sensitivity of HEDM [10–12]. Therefore, the use of reference compounds with known stability is important for estimation of the stability domain of the modeled materials.

In our recent work, we have shown the effectiveness of transformation of aminoaromatic and aminoheterocyclic compounds to the corresponding triazenes due to a diazoamination reaction [13]. Similarly, it is interesting to study such transformation towards the corresponding pentazoles. These compounds are known long ago as derivatives of arylamines (Scheme 1) [14,15]. It is known, however, that heterocyclic

amines can also form diazonium salts, which appear as intermediates in synthesis of pentazoles; this significantly expands possible domain of synthetically available pentazoles (Scheme 1) [16].

Usually, arylpentazoles further transform into *cyclo*-pentazolate salts by the cleavage of the C–N bond [17,18]. This is done mainly due to a low thermal stability of the corresponding pentazoles [14,15,19–22]. High-level density functional theory calculations showed that the decomposition of arylpentazoles to N_2 and azide is a first-order reaction, where the breaking of the N1–N2 bond is accompanied with cleavage of the N3–N4 bond [19,20]. A relationship between the arylpentazole stability and the relative intensity of the generated pentazolate anion in mass spectra was also established [21]. An unexpected increase in stability of phenylpentazole upon noncovalent binding to β-cyclodextrin was recently reported [22].

Arylpentazoles also decomposes by the UV light. Thus, the photolysis of *para*-methoxyphenyl pentazole in MeCN yields *para*-methoxyphenyl azide with subsequent formation of 4,4′-dimethoxyazobenzene [23]. A similar photolysis pattern was reported for 4-oxidophenylpentazole in MeCN, where the corresponding azobenzene was obtained along with arylamine. Meanwhile, in water, the final products are 4-oxidophenylazide and indophenol [24]. Geometry optimization of the first excited singlet state of 4-N(Me)$_2$ substituted phenylpentazole
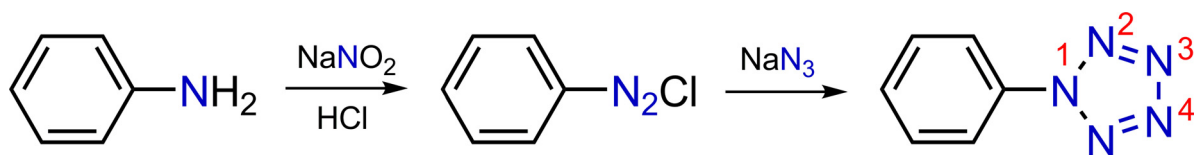
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Scheme 1. Sequence of chemical reactions leading from an amine to a pentazole (some atoms are numbered).

revealed a twisted structure of the latter with a pyramidalized Nα atom and lengthened Nα–Nβ bonds, while both Nβ–Nγ and Nγ–Nγ bonds are mainly remain unchanged [25].

These results of the photochemical degradation are in the complete agreement with the kinetic study of the thermal decomposition of a series of *p*-substituted phenylpentazoles in polar media, where a rate-determining cleavage of the Nα–Nβ bond giving an unstable azido-azo (pentazene) intermediate was found [26]. It was also shown earlier, that electron releasing groups (ERG) increase stability of arylpentazoles [15]. We should stress that the *cyclo*-N_5 group itself is a strong electron-withdrawing substituent with a Hammett ρ value equal +1.25 [26]. Recent quantum-chemical calculations revealed that formation of the N_5 ring also proceeds *via* cyclization at the Nα–Nβ bond and a substitution mode with the presence of a 4-O⁻ and a 3-ERG substituent (especially the –$C(CH_3)_3$ group) considerably facilitates the cyclization process enhancing the production of arylpentazoles [27].

Thus, in this work, we have tried to find a simple and reproducible descriptor of thermal stability as well as to estimate how the formation of pentazoles will change detonation properties of their amine precursors.

2. Computational details

The calculations presented herein were performed in terms of density functional theory (DFT) within the generalized gradient approximation (GGA) [28]. Prediction of chemical hardness (η) values was performed using calculations with the Gaussian09 package [29]. For this purpose, vacuum isolated molecules were first optimized using the long-range corrected hybrid functional with damped atom-atom dispersion corrections, namely, ωB97XD [30] along with the Pople's split-valence quasi-double-ζ in the valence shell basis set (6-31G) supplemented with polarization functions (d,p) [31]. The chemical hardness η values were calculated according to Eq. (1) [32].

$$\eta = I - A = -E_{HOMO} + E_{LUMO} \qquad (1)$$

where I, A, E_{HOMO} and E_{LUMO} are the ionization energy, electron affinity, energy of the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals, respectively.

Prediction of crystal densities and enthalpies of formation was performed with the Materials Studio 2017 program suite [33]. For this purpose, we have applied the Polymorph [34] and DMol³ [35] modules, respectively. In the Polymorph calculations we have applied *ab initio* force-field COMPASSII (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) [36], while in the DMol³ calculations, the total energies were calculated in terms of all-electron approximation using pure GGA functional due to Perdew-Burke-Ernzerhof (PBE) [37] along with a double numerical basis set, DNP [35]. Dispersion effects were taken into account using the Grimme form of the damped C_6 term [38]. A more detailed description of these procedures can be found in our recent papers [13,39].

Sampling of the Brillouin zones were performed using k-point grid generated by the Monkhorst-Pack method. Direct spacing between the k-points was specified to be 0.08 2πÅ⁻¹. Convergence quality parameters were as follows: total energy (5×10^{-6} eV atom⁻¹), force (0.01 eV Å⁻¹), stress (0.02 GPa) and displacement (5×10^{-4} Å).

3. Results and discussion

3.1. Theoretical analysis of the reaction efficiency with neglect of chemical structure

In a general case, the transformation of an amine to a pentazole of an arbitrary C–H–N–O composition can be expressed as:

$$C_xH_yN_zO_w \rightarrow C_xH_{y-2}N_{z+4}O_w \qquad (2)$$

Subsequently, taking into account the known empirical expressions for enthalpy of formation (ΔH_f) and crystal density (d_c) [40], one can write the following change in these two parameters as a result of transformation in Eq. (2):

$$\Delta\Delta H_f = 1.2845(4N - 2H) = 524.1 \text{ kJ mol}^{-1} \qquad (3)$$

$$\Delta d_c = \frac{2.398(a_1x + b_1y + c_1z - w)}{(a_2x + b_2y + c_2z + w)(a_2x + b_2y + c_2z + w + 4.386)}, \qquad (4)$$
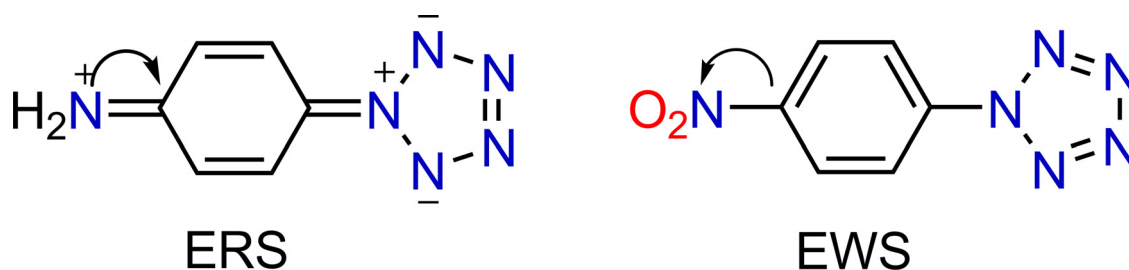
where $a_1 = 2.201$, $b_1 = 1.423$, $c_1 = 0.712$, $a_2 = 1.643$, $b_2 = 0.512$ and $c_2 = 1.355$.

It is easily seen that, with neglect of exact chemical structure, ΔH_f has a constant gain equal 524.1 kJ mol⁻¹ Eq. (3). Similarly, it can be found from Eq. (4) that the values of Δd_c must also always be positive. To confirm this, we have built an arbitrary set of 22 pentazoles obtained from the experimentally available aromatic and heterocyclic amines, both widely known and newly synthesized [41,42]. Chemical structures of the corresponding pentazoles are presented in Fig. S1 in the Supporting Information. Then, we have analyzed the ΔH_f, d_c values and the derivative properties, namely, detonation velocity (D, m s⁻¹) and pressure (P, GPa) calculated by means of the Kamlet-Jacobs method [43] for both pentazoles **1–22** and their amine precursors (Tables S1 and S2 in the Supporting Information). The numerical data on changes in these parameters obtained upon transformation of the amines into pentazoles are listed in Table 1. As one can see, the positive changes are observed in all the cases and vary in the range of 256–2447 m s⁻¹ for D and 2.2–9.6 GPa for P.

Of course, such a crude estimation is not enough to draw a conclusion about the efficiency of the chemical transformation and a more accurate analysis is required. On the other hand, this provides a guide indicating the most promising directions to be checked. Since the thermal stability problem for pentalozes is acute, this will be analyzed separately in this paper. However, in the case of any other family of compounds, which do not suffer from the lack of stability, one can be guided by the above-discussed compositional criterion analysis.

3.2. Quantification of the thermal stability of pentazoles

The low thermal stability of known arylpentazoles was the main reason for avoidance them as HEDM. Recently, interest in arylpentazoles has returned as high-level quantum chemical calculations (CBS-QB3) suggest that the barrier of N_2 loss for some compounds may be about 170.8 kJ mol⁻¹ [44]. The calculation of the decomposition reaction, however, is a complex task, which deserves a separate study. Therefore, in terms of the present work, we have tried to obtain simple DFT descriptors of the thermal stability on the basis of the known values of decomposition temperatures for six 4-X substituted phenylpentazoles

Scheme 2. The influence of ERS and EWS on resonance structure of arylpentazoles.

Table 1

Absolute changes in crystal density (Δd_c, g cm^{-3}), detonation velocity (ΔD, m s^{-1}) and pressure (ΔP, GPa) according to the compositional criterion analysis.

Molecule	Formula	Δd_c	ΔD	ΔP
1	$C_6H_4N_{10}O_6$	0.056	496	3.9
2	$C_4H_2N_{10}O_5$	0.058	497	4.3
3	$C_3H_4N_{12}$	0.114	776	5.9
4	$C_4H_2N_{12}O_2$	0.079	639	5.0
5	$C_4H_2N_{14}O_4$	0.053	402	3.6
6	$C_5H_6N_{14}$	0.091	639	4.6
7	$C_6H_9N_9$	0.130	1577	7.6
8	$C_6H_9N_9$	0.130	1577	7.6
9	$C_6H_9N_9$	0.130	1577	7.6
10	$C_6H_8N_8$	0.143	1909	8.5
11	$C_6H_7N_7$	0.159	2447	9.6
12	$C_6H_6N_8O_2$	0.110	973	5.8
13	$C_6H_5N_9O_4$	0.078	710	4.9
14	$C_6H_6N_8O_3$	0.098	797	5.1
15	$C_6H_2N_{10}O_6$	0.052	486	3.9
16	$C_4H_2N_{10}O_5$	0.058	497	4.3
17	$C_4H_2N_{12}O_3$	0.068	550	4.5
18	$C_4H_2N_{10}O_6$	0.048	265	2.6
19	$C_5H_3N_9O_5$	0.066	590	4.7
20	$C_8H_4N_{12}O_7$	0.045	408	3.2
21	$C_8H_4N_{12}O_7$	0.045	408	3.2
22	$C_8H_4N_{10}O_6$	0.043	282	2.2

Table 2

Thermal decomposition temperatures of some arylpentazoles and *cyclo*-pentazolate salts along with the corresponding numerical values of the possible descriptors.

X	T_{dec} (°C)	σ_p [46]	l_{N-N} (Å)	E_{HOMO} (eV)	E_{LUMO} (eV)	η (eV)
4-H	−4 [15]	0.00	1.37394	−6.860	−3.593	3.267
4-Cl	9 [15]	0.28	1.37115	−6.642	−3.225	3.417
4-Me	4 [15]	−0.17	1.37195	−6.600	−3.145	3.455
4-OMe	14 [15]	−0.27	1.36857	−6.414	−3.346	3.068
4-OEt	28 [15]	−0.24	1.36848	−6.175	−3.156	3.019
4-NMe$_2$	52 [15]	−0.83	1.36283	−5.236	−3.092	2.144
NH$_2$NH$_3^+$	100 [45]	–	1.35008	−7.216	−1.948	5.268
NH$_4^+$	106 [45]	–	1.34543	−6.915	−1.395	5.52
K$^+$	110 [45]	–	1.34722	−7.649	−2.007	5.642
R^2	–	0.69	0.98	0.18	0.89	0.64

[15] as well as some $X^+N_5^-$ *cyclo*-pentazolate salts (Table 2) [45]. First of all, we have checked the correlation of T_{dec} with the Hammett σ_p constants [46] as suggested by Zollinger [16]. As one can see in Table 2, a modest correlation ($R^2 = 0.69$) is observed, which is definitely not enough for prediction purposes.

Therefore, we have analyzed the changes in structural parameters (bond lengths), which can take place similarly to aryl diazonium salts [47,48], when the electron-releasing and withdrawing substituents favor different resonance structures (Scheme 2). Thus, the C–N bond lengths and valence vibrational frequencies do correlate with T_{dec}, which is following from the values in Table S3 in the Supporting Infor-

mation, but the R^2 values are still not applicable (0.62 and 0.88 for l_{C-N} and ν_{C-N}, respectively). Similarly, the energies of the highest occupied (E_{HOMO}) and the lowest unoccupied (E_{LUMO}) molecular orbitals, which determine ionization energy and electron affinity (the Koopmans' theorem), may demonstrate some correlation with T_{dec}. Indeed, electron-releasing (ERS) and withdrawing (EWS) substituents can narrow and expand the HOMO-LUMO gap (η), which reflects in rather good correlations of E_{HOMO} and η values with R^2 equal 0.91 and 0.95, respectively (Table S3 in the Supporting Information). But we should stress that values in Table S3 are calculated for 4-X substituted phenylpentazoles in vacuum [15]. When we have applied the calculations of E_{HOMO}, E_{LUMO} and η for the afore-mentioned compounds in the crystalline state (method PBE/DND) and included *cyclo*-pentazolate salts in the general correlation, the obtained R^2 values appear to be poor (Table 2). However, if one considers only 4-X substituted phenylpentazoles, the R^2 for E_{HOMO} will be 0.97.

This indicates that none of the above DFT parameters can be used as a universal descriptor of the thermal stability. On the other hand, *cyclo*-pentazolate salts demonstrate an increased thermal stability compared to the molecular forms, which is obviously caused by the formation of a quite robust aromatic *cyclo*-pentazolate anion. Since decomposition of both molecular and ionic pentazole compounds proceeds *via* breaking of the N–N bond, we have tried to examine the longest (trigger) N–N bond length as a possible descriptor. For this purpose, we have predicted crystal structures (space group *P*1) for all the compounds in Table 2 as it is described in Ref. [13] and completely relaxed the obtained asymmetric cells with the CASTEP code [49]. For more details of the calculation method applied, refer to our recent papers [6–9]. The pseudopotential method realized in CASTEP is superior to the all-electron method of DMol^3 in terms of the machine time. Therefore, the calculated trigger N–N bond lengths (l_{N-N}), which are listed in Table 2, are obtained with CASTEP code. As one can see, there is a clear and rigorous correlation ($R^2 = 0.98$) for the entire set of compounds as well as for molecular compounds only. Graphically, the correlation is presented in Fig. 1.

On the basis of the afore-mentioned correlation, we have obtained the following empirical regression (Eq. (5)), which was applied further to predict thermal stability.

$$T_{dec} = -4073.0 l_{N-N} + 5594.7 \tag{5}$$

To model possible thermally stable pentazoles, we have taken into account that pentazole is the most stable in the form of an anion. Therefore, we have examined a set of electron-rich *ortho*-, *meta*- and *para*-mono- as well as multi-substituted phenyl- and pyrrylpentazoles, all in the crystalline state (Fig. S2 in the Supporting Information). Empirically, we have found that substitution of the *ortho*-positions is unfavorable sterically since it leads to an out-of-plane position of the pentazole ring decreasing stabilization *via* the mesomeric effect. Moreover, introduction of too many amino groups also decreases stability due to their pronounced negative inductive effect. Thus, we have found that the most favorable substitution pattern is the presence of a carboxylate group in the *meta*-position and two amino groups in the *meta*- and *para*-positions of the benzene ring.
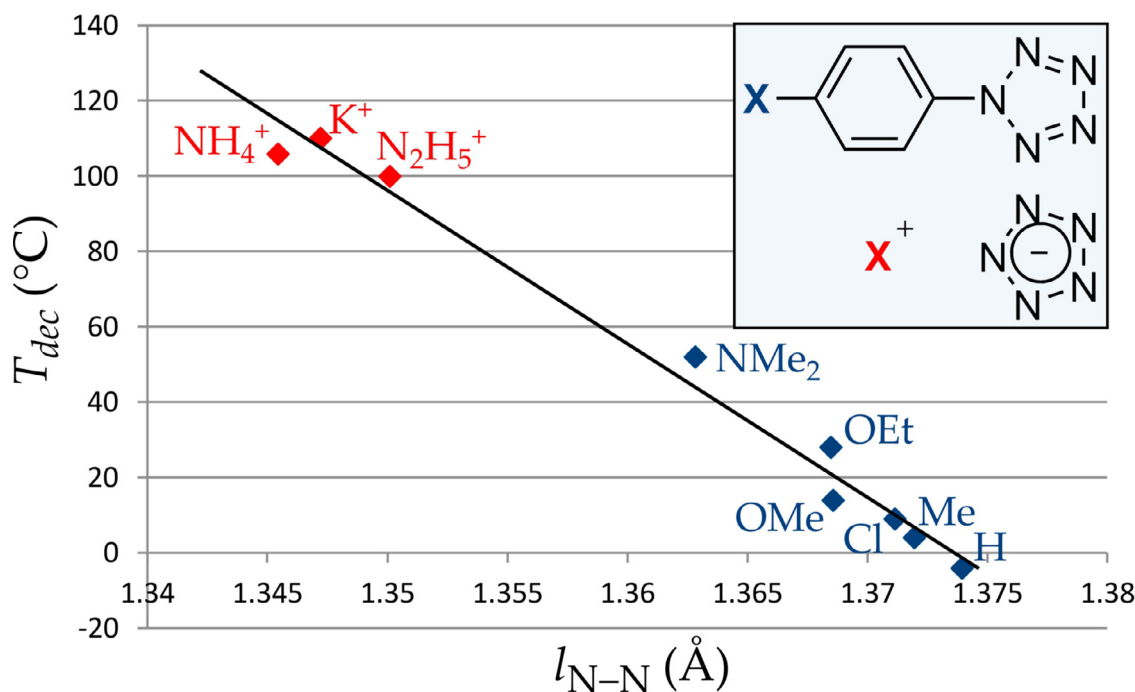
Fig. 1. Decomposition temperature of some pentazoles and pentazolate salts as a function of the longest N–N bond length.

Table 3

Lengths of the longest N–N bonds (Å) and the corresponding predicted decomposition temperatures (T_{dec}, °C) of the modeled compounds.

Molecule	l_{N-N} (Å)	T_{dec} (°C)	Molecule	l_{N-N} (Å)	T_{dec} (°C)
23	1.35562	73	**29**	1.36245	45
24	1.36075	52	**30**	1.35853	61
25	1.35792	64	**31**	1.36045	54
26	1.36201	47	**32**	1.35980	56
27	1.36313	43	**33**	1.35467	77
28	1.36109	51	**34**	1.36144	50

The calculated trigger N–N bond lengths and the predicted decomposition temperatures are listed in Table 3. As one can see, the predicted T_{dec} vary from 43 °C (compound **27**) to 77 °C (compound **33**). Actually, we have five compounds with T_{dec} within the range of 55–77 °C (compounds **23, 25, 30, 32** and **33**). Their T_{dec} are satisfactory for HEDM, which can be approved by a number of publication of new energetic materials with T_{dec} 80–140 °C [50–55] or even 58–65 °C [56,57]. Of course, for a more correct and precise estimation of the thermal stability, one need to perform molecular dynamics simulations at a set of temperatures, but this is not the primary goal of this work and we restrict ourselves with such an empirical description.

3.3. Quantum-chemical analysis of the most thermally stable structures

Thus, we have selected compounds **23, 25, 30, 32** and **33** for the higher level analysis using first-principles quantum-chemical calculations. The purpose of this analysis is to calculate more accurate ΔH_f and d_c values. We have applied procedure, which was adopted for the transformation of amines into triazenes and described in our recent paper [13]. This assumes estimation of these two parameters on the basis of empirical regression equations obtained by means of benchmarking a set of structurally similar compounds. These equations are the following [13]:

$$d_{theor} = 1.0144 d_{pred} - 0.0706 \qquad (6)$$

$$\Delta H_{f,theor} = 1.1142 \Delta H_{f,pred} - 44.657, \qquad (7)$$

where d_{pred} is the crystal density obtained after a crystal structure prediction (space group $P1$) with the COMPASSII forcefield; $\Delta H_{f,pred}$ is the solid-state enthalpy of formation obtained according to Eq. (8):

$$\Delta H_{f,pred} = E_{C_i H_j N_k O_l K_m Rb_n} - \left(i E_C + j E_H + k E_N + l E_O + m E_K + n E_{Rb} \right) \qquad (8)$$

Herein, $E_{CiHjNkOlKmRbn}$ is the total energy obtained by means of a fixed cell geometry optimization with the PBE/DND approach and E_X are the corresponding atomic increments. The values for C, H, N and O atoms are taken from our recent paper [13], whereas the values for E_K and E_{Rb} are estimated in this work benchmarking enthalpies of formations of the corresponding crystalline nitrates, carbonates and azides. Thus, the values of E_K and E_{Rb} are −599.73109 and −2939.747529 Ha, respectively.

Such approach for estimation of the ΔH_f and d_c values is very convenient and relatively fast since is assumes performing a single calculation for each single property. Unfortunately, due to a lack of experimental data on arylpentazoles, which is available only for the bare phenylpentazole (4-H) and 4-dimethylaminophenylpentazole (4-NMe$_2$) [58,59] we could not calibrate the method for this particular family of compounds. However, empirical equation obtained for triazenes (Eq. (6)) is applicable for pentazoles as it follows from the calculated values for 4-H and 4-NMe$_2$ (Fig. 2). As one can see, the absolute errors for the crystal density prediction are 0.059 and −0.027 g cm^{-3} for 4-H and 4-NMe$_2$, respectively. Thus, we speculate, such small errors cannot significantly distort results of the detonation properties calculation.

The optimized geometries of compounds **23, 25, 30, 32** and **33** in the crystalline phase are illustrated in Fig. 3. All the structures are characterized by the absence of imaginary frequencies in the vibrational spectra (Fig. S3 in the Supporting Information). As it follows from Fig. 3, the pentazole rings have almost planar alignments to the other molecule backbone. Otherwise, as we have mentioned above, the presence of the *ortho*-substituents cause steric hindrance and out-of-plane position of the pentazole ring. We should stress that this is a quite unfavorable molecular orientation which nullifies all mesomeric effects of the residues leading to a decrease in thermal stability.
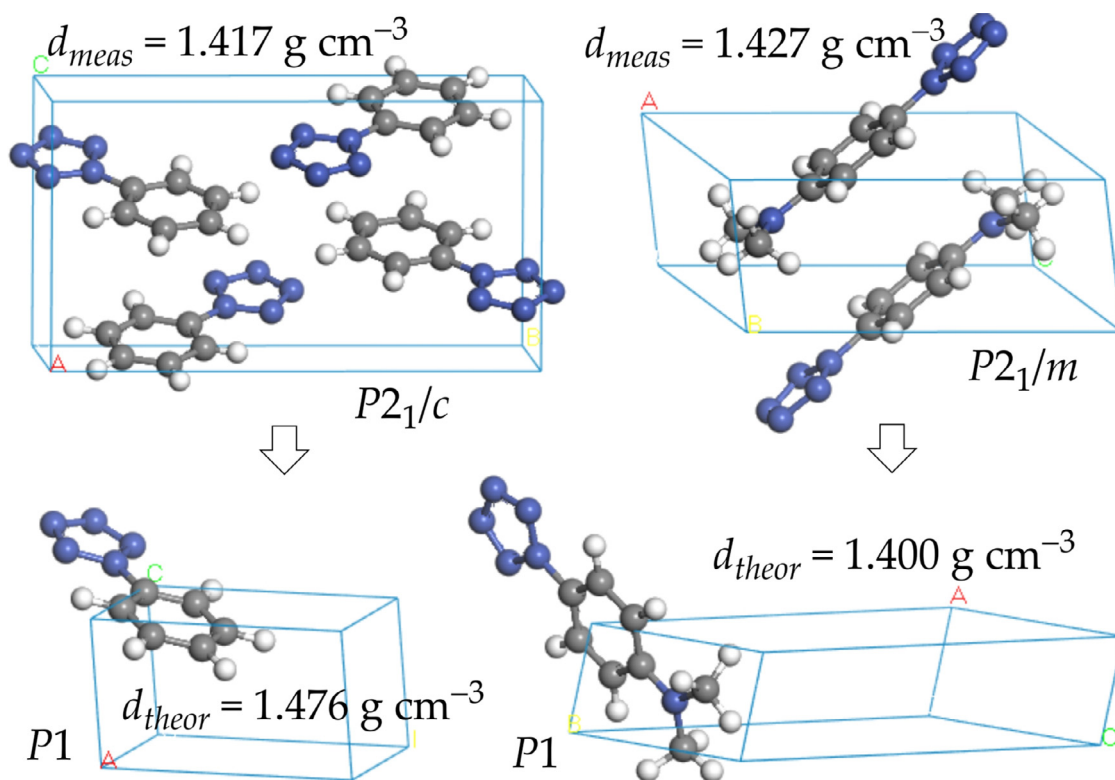
Fig. 2. Crystal structures and densities of the experimentally obtained (top) and modeled (bottom) arylpentazoles.

On the other hand, despite a good correlation of the C–N bond lengths for crystalline 4-X substituted phenylpentazoles with $R^2 = 0.93$ (Table S4 in the Supporting Information), an inclusion such the values for pentazoles **23, 25, 30, 32** and **33** decreases the correlation sharply ($R^2 = 0.36$), which is probably due to an ionic character of the latter compounds. A similar situation is for the E_{HOMO}, E_{LUMO} and η (Table S4 in the Supporting Information). Without three pentazolate salts, the correlation of η provides a noticeable correlation ($R^2 = 0.71$), but with the three above-mentioned values the correlation completely breaks. All of this suggests that one can easily obtain a false positive correlation; therefore, a careful analysis of all available experimental data is essential.

To estimate detonation properties of the modeled pentazoles **23, 25, 30, 32** and **33**, namely, detonation energy (Q, cal g^{-1}), D and P, we have used an extension of the Kamlet-Jacobs method for metal-containing compounds [60]. Within this scheme, Q can be expressed as the following

$$Q = -\frac{\left(\sum n\Delta H_f^P\right) - \Delta H_f^X}{MW},$$ (9)

where ΔH_f^X and ΔH_f^P are enthalpies of formation of the given explosive X and its detonation products P, scaled by their mole fractions n; MW is the molecular weight of X.

Along with the detonation properties, we have calculated propulsive characteristics, namely, combustion chamber temperature (CCT, K), specific impulse (I_{sp}), vacuum specific impulse (I_{vac}) and characteristic velocity (c^*) as described in our recent paper [61]. The results are listed in Tables 4 and 5, whereas some supplementary data for these calculations are presented in Fig. S4 and Tables S5 and S6 in the Supporting Information. To find out nature of the decomposition products, we have applied iterative procedure within the NASA CEA code [62] to obtain equilibrium distribution (Table 4), rather than extension of the arbitrary theory of the Kamlet-Jacobs method assuming a simple formation of the

metal oxides [60]. As one can see in Table 4, all the metal ions transform into the corresponding carbonates, rather than metal oxides. Only pentazole **30** demonstrates a positive value of the detonation energy, while the other compounds are expected to be not explosive. This conclusion is also supported by the values of Hirshfeld charges on cations at 100 GPa of hydrostatic compression (Fig. 3). All these values are higher than +0.1 e^-, indicating these salts as non-explosive [63].

At the same time, the latter pentazoles may be applied as mild gas-forming agents. In contrast to sodium azide (NaN$_3$), which has a high decomposition temperature (275 °C) and high volume of gaseous products (206.74 mL g^{-1}), compounds **23, 25, 32** and **33** may be useful for those applications where intensive gas formation is undesirable; for example, various solid foams, like aerated concrete, foamed plastics, etc. Meanwhile, all the studied pentazoles do not yield any dangerous and chemically aggressive products, like in the case of NaN$_3$.

Apart of the absolute values of the detonation and propulsive properties of compounds **23, 25, 30, 32** and **33**, it is interesting to track their changes when transforming from starting amines. For this purpose, we have applied the same procedure for the amine precursors to obtain the detonation and propulsive characteristics. The results are listed in Tables S7 and S8 in the Supporting Information. Since in the case of the studied chemical transformation, a single molecule yields another single molecule (not adduct), the efficiency can be easily estimated as absolute differences in the studied properties.

Thus the efficiency values expressed in per cents are listed in Tables 6 and 7. Since both the modeled compounds and precursors are non-explosives (except of pentazole **32**), we have estimated only the changes in detonation energy ΔQ, which can reach 600% (Table 6). For explosive pentazole **32**, ΔD and ΔP also equal 205.7 and 60.3%, respectively. Additionally, since three precursors do not demonstrate propulsive characteristics, we have estimated the relative enhancement only for compounds **30** and **32** (Table 7). As one can see, a positive change is tracked for all the estimated parameters.
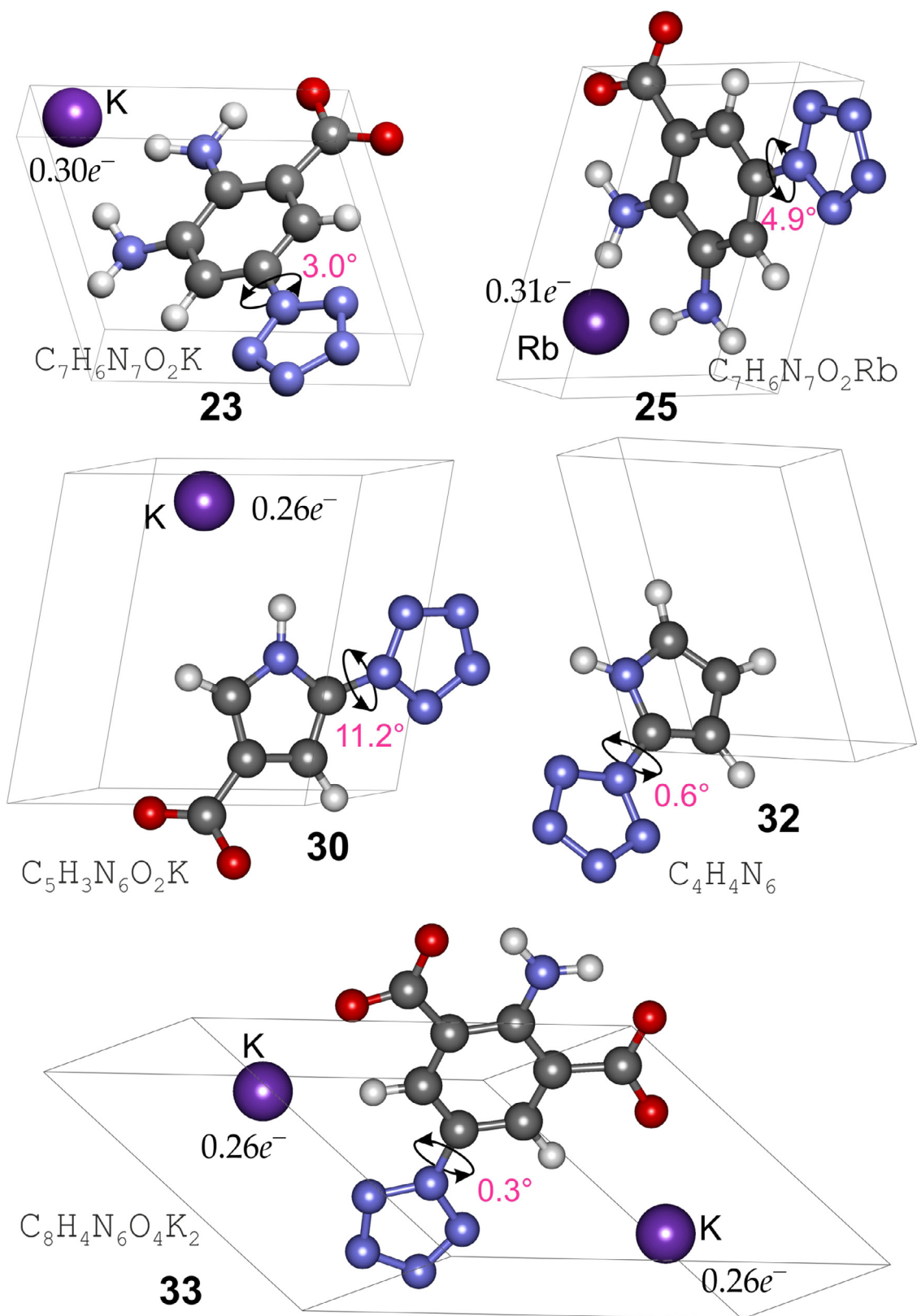
Fig. 3. Optimized asymmetric cells of the most promising structures in the crystalline state (space group *P*1).

Table 4

The calculated density (d_c, g cm^{-3}), enthalpy of formation (ΔH_f, kJ mol^{-1}), detonation energy (Q, cal g^{-1}) and volume of gaseous products (V_{gas}, mL g^{-1}) of the modeled pentazoles predicted using quantum-chemical calculations.

Molecule	Equilibrium distribution of the decomposition products	d_c	ΔH_f	Q	V_{gas}
23	$0.25960N_{2(g)} + 0.03152CO_{(g)} + 0.22135H_{2(g)} + 0.44836C_{(cr)} + 0.03917K_2CO_{3(cr)}$	1.893	−93.7	−41.6	44.36
25	$0.25973N_{2(g)} + 0.03164CO_{(g)} + 0.22135H_{2(g)} + 0.44823C_{(cr)} + 0.03905Rb_2CO_{3(cr)}$	2.184	−134.9	−68.2	37.63
30	$0.31307N_{2(g)} + 0.07357CO_{(g)} + 0.15523H_{2(g)} + 0.40417C_{(cr)} + 0.05101K_2CO_{3(cr)}$	1.777	−82.6	−17.2	55.45
32	$0.33337N_{2(g)} + 0.22219H_{2(g)} + 0.44444C_{(cr)}$	1.549	553.9	972.6	91.10
33	$0.23585N_{2(g)} + 0.06739CO_{(g)} + 0.15253H_{2(g)} + 0.46724C_{(cr)} + 0.07699K_2CO_{3(cr)}$	1.814	−753.8	−481.7	31.25

Table 5

The calculated propulsive properties of the modeled pentazoles.

Molecule	CCT	I_{sp}	I_{vac}	c^*
23	1152	145	160	855
25	1148	141	156	849
30	1180	141	157	833
32	2377	223	242	1344
33	1164	119	132	702

Table 6

The calculated enhancement of the detonation energy ΔQ (in %) of the modeled pentazoles.

23	25	30	32	33
519.9	301.3	605.2	41.8	12.6

Table 7

The calculated enhancement of the propulsive properties (in %) of the modeled pentazoles.

Molecule	ΔQ	ΔCCT	ΔI_{sp}	ΔI_{vac}	Δc^*
30	18.6	21.6	22.7	20.5	18.6
32	140.3	39.4	39.1	39.9	140.3

4. Conclusions and outlook

In summary, we have demonstrated in this paper how a simple and cheap two-step one-pot process can significantly increase detonation and propulsive properties of aromatic and heterocyclic amines. In all cases of the pentazoles formation, the changes in the above-mentioned properties are positive. But the problem of the low thermal stability of pentazoles is acute. Nevertheless, we have modeled five compounds with better stability, which is predominantly achieved due to the formation of alkaline metal salts. Synthetically, this is a convenient way since inclusion of the carboxylic groups facilitates diazoniation. Moreover, at the final stage, a neutralization of the formed pentazoles with alkalis readily yields the corresponding salts, which can be isolated as solid crystalline substances.

Using a powerful neural network, which can accurately predict the ΔH_f and d_c values from structural increments, the process described in this paper may be performed automatically. At the first level, the most promising compositions can be determined. At the second level, all possible chemical structures can be constructed and analyzed from these compositions. Thus, this algorithm can be applied for searching structure with the highest theoretical detonation performance and it will mean that detonation properties of any possible compound are predefined and known. Therefore, the development of such algorithm should be the issue of further studies in the field. Finally, another problem of any powerful explosive is its sensitivity, which is proportional to enclosed energy content. Fortunately, some efforts are already made in this direction, which aimed to search a balance between detonation proper-

ties and sensitivity. Thus, the account of sensitivity may also be included in the further algorithm.

Appendix A. Supplementary data

Crystal densities, optimized chemical structures, detonation properties, IR spectra, pressure dependence of thermodynamic functions, NASA coefficients

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.fpc.2021.09.002.

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