



Diazoamination: A simple way to enhance detonation performance of aminoaromatic and aminoheterocyclic energetic materials

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ABSTRACT

In this paper, we report a theoretical study of the change in detonation efficiency of energetic amines undergone diazoamination reaction. For this purpose, we selected 17 aminoaromatic and aminoheterocyclic energetic materials, both widely known and newly synthesized, and ranked all possible triazenes derived from them according to our recently developed compositional criterion evaluation algorithm. Then, top ten structures were calculated using quantum-chemical methods to obtain more accurate estimates of their detonation properties, which were calculated using the Kamlet-Jacobs equations. To ensure that input parameters, namely, crystal density (d_c) and enthalpy of formation (ΔH_f) are correct, we have benchmarked a number of experimentally known triazenes as well as other structurally similar compounds. As a result, we have obtained good regression coefficients, $R^2 = 0.91$ (for d_c) and $R^2 = 0.96$ (for ΔH_f). Applying the same quantum-chemical methods for structural building blocks (constituents of triazenes) we have found that diazoamination always increases detonation performance (2–15% for detonation velocity and 0–32% for pressure). Thus, transformation of aminoaromatic and aminoheterocyclic energetic materials into triazenes is a convenient method for enhancement of their detonation properties.

1. Introduction

Modern molecular engineering is increasingly using quantum-chemical methods since the latter are convenient, versatile and safe for a fast preliminary evaluation of detonation properties of a potential high-energy density material (HEDM) [1]. Simple static molecular calculations, however, are inferior to calculations of chemical transformations since the latter assume a specific chemical route to the desired HEDM and, therefore, allow a more precise estimation of the availability-efficiency compromise [2]. The efficiency of a HEDM means calculations of detonation properties, namely, heat of detonation, detonation pressure, velocity and temperature, Gurney energy and power (strength) [3, 4]. However, the most frequently estimated parameters are detonation velocity (D , m s⁻¹) and pressure P (GPa) [5, 6].

Since many energetic materials bear primary amino group at the aromatic or heterocyclic ring [7, 8], it is interesting to study possible transformation of such aminoaromatic and aminoheterocyclic energetic materials into the corresponding triazenes, which can be synthesized via a simple and cheap two-step one-pot process involving a diazonium salt as an intermediate (Scheme 1) [9]. Herein, R can be both aromatic/heterocyclic and aliphatic, which pushes the limits of possible building blocks applied. We should stress, however, that synthetic routes to triazenes are not limited with Scheme 1 [10, 11].

Triazenes are usually appearing as stable solids, for which crystalline structures were determined in a number of cases [12, 13] (see Supporting Information for more details). Flexibility of Scheme 1 also allows obtaining bis-triazenes via both bis-diazonium salts and diamines [14]. Due to the detachment of a hydrogen atom at the N3 site, triazenes also form stable crystalline complexes with transition metals, Rh [15, 16] and Ru^I [17]. Moreover, replacement of the hydrogen atom by an acyl group or an oxygen atom yields the corresponding acyl derivatives [18] and oxides [19, 20]. The latter compounds are especially interesting as HEDMs, since are bearing an oxygen atom, which is useful in the case of the negative oxygen balance precursors.

Meanwhile, triazenes are physiologically active compounds known for a long time. Despite these were reported as tumors inducing agents in far 1947 [21], later studies revealed an opposite effect along with a wide pattern of other useful physiological activities, namely, antitumor, anorectic, antifungal, antimicrobial, antiviral and cytotoxic [22–31].

It is known from X-ray studies that the most stable isomer has a *trans*-conformation at the N=N bond [32]. Quantum-chemical calculations also supported this conclusion and shown that *E*-azo,*s-trans* structure of berenil predominates in the gas phase and in aqueous solution with the energy difference between conformers equal 95.4 kJ mol⁻¹ [33]. The process of *cis-trans* isomerization, however, is catalyzed by acids and bases as a result of acid/base-promoted 1,3-prototropic rearrangements

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[34]. Significant difference in conductance appearing in the *cis* and the *trans* form makes triazenes as a possible optical molecular switch [35].

Thus, such simple synthetic methods of the triazene preparation along with increasing of the nitrogen content makes this family of compounds desired candidates as potential HEDM. To the best of our knowledge, triazenes are still not studied in this context, except of one experimental work, where 1,3-bis(2-methyltetrazol-5-yl)triazene was transformed into 2,2'-dimethyl-5,5'-azoxybistetrazole [36] and one theoretical work, where hypothetical 1-nitro-1-triazene was estimated as a potential HEDM [37]. Therefore, in the present work we have performed a comprehensive theoretical study of triazenes as possible HEDM and compared their performances with the corresponding NH_2 -containing precursors, which is reported for the first time.

2. Computational details

Quantum-chemical calculations performed in this work were done in terms of density functional theory (DFT) by using both the Gaussian09 [38] and Materials Studio 2017 [39] suite of programs. For predictions of condensed-phase densities, vacuum isolated molecules were first optimized using the range separated hybrid functional with dispersion correction based on C_6 , namely, ωB97XD [40]. We have applied the Pople's split-valence quasi-double- ζ in the valence shell basis set (6-31G) along with polarization functions (d,p) [41]. Thereafter, Merz-Kollman electrostatic potential fitting partial charges were obtained and assigned to atoms for the next step.

Then crystal structure predictions were performed with the Polymorph module of the Materials Studio 2017 program suite using *ab initio* forcefield COMPASSII (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) [42]. This procedure includes four steps: 1) simulated annealing assuming construction and random modification of thousands of initial crystal structures; 2) clustering when all available frames for the specified space groups are clustered; 3) geometry optimization with the complete relaxation of all degrees of freedom; 4) final clustering.

The total energies of condensed-phase molecules were calculated in terms of all-electron approximation using pure GGA functional due to Perdew-Burke-Ernzerhof (PBE) [43] along with a double numerical basis set, DND, as implemented in the DMol³ code [44]. The latter code allows treating both periodic and non-periodic systems with the same method without use of supercell approximation. Sampling of the Brillouin zones were performed using k-point mesh generated by the Monkhorst-Pack algorithm. Direct spacing between k-points was specified to be $0.08\ 2\pi\text{\AA}^{-1}$. Convergence quality parameters are as follows: total energy (5×10^{-6} eV atom⁻¹), force (0.01 eV \AA^{-1}), stress (0.02 GPa) and displacement (5×10^{-4} \AA). Dispersion effects were taken into account using the Grimme form of the damped C_6 term [45].

3. Results and discussion

3.1. Calibration of the calculation methods

In this work, we have performed estimation of detonation properties using the Kamlet-Jacobs (K-J) empirical scheme [46], which demonstrate a good predictive force despite its simplicity [1, 5]. The K-J scheme uses two input parameters, namely, crystal density (d_c) and enthalpy of formation (ΔH_f); the latter, along with empirical formula (internal oxidation ability), are sufficient parameters for estimation of detonation energy (Q , cal g^{-1}), velocity (D , m s^{-1}) and pressure P (GPa) [46].

First of all, we have tried to calibrate the method for calculation of the crystal density. Recently, we have shown that this parameter is one of the most important; therefore, estimation of the density must be done very carefully. Despite a number of methods for crystal density calculation are described in the literature, we are using the method,

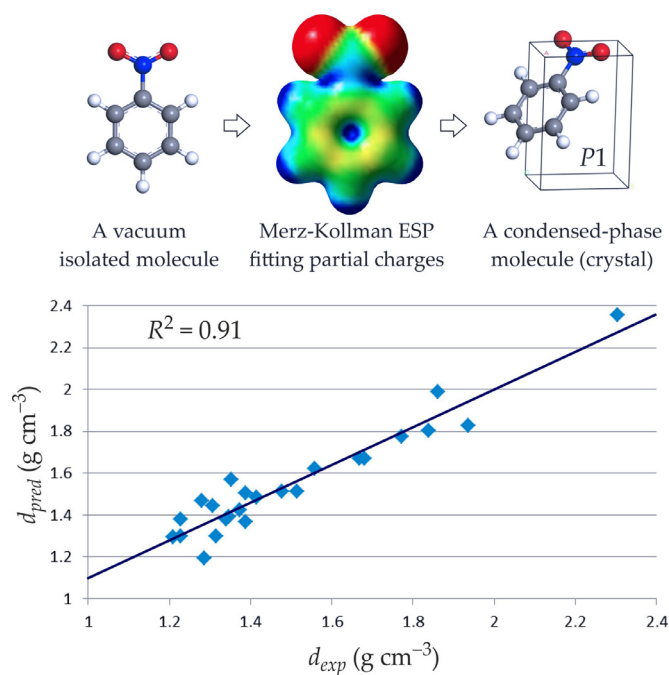


Fig. 1. Sequence of isolated-to-condensed phase molecule transformation (top) and correlation of the predicted and experimental crystal densities (bottom)

which is based on the condensed (crystal) phase optimization. The applied sequence is presented graphically in Fig. 1. By using accurate ESP fitting charges, the predicted densities (d_{pred}) are obtained as densities of the completely relaxed asymmetric cells (space group $P1$) of the studied compounds. Thus, in this approach we are neglecting the difference between densities of possible polymorphs since for majority of organic crystals it equals 0-2% [47], whereas an accurate crystal structure prediction with correct space group and architecture is very complex task, which, moreover, can scarcely be performed in 100% of cases.

Thus, to calibrate the method, we have performed crystal structure prediction for a series of 24 compounds (18 triazenes and 6 aromatic and heterocyclic amines) with available crystal structures (Fig. S1 and Table S1 in the Supporting Information). The calculated crystal densities of the benchmark set molecules correlate well with the experimental data providing $R^2 = 0.91$ (Fig. 1). On the basis of this correlation, we have obtained an empirical regression (Eq. (1)) for corrected values (d_{theor}):

$$d_{theor} = 1.0144d_{pred} - 0.0706 \quad (1)$$

The numerical data on the experimental and calculated densities are gathered in Table 1. As one can see, the corrected values of density (d_{theor}) are very close to the experimental ones. A statistical treatment of the absolute errors gives the following estimates: $\Delta_{max} = 0.167$, $\Delta_{min} = -0.155$, mean = 0.000125 and median = -0.0025. We should stress, however, that fluorine-containing species are predicted very poor, which is a drawback of the COMPASSII forcefield. Thus, one should avoid calculations of such compounds along with fluorine-free compounds, since these require a separate calibration. To ensure that the difference between the densities of polymorphs can be neglected, we have performed a set of the density predictions using the exact experimentally found space groups. The calculated values (d'_{theor}) are listed in Table S1 in the Supporting Information. As one can see, the differences between densities of the possible polymorphs are small enough to be neglected in the present study.

Similarly to the crystal density, enthalpy of formation can also be calculated using a number of methods, which include isodesmic reactions, lattice energies, atomic increments, etc. In the present work, however, we have tried to avoid any multistep calculation scheme and applied

Table 1
Numerical data on the density (g cm^{-3}) estimation results for the benchmark set compounds ($\Delta = d_{\text{theor}} - d_{\text{exp}}$)

Crystal	d_{exp}	d_{pred}	d_{theor}	Δ
T1	2.304	2.356	2.319	0.015
T2	1.209	1.294	1.242	0.033
T3	1.228	1.297	1.245	0.017
T4	1.353	1.568	1.520	0.167
T5	1.515	1.514	1.465	-0.050
T6	1.388	1.506	1.457	0.069
T7	1.478	1.513	1.464	-0.014
T8	1.374	1.424	1.374	0.000
T9	1.316	1.297	1.245	-0.071
T10	1.559	1.621	1.574	0.015
T11	1.415	1.484	1.435	0.020
T12	1.285	1.195	1.142	-0.143
T13	1.346	1.391	1.341	-0.005
T14	1.280	1.470	1.420	0.140
T15	1.388	1.369	1.318	-0.070
T16	1.307	1.446	1.396	0.089
T17	1.340	1.378	1.327	-0.013
T18	1.228	1.380	1.330	0.102
DTBT	1.669	1.671	1.624	-0.045
MATB	1.773	1.773	1.728	-0.045
DATB	1.839	1.801	1.757	-0.082
TATB	1.937	1.826	1.782	-0.155
TetNA	1.861	1.988	1.946	0.085
ATZ	1.681	1.672	1.625	-0.056

Table 2
Numerical data on the ΔH_f (kJ mol^{-1}) estimation results for the benchmark set compounds

Crystal	$\Delta H_{f,\text{exp}}$	$\Delta H_{f,\text{pred}}$	$\Delta H_{f,\text{theor}}$	Δ
1	331.6	327.9	320.7	-10.9
2	411.7	396.4	397.1	-14.6
3	-66.1	-30.4	-78.5	-12.4
4	457.9	440.7	446.4	-11.5
5	-86.6	12.6	-30.6	56.0
6	-72.8	146.6	118.6	191.4
7	-74.7	-151.7	-213.6	-138.9
8	-11.7	28.6	-12.7	-1.0
9	207.8	330.0	323.0	115.2
10	-50.6	-44.1	-93.8	-43.2
11	79.1	76.3	40.4	-38.7
12	75.0	73.1	36.8	-38.2
13	-538.5	-377.1	-464.8	73.7
14	41.0	55.9	17.6	-23.4
15	754.6	746.8	787.4	32.8
16	184.4	166.1	140.4	-44.0
17	-296.9	-260.4	-334.8	-37.9
18	-487.2	-374.1	-461.5	25.7
19	-792.1	-656.5	-776.1	16.0
20	606.0	497.7	509.9	-96.1

was obtained to calculate the corrected $\Delta H_{f,\text{theor}}$ values (Eq. (2)).

$$\Delta H_{f,\text{theor}} = 1.1142\Delta H_{f,\text{pred}} - 44.657 \quad (2)$$

The corresponding numerical data are listed in Table 2. As one can see, there is a significant mismatch in the case of compounds 6, 7 and 9. This can be ascribed to an unbalanced account of the hydrogen bonding in the P1 crystal models compared to real ones, when this effect contributes strongly. Meanwhile, the benchmark set compounds 1 and 2 bearing a triazene linkage have small errors equal -10.9 and -14.6 kJ mol^{-1} , respectively. Moreover, as we have recently shown, within a 1% error for D and P , ΔH_f can vary in rather wide ranges. For example, for RDX these ranges are -220.2-42.0% and -53.0-26.4% for D and P , respectively [1]. Therefore, we can conclude that our present results of the $\Delta H_{f,\text{theor}}$ values prediction are good enough. A statistical treatment provides the following estimates: $\Delta_{\text{max}} = 191.4$, $\Delta_{\text{min}} = -138.9$, mean = 7.1×10^{-16} and median = -11.95.

Of course, the values of solid-state enthalpies of formation can be obtained involving a more accurate method applied in this work, namely, $\omega\text{B97XD}/6\text{-}31\text{G(d,p)}$. But this scheme assumes the calculations of gas-phase enthalpies of formation followed by the calculation of sublimation enthalpies. Since in our case the latter can be obtained using the PBE/DND method only, the total accuracy of the prediction of solid-state enthalpies of formation will be controlled by the sublimation energy prediction accuracy. Thus, in this case, one obtains a more computationally expensive scheme without any significant gain in accuracy.

3.2. Level 1: Efficiency estimation based on the compositional criterion

This section describes how to perform an express estimation of the transformation efficiency based on empirical formulas only. Since we do not assume any chemical structures, this means that such an analysis can be performed without quantum-chemical calculations. Recently, we have shown quantitatively that compositional criterion (internal oxidation ability) is a very important determinant of the detonation performance of a HEDM. Thus, using various additive schemes, we have provided a crude prediction of d_c , ΔH_f , Ω_{CO_2} , Q , D , and P values for all compositions up to $\text{C}_{30}\text{H}_{30}\text{N}_{30}\text{O}_{30}$ [1].

Assume we want to transform an amine to a triazene. Then, this process can be schematically described as follows:

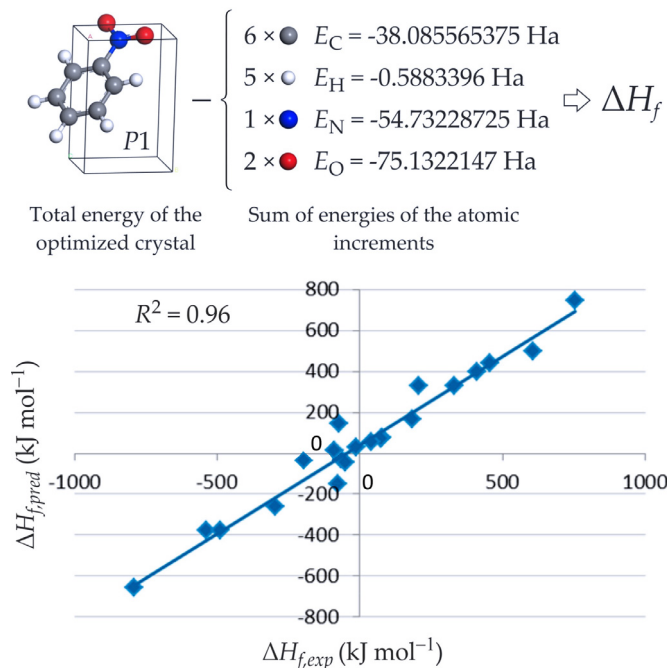


Fig. 2. Enthalpy of formation calculation approach (top) and correlation of the predicted and experimental ΔH_f values (bottom)

an approach, which is schematically illustrated in Fig. 2. It allows a direct estimation of enthalpy of formation using total energies obtained by means of fixed cell geometry optimizations with the PBE/DND approach.

The obtained values ($\Delta H_{f,\text{pred}}$) were then corrected benchmarking with a set of 20 molecules bearing various structurally-similar motifs and with the known solid-state enthalpies of formation taken from the NIST Chemistry WebBook (Fig. S2 in the Supporting Information) [48]. It was found that $\Delta H_{f,\text{pred}}$ correlate well ($R^2 = 0.96$) with the experimental ones (Figure 2). On the basis of this correlation, a regression equation

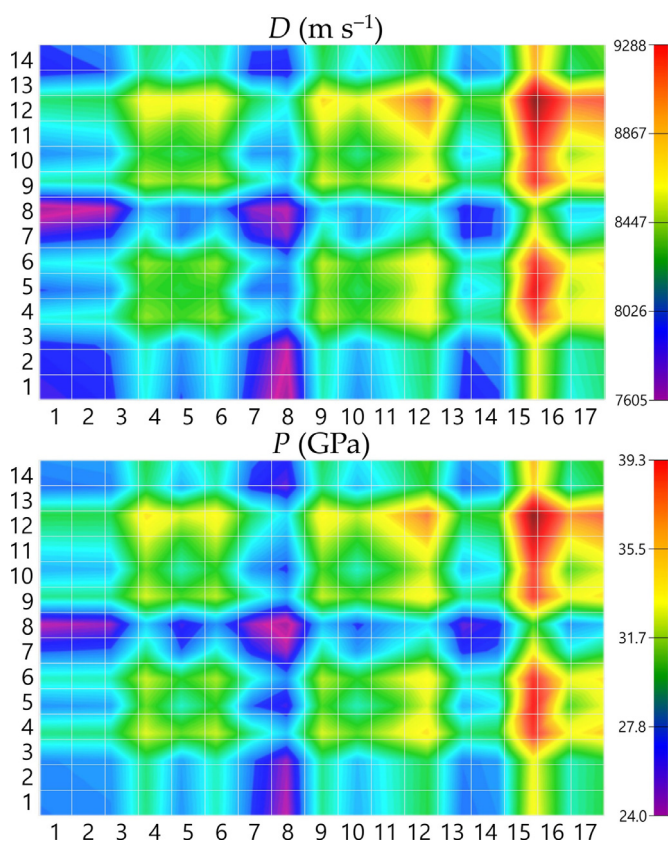


Fig. 3. Contour plots of the predicted D and P values for a 14×17 triazene matrix.

As a result, expected differences in enthalpy of formation and crystal density can be expressed as in Eq. (4) and (5) [1]:

$$\Delta\Delta H_f = -1.2845(-32x + 26y - 89z + 56w - 167) \quad (4)$$

$$\Delta d_c = \frac{1.020(a_1x + b_1y + c_1z + w)}{(a_2x + b_2y + c_2z + w)(a_2x + b_2y + c_2z + w - 0.091)}, \quad (5)$$

where $a_1 = 1.457$, $b_1 = 0.418$, $c_1 = 1.255$, $a_2 = 1.643$, $b_2 = 0.512$, $c_2 = 1.355$. One can easily ascertain that the expected values $\Delta\Delta H_f$ and Δd_c are always positive meaning the higher D and P as a result of such an amine-to-triazene transformation.

Thus, we have selected 17 amines including aromatic, heterocyclic and aliphatic compounds, which are either well-known energetic materials (1-4, 5, 15-17) [7, 49, 50] or recently synthesized nitrogen-rich HEDM (6-14) [8]. Structural formulas and the corresponding numbering are presented in Fig. S3 in the Supporting Information. Since amines 15-17 are aliphatic, these can serve only as an amine component, not diazonium component (Scheme 1). Therefore, one can expect 14×17 possible triazenes formed. Using our above-described method [1], we have built contour plots of the predicted D and P values using Matlab r2014a (Fig. 3) and the corresponding numerical values are listed in Tables S2 and S3 in the Supporting Information. Thus, top 10 structures from the total 238 were selected for a higher-level estimation by means of first-principles quantum chemical calculations.

3.3. Level 2: Accurate efficiency estimation with account of chemical structure

As it follows from Tables S2 and S3, the most promising structures must be constructed from building blocks (diazonium and amine components), which are listed in Table S4 in the Supporting Information. The

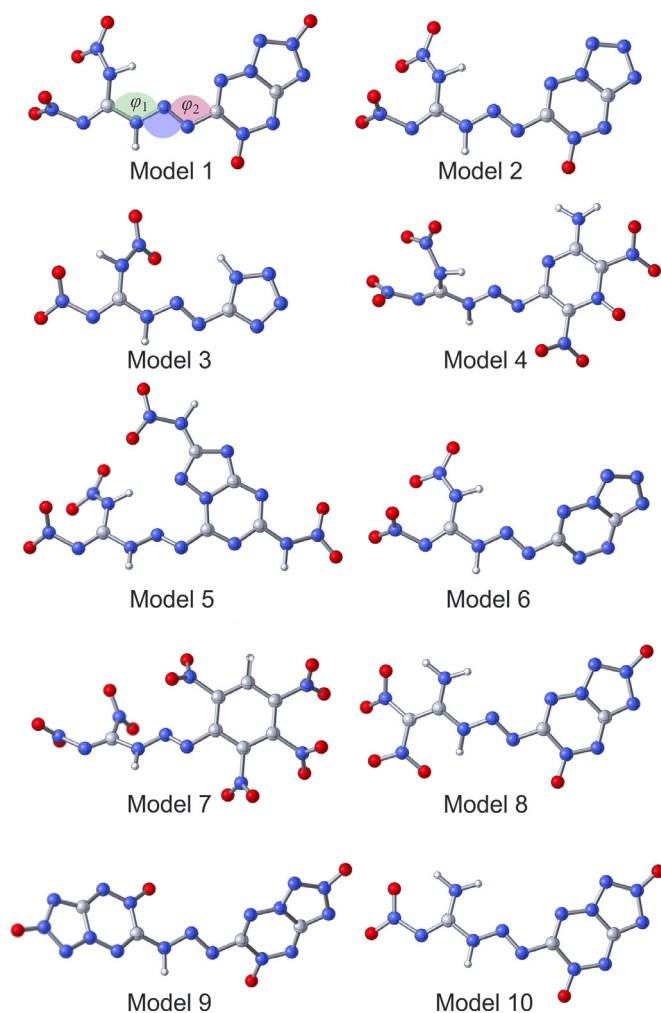
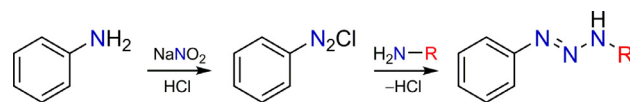


Fig. 4. The gas-phase optimized chemical structures of the top 10 triazenes selected for the higher-level estimation



Scheme 1. Schematic presentation of the diazoamination reaction

optimized structures of these triazenes (Models 1-10) are illustrated in Fig. 4. As one can see, the triazene linkage remains linear *trans*-conformation in the gas phase, but in the condensed phase, the torsion angles $|\varphi_1|$ and $|\varphi_2|$ can be much less than 180° , which is determined by steric hindrance of the amine residuals (Fig. 4). We have performed geometry optimization of Models 1-10 in crystalline state with a subsequent frequency analysis to check the absence of imaginary modes in the IR spectra. The latter are illustrated in Fig. S4 in the Supporting Information.

Thus, the calculated densities (d , g cm^{-3}), enthalpies of formation (ΔH_f , kJ mol^{-1}), detonation energies (Q , cal g^{-1}), velocities (D , m s^{-1}) and pressures (P , GPa) for Models 1-10 are listed in Table 3. As one can see, all triazenes, except of Model 10, demonstrate excellent detonation properties, which approaches to the most powerful non-nuclear explosive, ϵ -hexanitrohexaazaisowurtzitane (HNIW or CL-20). This is achieved due to high densities, balanced internal redox ratio and high enthalpies of formation (Table 3). At the same time, despite Model 10 is structurally similar to Models 2 and 8, it has a relatively low density

Table 3
The calculated detonation properties of Models 1-10

Model	d_{theor}	$\Delta H_{f,theor}$	Q	D	P
1	1.923	1093.2	1678.7	9511	41.7
2	2.029	1084.3	1607.7	9731	45.0
3	1.958	676.8	1493.2	9444	41.5
4	2.134	583.4	1553.1	9883	47.7
5	2.069	824.8	1429.3	9490	43.2
6	1.971	1145.4	1585.2	9442	41.7
7	2.044	493.1	1657.1	9491	43.0
8	2.040	929.7	1581.4	9610	44.0
9	2.018	1625.3	1657.2	9572	43.4
10	1.786	1000.8	1555.2	8771	34.0

Table 4
The estimated efficiency of diazoamination as a result of formation of Models 1-10

Model	Enhancement (%)		Model	Enhancement (%)	
	ΔD	ΔP		ΔD	ΔP
1	5.04	9.39	6	7.43	16.35
2	12.64	31.71	7	7.25	17.22
3	14.77	31.23	8	7.49	17.01
4	7.54	16.52	9	7.24	17.30
5	8.89	20.26	10	2.14	0.11

1.786 g cm⁻³ and a more negative Ω_{CO_2} , which is the main reason of a lower detonation performance (Table 3).

Of course, to be more precise in the comparison of the D and P values of triazenes and CL-20, one needs to apply the calculated detonation properties of the latter within the same approach rather the experimentally measured values. On the other hand, we have recently predicted crystal density of CL-20 using the same method and obtained the value 1.982 g cm⁻³. Using the empirical correction applied in the present work, the theoretical crystal density is 1.940 g cm⁻³. It's easily to check that replacement of the experimental (2.055 g cm⁻³ [51]) density by the theoretical one and leaving the experimental ΔH_f (377.4 kJ mol⁻¹) gives the reference values of D and P for CL-20 being much lower. In this case it's not necessary to re-calculate ΔH_f , since its influence is very little to change the D and P significantly [1]. For example, to increase the D and P values up to the initial level with the theoretical density (1.940 g cm⁻³), the calculated enthalpy of formation must be about 900 kJ mol⁻¹ ($\delta = 138.5\%$), which lies outside of any possible error ranges.

But such high performance of the resulting triazenes does not mean that the modeled diazoamination reaction is really needed. Indeed, the corresponding precursors (starting amines) can also have high detonation properties; hence, the chemical reaction may not have sense or even be counterproductive. Thus we have performed an analogous prediction of the detonation properties for the corresponding precursors and the results are gathered in Table S5 in the Supporting Information. Since triazenes are bearing residues of two amines, their contributions must be accounted according to their molar masses (M). Mathematically, this can be expressed as in Eq. (6) and (7) for ΔD and ΔP , respectively.

$$\Delta D = D_X \frac{M_1 + M_2}{M_1 D_1 + M_2 D_2} - 1 \quad (6)$$

$$\Delta P = P_X \frac{M_1 + M_2}{M_1 P_1 + M_2 P_2} - 1, \quad (7)$$

The results of this analysis are listed in Table 4. As one can see, the diazoamination reaction has positive effect in all the cases, which confirm the conclusion drawn on the basis of general considerations in the previous section. Such chemical transformation provides the relative enhancement of D equals 8.0% as an average. This is a significant gain in detonation performance, which is worth to be acquired with such a simple reaction. Meanwhile, the relative enhancement of P is even higher and equals 17.7% as an average. We should stress that ΔD and ΔP values may appear even higher, taking into account that we have selected

the most promising candidates at Level 1. Indeed, triazenes composed from lower-performance precursors appeared out of consideration. At the same time, it is expected that the relative enhancement will be more pronounced precisely for such compounds.

4. Conclusions

In summary, we have presented in this paper a theoretical analysis of the possible enhancement of detonation performance in energetic amines due to their chemical transformation into triazenes, a diazoamination reaction. The performed two-level analysis unambiguously indicates a positive effect of such a transformation. For a set of nitrogen-rich amines used, the calculated effectiveness was found to be $\Delta D = 8\%$ and $\Delta P = 17.7\%$ as an average. Although, we did not set ourselves the goal of covering the widest possible number of precursors, but selected those, whose expected performance should exceed most known energetic materials. For low-energetic precursors, the calculated enhancement is expected to be even higher.

This work provides a short guide for the analysis of such chemical transformations in order to find the most powerful energetic materials. However, it must be kept in mind that increasing detonation properties usually lead to decrease in sensitivity due to higher energy content [52–55]. Therefore, a delicate balance between performance and sensitivity is of primary importance for molecular design and engineering [56, 57]. Fortunately, triazenes are expected to be stable compounds; however, the other related diazonium derivatives, pentazolates, which also possess a high energy density, are known to be quite unstable. Consequently, before performing of such analyses one needs to estimate possible change in sensitivity, which must be the issue of further study.

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.2021.05.001.

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