

Article

Impact of Incremental Methylene Groups on the Energetic Properties of Aromatic Nitramines

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Abstract: The investigation of a series of secondary aromatic nitramines was performed to reveal the impact of incremental methylene groups on the stability, shock impulse, and energetic properties of these compounds. Becke's three-parameter hybrid functional approach with non-local correlation provided by Lee, Yang, and Parr and a cc-pVTZ basis set was used to obtain the geometry, total energy, and heat of formation of the most stable conformers of these aromatic nitramines. These parameters were used to evaluate the density, resistance to shock stimuli, detonation pressure, and velocity of the nitramines under study. Referring to the results obtained, we concluded that the thermal stability and resistance to shock stimuli of the compound investigated was directly CH₂ chain length-dependent, while their energetic- properties, such as detonation pressure and velocity, were worsened due to this chain increase. We also found that the stability of the compounds increases more significantly than the worsening energetic properties of aromatic nitramines. The results obtained reveal that in some cases the number of CH₂ in the chain should be smaller than three so that the explosive properties of the compounds under study would not be worse than TNT.

Keywords: aromatic nitramines; methylene group; energetic properties; stability; resistance to shock stimuli



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1. Introduction

High-energy materials are a class of materials with a high amount of stored chemical energy that can be released [1–10]. Various types of high energy materials (HEMs) are used for civil and military purposes due to their unique properties [11–16]. Most of currently known popular HEMs contain in their structures three typical, so called, explosoforic groups: NO₂ (nitro), ONO₂ (nitrate), and >N-NO₂ (nitramine) [17–21]. The last type of energetic compounds, “nitramines”, can be divided into two subgroups: primary nitramines (R-NH-NO₂) and secondary nitramines (R₁R₂N-NO₂) [11,12,22–31]. Thus, many high-energy materials are similar in that they mostly contain nitro groups [1,3,14,19,32–35], but they can have very different properties that are substitution depended [23,36,37]. For example, primary nitramines, and their typical representatives methylnitramine (CH₃-NHNO₂) and ethylene dinitramine (O₂NNH-CH₂CH₂-NHNO₂, EDNA), possess good energetic characteristics and both are powerful explosives [2,8,9,26,38]; however, from the practical point of view, they suffer from poor thermal stability and high shock sensitivity [39–50]. Moreover, due to the acidic nature of the proton (NH-NO₂), primary nitramines are comparatively strong organic acids, and they can induce corrosion for metals [28,47,51–53]. While nitramines have long been used as powerful explosives, their poor thermal stability and high shock sensitivity have limited their practical applications. As such, there is a growing interest in exploring the potential of nitramines, which possess more favorable energetic properties and improved stability.

As the demand for high-energy materials continues to grow, scientists have focused on the search for high-energy materials with a combination of properties such as safety, reliability, stability, cost-effectiveness, and eco-friendliness; i.e., there is a rising interest in exploring the potential of secondary nitramines, which possess more favorable energetic properties and improved stability [4,9,12,17,24,53]. To approach their goal, the synthesis of energetic metal complexes, the modification of the existing primary HEMs with insensitive materials, coordination polymerization, etc., are performed [22,23,45,54,55]. However, there remains much to be understood about the fundamental chemistry behind these compounds and their properties, particularly in the case of secondary nitramines.

This study is dedicated to the investigation of energetic-property peculiarities of some secondary nitramines. More strictly, we have selected for the current theoretical investigation a series of secondary aromatic nitramines, possessing as the main substituents traditional 2,4,6-trinitrophenyl moiety and varying lengths of the CH₂ (methylene) chain, attached to the nitramine group nitrogen, aiming to improve the stability and resistance to shock stimuli and to identify the optimal chain length for maximizing both their energetic properties and stability. We carried out this investigation because there is a lack of information on the dependence of the energetic properties of the aromatic nitramines on the -CH₂ chain length. The results of our study will indicate how long the -CH₂ length should be in order that the stability and resistance to shock stimuli of the aromatic nitramines would be high along with energetic properties. The insight gained from this research could pave the way for the development of new and improved high-energy materials in the future.

2. Materials and Methods

At least two different geometric structures of the compounds under study were modeled to obtain the most stable conformer by using the Berny optimization without any symmetry constraints (all bond's length, angles, and dihedral angles are changed). The vibration frequencies analysis was performed so as to be sure that the equilibrium point was found. The results of the comparison of the total energy allowed us to select the most stable conformers for further study. Becke's three-parameter hybrid functional approach with non-local correlation provided by Lee, Yang, and Parr (B3LYP) and the cc-pVTZ basis set implemented in a GAUSSIAN package was applied in our studies [56–58]. This approach described well the geometric and electronic structure of various molecules and their derivatives [59–67]. To predict the stability and sensitivity of the materials and foresee how these properties are changed due to various modifications, we calculated and compared the binding energy per atom, chemical hardness, softness, electronegativity, and hardness index [68,69]. The oxygen balance was calculated, too.

The density of the materials under investigation was obtained by both approaches implemented in the ACD/Labs program as suggested by M.S. Keshavarz to avoid unexpected errors [70,71]. In the ACD/Labs program, the density is equal to the division of molecular weight from molar volume. Molar volume was calculated by molar division from additive increments. The additive atomic increments were obtained using a database implemented in this program.

The detonation velocity was also calculated by using several empirical approaches described in [72]. The Equations for the evaluation of this parameter are given below. We used these various approaches because there is no possibility to predict which of them is more accurate for the compound under study. Even though there are other methods to assess detonation velocities, these methods are also imprecise and necessitate fixed parameters. On the other hand, if we use the same approach to determine the detonation velocities of all the molecules under investigation, we can ensure that the statistical errors in the velocities for each molecule will be similar. This allows us to compare the detonation velocities of the compounds studied here, regardless of the model used to compute them, and subsequently rank those molecules. Moreover, the data obtained by different approaches allow us to reveal general features.

When the detonation velocity is known, its pressure can be evaluated as follows:

$$P(\text{kbar}) = 15.58 (D \rho / (1.01(1 + 1.30 \rho)))^2$$

where D is the detonation velocity and ρ is the density of the compounds. A detailed description of the methodology used to evaluate and interpret the results is presented in our paper [36]. The main points of the methodology are as follows:

- The lowest value of total energy indicates the most stable conformers for further study;
- A higher value of the binding energy per atom shows higher thermal stability;
- Obtaining larger values of the HOMO–LUMO gap and chemical hardness points to increasing chemical stability;
- A low chemical softness value denotes a high tendency of the molecule to degrade;
- A higher electronegativity reflects the higher tendency of a compound to form a bond;
- A high negative value of oxygen balance exhibits a low sensitivity of an explosive molecule to shocks. Oxygen balance also expresses the degree to which an explosive can be oxidized and provides information on the strength and brisance of high-energy materials;
- A low value of the impact sensitivity reveals a low resistance to impact;
- The hardness index indicates the resistance to indentation and deformation under mechanical stress and durability. A higher value indicates higher resistance.

It is important that the calculated detonation velocity of Tetryl coincides well with that of 7.59–7.7 km/s presented by other researchers, which indicates the reliability of the approaches used for our study [73–77].

3. Results

As is mentioned above, the density of the materials under study was calculated using two approaches. To simplify the communications, we use indexes I and II to denote results obtained when the density value used was calculated by ACD/Labs and the M.S. Keshavarz approach, respectively. The obtained densities are presented in Appendix A.

We separated our investigated compounds into three groups to foresee the influence of CH_2 chain length on the energetic properties of Tetryl and to obtain whether the main features obtained remain when this compound is substituted by $-\text{NH}_2$. The first group (a) consists of Tetryls with different $-\text{CH}_2$ chain lengths ($n = 1-5$) [(2,4,6-trinitrophenyl- $(\text{O}_2\text{N})\text{N}(\text{CH}_2)_n \text{H}$]. Bis-aromatic nitramine homologs of chain length variation $(\text{CH}_2)_n$ of [(2,4,6-trinitrophenyl- $\text{N}(\text{NO}_2)_2(\text{CH}_2)_n$ ($n = 1-5$) joined per different lengths of the $-\text{CH}_2$ chain belong to the second group (b). The third group (c) is formed like the first one, but in this case, Tetryl is substituted by $-\text{NH}_2$, i.e., 3-Amino derivatives of chain length variation $\text{N}(\text{CH}_2)_n$ ($n = 1-5$) analogs of 2,4,6-trinitrophenyl- N -nitramine were investigated. The details of the compounds and their chemical composition are presented in Appendix B. The parameters revealing the chemical and thermal stability are presented in Table 1.

To evaluate the resistance to impact, the oxygen balance [78] and impact sensitivity were calculated. The impact sensitivity is obtained as follows:

$$\log h_1 = (11.76a + 61.72b + 26.89c + 11.48d)/M$$

$$\log h_2 = (47.33a + 23.50b + 2.357c - 1.105d)/M$$

where a , b , c , and d indicate the number of C, H, N, and O atoms, respectively, and M is the molar mass of compounds [79–81]. The results achieved are presented in Table 2.

Table 1. The parameters describing the chemical and thermal stability of the compounds belonging to. (a) Homologous aromatic *N*-nitramines, tetryl derivatives [(2,4,6-trinitrophenyl-(O₂N)N(CH₂)_{*n*} H, *n* = 0–5]. (b) Bis-aromatic homologs of chain length variation (CH₂)_{*n*} of [(2,4,6-trinitrophenyl-N(NO₂))₂(CH₂)_{*n*}, (*n* = 1–5)]. (c) 3-Amino derivatives of tetryl with chain length variation [(3-amino-2,4,6-trinitrophenyl-(O₂N)N(CH₂)_{*n*} H, *n* = 1–5)] homologs. The results are discussed in the next section of this paper.

(a)					
Compound	Binding Energy per Atom, eV	Hardness, eV	Softness, eV	Electronegativity, eV	Hardness Index Y
2,4,6-Trinitrophenyl- <i>N</i> -nitramine	4.344	2.222	0.225	6.441	0.90
Tetryl	4.835	2.171	0.230	6.193	0.89
Ethyltetryl	5.339	2.130	0.235	6.127	0.89
Propyltetryl	5.841	2.111	0.237	6.095	0.89
Propyltetryl ¹	5.840	2.109	0.237	6.119	0.89
Butyltetryl	6.396	2.161	0.231	6.183	0.89
Amyltetryl	6.845	2.160	0.232	6.173	0.89
(b)					
Compound	Binding Energy per Atom, eV	Hardness, eV	Softness, eV	Electronegativity, eV	Hardness Index Y
Bis-tetryl-CH ₂	9.233	2.191	0.228	6.545	0.90
Bis-tetryl-CH ₂ CH ₂	9.769	2.098	0.238	6.375	0.89
Bis-tetryl-CH ₂ CH ₂ CH ₂	10.305	2.071	0.241	6.375	0.88
Bis-tetryl-CH ₂ CH ₂ CH ₂ CH ₂	10.299	2.191	0.228	6.545	0.90
Bis-tetryl-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂	11.362	2.072	0.241	6.256	0.88
(c)					
Compound	Binding Energy per Atom, eV	Hardness, eV	Softness, eV	Electronegativity, eV	Hardness Index Y
3-Amino-tetryl	5.207	2.130	0.253	6.127	0.86
3-Amino-tetryl ¹	5.207	1.984	0.252	5.913	0.87
3-Amino- <i>N</i> -ethyltetryl	5.709	1.918	0.261	5.872	0.86
3-Amino- <i>N</i> -propyltetryl	6.209	1.917	0.261	5.876	0.86
3-Amino- <i>N</i> -butyltetryl	6.712	1.984	0.252	5.913	0.87
3-Amino- <i>N</i> -amyltetryl	7.213	1.894	0.264	5.858	0.86

¹ denotes the other conformer of the Propyltetryl obtained by us.

Table 2. The parameters describing the resistance to the impact of the compounds belonging (a) Homologous aromatic *N*-nitramines, tetryl derivatives [(2,4,6-trinitrophenyl-(O₂N)N(CH₂)_{*n*} H, *n* = 0–5]. (b) Bis-aromatic homologs of chain length variation (CH₂)_{*n*} of [(2,4,6-trinitrophenyl-N(NO₂))₂(CH₂)_{*n*}, (*n* = 1–5)]. (c) 3-Amino derivatives of tetryl with chain length variation [(3-amino-2,4,6-trinitrophenyl-(O₂N)N(CH₂)_{*n*} H, *n* = 1–5)] homologs. The results are discussed in the next section of this paper.

(a)			
Compound	Oxygen Balance, %	log _h ₁	log _h ₂
2,4,6-Trinitrophenyl- <i>N</i> -nitramine	−32.22	1.545	1.309
Tetryl	−47.36	1.906	1.573
Ethyltetryl	−61.09	2.233	1.813
Propyltetryl	−73.60	2.530	2.032
Butyltetryl	−85.05	2.803	2.232
Amyltetryl	−95.56	3.053	2.415
(b)			
Compound	Oxygen Balance, %	Log _h ₁	Log _h ₂
Bis-tetryl-CH ₂	−37.26	1.515	1.365
Bis-tetryl-CH ₂ CH ₂	−44.73	1.697	1.497
Bis-tetryl-CH ₂ CH ₂ CH ₂	−51.85	1.870	1.622
Bis-tetryl-CH ₂ CH ₂ CH ₂ CH ₂	−58.63	2.035	1.741
Bis-tetryl-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂	−61.11	2.192	1.855
(c)			
Compound	Oxygen Balance, %	Log _h ₁	Log _h ₂
3-Amino-tetryl	−47.66	2.104	1.581
3-Amino- <i>N</i> -ethyltetryl	−60.72	2.407	1.809
3-Amino- <i>N</i> -propyltetryl	−72.68	2.684	2.018
3-Amino- <i>N</i> -butyltetryl	−83.66	2.938	2.210
3-Amino- <i>N</i> -amyltetryl	−93.78	3.173	2.386

The parameters indicating the effectiveness of energetic properties are presented in Tables 3 and 4. It is necessary to mention that the detonation velocity and consequently the detonation pressure were evaluated by using different expressions. We remind the reader

that the density of the materials under study was also calculated by applying two different approaches. Thus, detonation velocities denoted as D_1 and D_2 are calculated followingly:

$$D_1^2 = -393.6877 - 0.2454 \left(\frac{NE}{M} \right) - 114.0793 \frac{E}{M} \quad (1)$$

$$D_2^2 = -372.4122 - 1.31980 \left(\frac{NE}{M} \right) - 106.8382 \frac{E}{M} \quad (2)$$

where N is the number of $-NO_2$ groups in the molecule, E is total energy, a.u., and M is molar mass, g/mol. These equations are given by Türker [82].

The detonation velocity denoted as D_3 is calculated by using the following equation:

$$D_3 = 1.9 + \left(\frac{-2.97a + 9.32b + 27.68c + 98.9d + 1.22\Delta H_f}{M} \right) \rho \quad (3)$$

presented in [72]. Here, a , b , c , and d indicate the number of C, H, N, and O atoms, respectively, ρ is density in g/cm^3 , and ΔH_f is the gas phase heat of formation of the energetic compound. The very well know Kamlet–Jacobs equation of the detonation velocity was also used to calculate this parameter [83]:

$$D_4 = 1.01\varphi^{1/2}(1 + 1.30\rho) \quad (4)$$

where $\varphi = nM^{1/2}Q^{1/2}$.

Here, n is the number of moles of gaseous products of detonation per gram of explosive, M is the average molecular weight of the gas found from the chemical reaction equations with an assumed equilibrium composition, Q is the heat of detonation in calories per gram of explosive, and ρ is loading density. The values obtained by this approach are marked as D_4 . The obtained detonation velocity is presented in Table 3.

Table 3. The detonation velocity of the compounds (a) Homologous aromatic N-nitramines, tetryl derivatives [(2,4,6-trinitrophenyl-(O₂N)N(CH₂)_nH, $n = 0-5$). (b) Bis-aromatic homologs of chain length variation (CH₂)_n of [(2,4,6-trinitrophenyl-N(NO₂))₂(CH₂)_n, ($n = 1-5$). (c) 3-Amino derivatives of tetryl with chain length variation [(3-amino-2,4,6-trinitrophenyl-(O₂N)N(CH₂)_nH, $n = 1-5$] homologs.

(a)						
Compound	D_1 , km/s	D_2 , km/s	* D_{3I} , km/s	* D_{4I} , km/s	** D_{3II} , km/s	** D_{4II} , km/s
2,4,6-Trinitrophenyl-N-nitramine	8.44	8.73	8.62	8.56	8.21	8.18
Tetryl	8.07	8.64	7.94	7.98	7.83	7.88
Ethyltetryl	7.67	8.28	7.47	7.56	7.50	7.59
Propyltetryl	7.29	7.93	7.33	7.21	7.46	7.34
Butyltetryl	6.91	7.60	6.38	6.91	6.57	7.10
Amyltetryl	6.55	7.28	6.46	6.64	6.71	6.88
(b)						
Compound	D_1 , km/s	D_2 , km/s	* D_{3I} , km/s	* D_{4I} , km/s	** D_{3II} , km/s	** D_{4II} , km/s
Bis-tetryl-CH ₂	8.55	9.99	8.81	8.72	7.99	7.97
Bis-tetryl-CH ₂ CH ₂	8.55	10.00	8.81	8.72	8.00	7.97
Bis-tetryl-CH ₂ CH ₂ CH ₂	8.40	9.86	8.47	8.45	7.81	8.45
Bis-tetryl-CH ₂ CH ₂ CH ₂ CH ₂	8.20	9.69	8.17	8.19	7.64	8.19
Bis-tetryl-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂	8.00	9.52	7.91	7.91	7.48	7.96
(c)						
Compound	D_1 , km/s	D_2 , km/s	* D_{3I} , km/s	* D_{4I} , km/s	** D_{3II} , km/s	** D_{4II} , km/s
Tetryl #	8.07	8.64	7.94	7.98	7.83	7.88
3-Amino-tetryl	7.97	8.55	8.09	8.19	7.80	7.92
3-Amino-tetryl * ¹	7.97	8.55	8.09	8.19	7.80	7.92
3-Amino-N-ethyltetryl	7.58	8.20	7.61	7.76	7.49	7.65
3-Amino-N-propyltetryl	7.21	7.87	7.21	7.40	7.21	7.40
3-Amino-N-butyltetryl	6.85	7.55	6.87	7.08	6.96	7.16
3-Amino-N-amyltetryl	6.10	7.24	6.18	6.42	6.73	6.95

* 'I' denotes detonation velocity obtained by density calculated by applying the approach implemented in ACD/Labs program. ** 'II' denotes detonation velocity obtained by density calculated by applying the approach suggested in [84]. # Here and below, the parameters of tetryl are included in the table for the convenience of readers, i.e., to show the influence of the NH₂ substituent in a more suitable way. ¹ means that the parameter of the other conformer is presented, too.

We remind the reader that the detonation pressure was calculated as follows:

$$P(\text{kbar}) = 15.58 (D \rho / (1.01(1 + 1.30 \rho)))^2$$

As detonation velocity and density were calculated by different approaches, we have several values of these parameters, as presented in Table 4.

Table 4. The detonation pressure of the compounds belonging to (a) Homologous aromatic *N*-nitramines, tetryl derivatives [(2,4,6-trinitrophenyl-(O₂N)N(CH₂)_n H, *n* = 0–5]. (b) Bis-aromatic homologs of chain length variation (CH₂)_n of [(2,4,6-trinitrophenyl-N(NO₂))₂ (CH₂)_n, (*n* = 1–5)]. (c) 3-Amino derivatives of tetryl with chain length variation [(3-amino-2,4,6-trinitrophenyl-(O₂N)N(CH₂)_n H, *n* = 1–5)] homologs.

(a)								
Compound	* P(D _{1I}), kbar	P(D _{1II}), kbar	P(D _{2I}), kbar	P(D _{2II}), kbar	P(D _{3I}), kbar	P(D _{3II}), kbar	P(D _{4I}), kbar	P(D _{4II}), kbar
2,4,6-Trinitrophenyl- <i>N</i> -nitramine	330.00	317.94	353.21	340.3	342.40	300.88	339.72	298.83
Tetryl	289.38	286.11	331.73	318.37	274.22	263.95	282.59	272.11
Ethyltetryl	253.14	254.04	294.89	291.98	230.19	232.86	246.16	248.98
Propyltetryl	222.28	225.79	263.50	267.65	196.27	217.28	217.67	228.82
Butyltetryl	199.86	203.05	241.65	246.01	169.46	168.15	194.82	211.16
Amyltetryl	171.00	177.09	211.32	218.85	147.53	164.34	175.80	195.48
(b)								
Compound	* P(D _{1I}), kbar	P(D _{1II}), kbar	P(D _{2I}), Kbar	P(D _{2II}), kbar	P(D _{3I}), kbar	P(D _{3II}), kbar	P(D _{4I}), kbar	P(D _{4II}), kbar
Bis-tetryl-CH ₂	384.62	324.43	476.26	425.53	363.07	281.88	6362.59	282.09
Bis-tetryl-CH ₂ CH ₂	329.97	310.26	476.26	425.76	326.99	264.17	333.81	270.18
Bis-tetryl-CH ₂ CH ₂ CH ₂	308.98	293.21	431.50	400.01	296.36	247.88	308.40	258.32
Bis-tetryl-CH ₂ CH ₂ CH ₂ CH ₂	289.57	277.15	409.92	386.35	269.91	232.90	286.27	247.39
Bis-tetryl-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂	233.0	258.38	339.01	370.93	234.61	209.47	282.80	226.82
(c)								
Compound	* P(D _{1I}), kbar	P(D _{1II}), kbar	P(D _{2I}), kbar	P(D _{2II}), kbar	P(D _{3I}), kbar	P(D _{3II}), kbar	P(D _{4I}), kbar	P(D _{4II}), kbar
Tetryl #	289.38	286.11	331.73	318.37	274.22	263.95	282.59	272.11
3-Amino-tetryl * ¹	287.90	331.37	279.82	311.25	295.06	267.79	304.35	276.46
3-Amino- <i>N</i> -ethyltetryl	252.91	295.74	249.56	286.42	248.40	237.62	265.19	253.81
3-Amino- <i>N</i> -propyltetryl	222.53	264.78	222.49	263.70	211.96	211.82	234.12	233.96
3-Amino- <i>N</i> -butyltetryl	196.05	237.79	198.17	242.83	183.20	189.58	209.29	216.48
3-Amino- <i>N</i> -amyltetryl	225.83	176.24	263.07	218.35	133.33	170.30	158.01	200.99

* Here D_n, where *n* = 1–4, denotes the equation used to calculate detonation velocity, while “I” and “II” denote that detonation pressure obtained by density calculated by applying the approach implemented in ACD/Labs program and that suggested in [84], respectively. We remind one that the parameters of tetryl (Tetryl #) are included in the table to show the influence of the NH₂ substituent in a more suitable way. ¹ indicate that the parameters of conformer is presented.

4. Discussion

Let us remind the reader that our investigated compound could be addressed to C_aH_bN_cO_d group derivatives. Most often, this type of explosives generally have crystal densities of 1.7–1.9 g/cm³, and they are generally used at high fractions of theoretical maximum density [85]. According to our calculation results, the density of Bis-tetryl-CH₂ and Bis-tetryl-CH₂CH₂ is higher than 1.9 g/cm³, while that of 3-Amino-*N*-butyltetryl, Amyltetryl, and Butyltetryl are lower than 1.7 g/cm³. Thus, the densities obtained by using the approach implemented in ACD/Labs laboratory could be overestimated or undervalued, more probably in the case of insufficient data in the database implemented. The results have been considered when the detonation pressure and velocity were evaluated and compared.

The hardness index of 0.80–0.90 indicates that the compounds under investigation are chemically and thermally stable. The binding energy per atom revealed that the thermal stability of the compound investigated also increased when the CH₂ chain length increased. It occurred in all compounds investigated. We did not find strict dependence of the chemical stability of the compound under study on the -CH₂ length. Referring to the results presented in Table 1, we may state that chemical stability is related to the geometrical structure of the compound, for example, the conformers of 3-Amino-tetryl with different bending of NO₂-N-CH₃ substitution. The analysis of values of chemical hardness, softness, and electronegativity indicates that one of these conformers (3-Amino-tetryl) is more resistant to deformation or change than another (3-Amino-tetryl *), better attracting shared electrons (or electron density) when forming a chemical bond. Briefly, the bonding

chemical reactions should be faster if 3-Amino-tetryl will be involved in them; however, 3-Amino-tetryl * activation could be easier than that of 3-Amino-tetryl. We speculate that the occurrence of less stable conformers could lead to faster aging of this type of explosives.

The bending, not only of the abovementioned substitution but also of the $-\text{CH}_2$ chain, could lead to higher stability. The parameters revealing the stability of the (b) compound group clearly indicate this finding. In the case when the CH_2 chain is bending in this way, the initial (gem/mother) molecules displace above each other (see Figure 1, $n = 1, 3$ cases), and the chemical and thermal stabilities of the compounds increase.

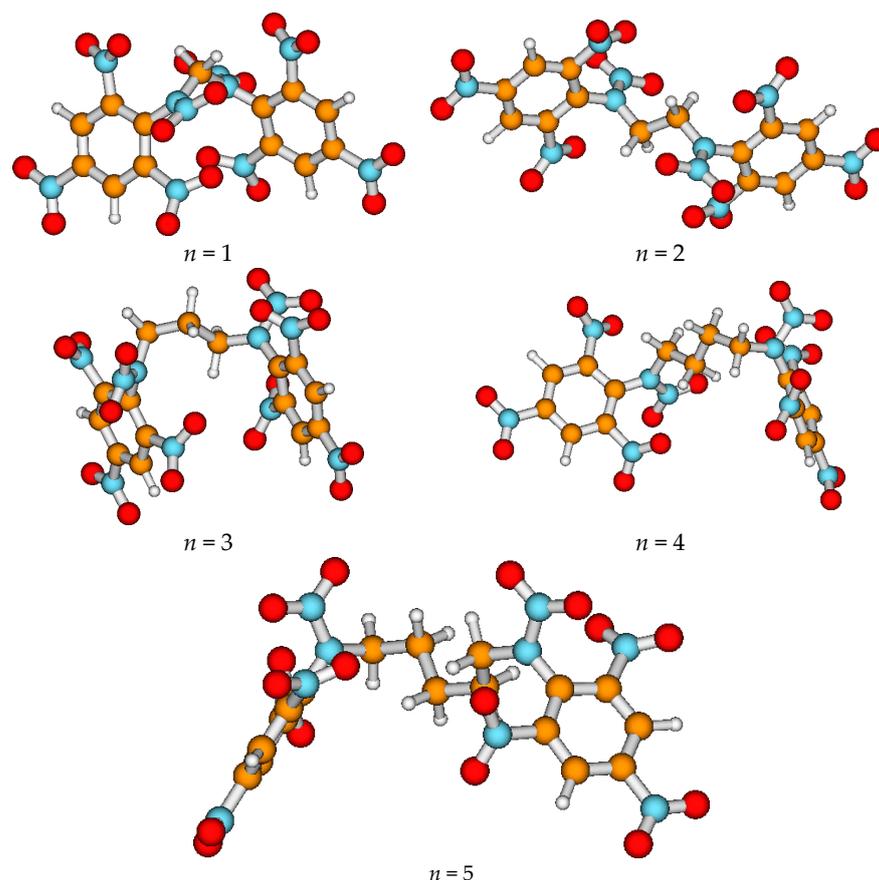


Figure 1. Views of the most stable conformers of bis-aromatic homologs of chain length variation $(\text{CH}_2)_n$ ($n = 1-5$) of $[(2,4,6\text{-trinitrophenyl-N}(\text{NO}_2))_2(\text{CH}_2)_n]$. The Figure was drawn by Molden [86].

The values of oxygen balance representing the brisance, strength, and sensitivity to shock stimuli increase with the enlargement of the CH_2 chain length in the compound investigated (Table 2). It allows us to conclude that the brisance and strength of the materials under study tend to approach their maxima as the oxygen balance approaches a more negative value. The \log_1 and \log_2 values revealed that the $-\text{CH}_2$ chain length of Tetryl leads to higher resistance to shock stimuli. Let us remind the reader that the value of the oxygen balance of TNT, which is considered a standard reference for many purposes, is equal to -74% [87]. Thus, the properties of the HEMs' power of group (a) and (c) materials are greater than TNT when the number of $-\text{CH}_2$ is smaller than 3. However, these materials are more sensitive to stimuli than indicated by the calculated values of \log_1 and \log_2 . In the case of group (b) materials, the abovementioned parameter's values indicate their better energetic properties and higher sensitivity than TNT, but these properties are worse than nitromethane (oxygen balance -39%), and PETN (-10%), along with higher resistance to the shock stimuli. The comparison of the parameters representing the effectiveness of explosion and resistance for stimuli of the (a) and (c) group materials leads to a conclusion that the inclusion of NH_2 insignificantly changes explosive properties and resistance to

shock stimuli. It leads to a presumption that certain combinations of substituents and CH₂ could allow one to design brisance and insensitive materials.

The calculated values of detonation velocity and pressure (Tables 3 and 4) also revealed the worseness of the energetic properties with increasing -CH₂ chain length. These results show that an increasing -CH₂ chain length leads to decreasing in detonation velocity and pressure, which indicates a decrease in explosive effectiveness. The exception is the cases when the density of the materials is inaccurately calculated due to a lack of data in the database used. However, considering the 6.9 km/s detonation velocity of TNT [88] (in comparison to our calculated 7.31–7.69 km/s), we could foresee that (b) materials possess better energetic properties than TNT despite their worseness due to -CH₂ chain length increases. In the case of (a) and (c) group materials, the above properties remain better than those of TNT when the -CH₂ number in the compound is not larger than 3. Moreover, the detonation velocities for high explosives range from 3300 to 29,900 fps (1.01 to 9.11 km/s). Hence, the results obtained indicate that the compounds under investigation remain highly energetic despite the decrease in explosive effectiveness due to CH₂ chain length increases. This conclusion is also supported by the results of the detonation pressure calculations that showed that values are higher than those of TNT in most of the material investigated. For comparison, the detonation pressure of TNT is equal to 171.8 kbar in a liquid state [89] and 213–259 kbar in a solid state, and is used as a standard; the detonation pressure evaluated by us varies from 133 to 364 kbar. However, only group (a) and (b) materials' detonation pressures are below that of TNT when the CH₂ number in the chain is higher than 3, and these values depended on the approach used. Hence, as is mentioned above, increasing CH₂ chain length in the Tetryl should increase the stability of the compounds more significantly than worsening the explosion properties.

5. Conclusions

Our study was performed to reveal if and how varying lengths of the CH₂ (methylene) chain, attached to the nitramine group nitrogen gaining, improves the stability and resistance for shock stimuli as well as explosive properties of the series of secondary aromatic nitramines, possessing as the main substituents traditional 2,4,6-trinitrophenyl moiety. Referring to the results obtained, we may state that the thermal stability and resistance to shock stimuli of the compound investigated are directly dependent on the CH₂ chain length, while their explosive properties are worsened due to this chain lengthening. The results of our study also show that the case of Tetryl with different -CH₂ chain lengths ($n = 1-5$) [(2,4,6-trinitrophenyl-(O₂N)N(CH₂)_n H)] ((a) group) could not be longer than 3 in order for the detonation pressure of these compound not to be below that of TNT. A similar conclusion follows from the results of the investigation of Bis-aromatic nitramine homologs of chain length variation (CH₂)_n of [(2,4,6-trinitrophenyl-N(NO₂))₂(CH₂)_n ($n = 1-5$)- joined per different lengths of the -CH₂ chain ((b) group). However, the stability of the compounds increases more significantly than the worsening of the explosive properties. These results were proven by the different approaches applied.

Author Contributions: Conceptualization, J.S. and J.T.; methodology, J.T.; validation, J.S. and J.T.; formal analysis, J.S. and J.T.; investigation, J.S.; resources, J.T.; data curation, J.S. and J.T.; writing—original draft preparation, J.S. and J.T.; writing—review and editing, J.S. and J.T. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data supporting the reported results can be received upon request from the authors.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1. The values of density for the studied compounds, obtained using the approach implemented in the ACD/Labs program (denoted as ρ_1) and that suggested by M.S. Keshavarz (denoted as ρ_2).

Compound	$\rho_1, \text{g/cm}^3$	$\rho_2, \text{g/cm}^3$	Deviation, %
2,4,6-Trinitrophenyl- <i>N</i> -nitramine	1.574	1.642	-4.30
Tetryl	1.803	1.769	1.87
Ethyltetryl	1.713	1.723	-0.57
Propyltetryl	1.523	1.606	-8.30
Butyltetryl	1.639	1.680	-2.53
Amyltetryl	1.870	1.782	4.69
Bis-tetryl-CH ₂	2.041	1.800	11.80
Bis-tetryl-CH ₂ CH ₂	1.973	1.775	10.03
Bis-tetryl-CH ₂ CH ₂ CH ₂	1.913	1.751	8.4
Bis-tetryl-CH ₂ CH ₂ CH ₂ CH ₂	1.859	1.728	7.04
Bis-tetryl-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂	1.765	1.669	5.45
3-Amino-tetryl	1.870	1.782	4.69
3-Amino- <i>N</i> -ethyltetryl	1.776	1.737	2.17
3-Amino- <i>N</i> -propyltetryl	1.697	1.696	0.03
3-Amino- <i>N</i> -butyltetryl	1.631	1.659	-1.70
3-Amino- <i>N</i> -amyltetryl	1.765	1.669	5.45

Appendix B

Table A2. The view of the molecules belonging to (a) Homologous aromatic *N*-nitramines, tetryl derivatives [(2,4,6-trinitrophenyl-(O₂N)N(CH₂)_n H, $n = 0-5$]. (b) Bis-aromatic homologs of chain length variation (CH₂)_n of [(2,4,6-trinitrophenyl-N(NO₂))₂, (CH₂)_n ($n = 1-5$)]. (c) 3-Amino derivatives of tetryl with chain length variation [(3-amino-2,4,6-trinitrophenyl-(O₂N)N(CH₂)_n H, $n = 1-5$)] homologs. their names, structures, chemical compositions and molecular weights (g/mol).

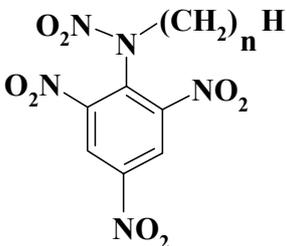
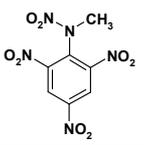
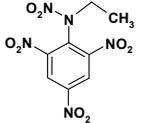
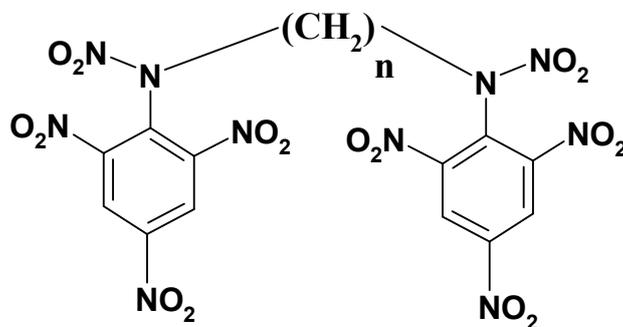
(a)					
No.	Name	Structural Formula	Molecular Formula	Molecular Weight	Molecular Composition
1.	2,4,6-Trinitrophenyl- <i>N</i> -nitramine $n = 0$		C ₆ H ₃ N ₅ O ₈	273.12	C 26.39% H 1.11% N 25.64% O 46.86%
2.	Tetryl $n = 1$		C ₇ H ₅ N ₅ O ₈	287.15	C 29.28% H 1.76% N 24.39% O 44.57%
3.	Ethyltetryl $n = 2$		C ₈ H ₇ N ₅ O ₈	301.17	C 31.90% H 2.34% N 23.25% O 42.50%

Table A2. Cont.

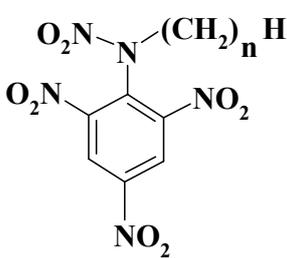
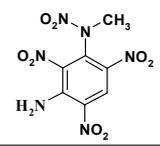
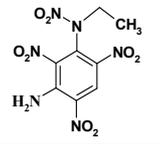
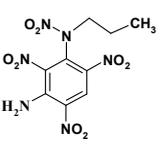
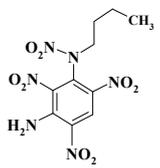
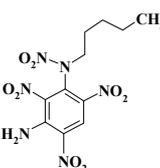
4.	Propyltetryl $n = 3$		$C_9H_9N_5O_8$	315.20	C	34.30%
					H	2.88%
					N	22.22%
					O	40.61%
5.	Butyltetryl $n = 4$		$C_{10}H_{11}N_5O_8$	329.23	C	36.48%
					H	3.37%
					N	21.27%
					O	38.88%
6.	Amyltetryl $n = 5$		$C_{11}H_{13}N_5O_8$	343.25	C	38.49%
					H	3.82%
					N	20.40%
					O	37.29%

(b)



No.	Name	Structural Formula	Molecular Formula	Molecular Weight	Molecular Composition	
1.	Bis-tetryl- CH_2 $n = 1$		$C_{13}H_6N_{10}O_{16}$	558.25	C	27.97%
					H	1.08%
					N	25.09%
					O	45.86%
2.	Bis-tetryl- CH_2CH_2 $n = 2$		$C_{14}H_8N_{10}O_{16}$	572.28	C	29.38%
					H	1.41%
					N	24.48%
					O	44.73%
3.	Bis-tetryl- $CH_2CH_2CH_2$ $n = 3$		$C_{15}H_{10}N_{10}O_{16}$	586.30	C	30.73%
					H	1.72%
					N	23.89%
					O	43.66%
4.	Bis-tetryl- $CH_2CH_2CH_2CH_2$ $n = 4$		$C_{16}H_{12}N_{10}O_{16}$	600.33	C	32.01%
					H	2.01%
					N	23.33%
					O	42.64%
5.	Bis-tetryl- $CH_2CH_2CH_2CH_2CH_2$ $n = 5$		$C_{17}H_{14}N_{10}O_{16}$	614.36	C	33.24%
					H	2.30%
					N	22.80%
					O	41.67%

Table A2. Cont.

(c)													
													
No.	Name	Structural Formula	Molecular Formula	Molecular Weight	Molecular Composition								
1.	3-Amino-tetryl $n = 1$		$C_7H_6N_6O_8$	302.16	<table border="1"> <tr><td>C</td><td>27.83%</td></tr> <tr><td>H</td><td>2.00%</td></tr> <tr><td>N</td><td>27.81%</td></tr> <tr><td>O</td><td>42.36%</td></tr> </table>	C	27.83%	H	2.00%	N	27.81%	O	42.36%
C	27.83%												
H	2.00%												
N	27.81%												
O	42.36%												
2.	3-Amino-N-ethyltetryl $n = 2$		$C_8H_8N_6O_8$	316.19	<table border="1"> <tr><td>C</td><td>30.39%</td></tr> <tr><td>H</td><td>2.55%</td></tr> <tr><td>N</td><td>26.58%</td></tr> <tr><td>O</td><td>40.48%</td></tr> </table>	C	30.39%	H	2.55%	N	26.58%	O	40.48%
C	30.39%												
H	2.55%												
N	26.58%												
O	40.48%												
3.	3-Amino-N-propyltetryl $n = 3$		$C_9H_{10}N_6O_8$	330.22	<table border="1"> <tr><td>C</td><td>32.74%</td></tr> <tr><td>H</td><td>3.05%</td></tr> <tr><td>N</td><td>25.45%</td></tr> <tr><td>O</td><td>38.76%</td></tr> </table>	C	32.74%	H	3.05%	N	25.45%	O	38.76%
C	32.74%												
H	3.05%												
N	25.45%												
O	38.76%												
4.	3-Amino-N-butyltetryl $n = 4$		$C_{10}H_{12}N_6O_8$	344.24	<table border="1"> <tr><td>C</td><td>34.89%</td></tr> <tr><td>H</td><td>3.51%</td></tr> <tr><td>N</td><td>24.41%</td></tr> <tr><td>O</td><td>37.18%</td></tr> </table>	C	34.89%	H	3.51%	N	24.41%	O	37.18%
C	34.89%												
H	3.51%												
N	24.41%												
O	37.18%												
5.	3-Amino-N-amyltetryl $n = 5$		$C_{11}H_{14}N_6O_8$	358.27	<table border="1"> <tr><td>C</td><td>36.88%</td></tr> <tr><td>H</td><td>3.94%</td></tr> <tr><td>N</td><td>23.46%</td></tr> <tr><td>O</td><td>35.73%</td></tr> </table>	C	36.88%	H	3.94%	N	23.46%	O	35.73%
C	36.88%												
H	3.94%												
N	23.46%												
O	35.73%												

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