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Research paper

N-N Bond Lengths and Initiation Reactivity of Nitramines

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Abstract: For the 16 selected nitramines, it is shown that an increase in the energy content of these molecules (represented by enthalpies of formation) is connected with an increase in the lengths of the longest N–N bonds in the molecules. These lengths are directly proportional to the activation energies of the low-temperature thermal decomposition of the pure nitramines in all states of matter for this reaction. Raising the energy content also leads to reductions in the rate constants of thermal decomposition. Both of these facts are in contrast to expectations and also with similar published findings concerning thermal decomposition of nitramines in solution, which can be explained by the solvation effect and termination of the emerging aza-radicals in solutions. The calculated dissociation energies of the weakest N–N bonds yielded a relatively good reciprocal conformity with the lengths of the longest N–N bonds of the nitramines studied, especially when using the UB3LYP/6-31G* method. The relationship between the impact sensitivity of these nitramines and the lengths of their longest N–N bond is not completely clear. Such lengths cannot be a measure of impact reactivity, because the longest N–N bond might be stabilized in some cases by suitable intermolecular interactions with adjacent molecules in the crystal lattice.

Keywords: bond length, impact sensitivity, nitramines, reactivity, thermal decomposition, X-ray analysis

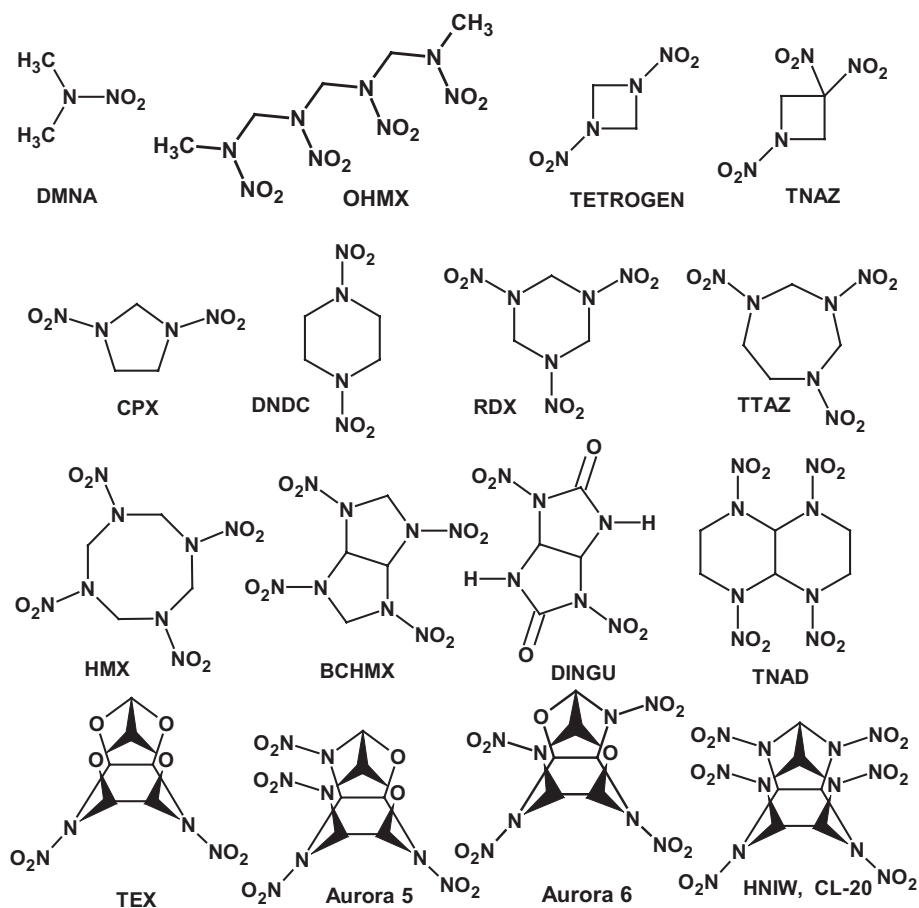
1 Introduction

It is intuitively possible to state that the greater the length of the N-N bond in nitramine molecules, the greater will be their initiation reactivity. We have tentatively addressed this problem in reference [1], in which we found a direct proportional relationship between the length of the longest N–N bond in a selection of nitramines and the activation energy (E_a) values of their low-temperature mono-molecular non-autocatalyzed decomposition in the condensed state. A recent response to the above cited paper claimed that a relationship between the E_a of decomposition and the length of the N–N bond in nitramines did not produce precise results [2], and another stated that this direct correlation failed because of the significant scattering of the experimental data [3]. The work described in the present study was designed to explore the reality of this relationship, taking a broader view of initiation reactivity. The fact that the initiation reactivity of energetic materials has a relationship, mostly inverse, to the molecules' energy content [4-6] needs to be taken into account. To this end, we have taken advantage of a considerable amount of information/data compared with reference [1], and in our work we have used enthalpies of formation (as representative of the energy content), kinetic data for low temperature decomposition and impact sensitivity. This approach corresponds to that of Physical Organic Chemistry.

2 Data Sources

2.1 Nitramines studied

The data used for the study of each nitramine were taken from published literature and are grouped in Tables 1 and 2 (see p. 2.2 and 2.5, respectively). The individual nitramines studied are shown in Scheme 1:



Scheme 1. Structural formulae of the nitramines studied, see Table 1

2.2 Bond dissociation energies

The calculations of *BDEs* were performed by means of the UB3LYP/6-31G* and UB3LYP/6-31+G*//PM3 (UHF) methods [7, 8] in reference [9]: the values obtained by these two methods for isolated molecules are denoted by the codes *BDE^a* and *BDE^b*, respectively and are included in Table 1. All of these calculations were performed using the Spartan 06 package program [7]. On the basis of X-ray measurements of 1,3,5-trinitro-1,3,5-triazepane (TTAZ, Figures 3(b) and 11), the *BDE^a* value was calculated for its dimer only, by means of the UB3LYP/6-31G* method; the results are collected in Table 2.

Table 1. A list of the nitramines studied, with their impact sensitivities and the bond dissociation energies, BDE^a and BDE^b , of the weakest N–N bonds

Data No.	Chemical name of nitramine	Code designation	Impact sensitivity		Bond dissociation energy	
			E_{th} [J]	Ref.	BDE^a	BDE^b
1	2-Nitro-2-azapropane	DMNA	49.0*	[10]	172.3	161.6
2	2,4,6,8-Tetranitro-2,4,6,8-tetraazanone	OHMX	9.5	[11]	154.8	134.1
3	1,3-Dinitro-1,3-diazetidene	TETROGEN	9.9	[12]	145.8	147.7
4	1,3,3-Trinitroazetidene	TNAZ	6.9	[13]	160.1	158.8
5	1,3-Dinitroimidazolidine	CPX	17.9	[9]	142.6	134.2
6	1,4-Dinitropiperazine	DNDNC	11.6		171.0	179.1
7	1,3,5-Trinitro-1,3,5-triazinane	RDX	5.6	[14]	153.6	174.5
8	1,3,5-Trinitro-1,3,5-triazepane	TTAZ	4.5	[9]	152.1	145.3
9.1	β -1,3,5,7-Tetranitro-1,3,5,7-tetraazocane	β -HMX	6.4	[14]	153.7**	135.6**
9.2	α -1,3,5,7-Tetranitro-1,3,5,7-tetraazocane	α -HMX	1.9	[9]	153.7**	135.6**
10	<i>cis</i> -1,3,4,6-Tetranitrooctahydro-imidazo[4,5-d]-imidazole	BCHMX	3.0		140.3	131.9
11	1,4-Dinitrotetrahydroimidazo-[4,5-d]imidazol-2,5(1 <i>H</i> ,3 <i>H</i>)dione	DINGU	24.6	[14]	159.7	126.7
12	<i>trans</i> -1,4,5,8-Tetranitrodecahydro-pyrazino[2,3- <i>b</i>]-pyrazine	TNAD	8.6	[15]	137.0	98.4
13	4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane	TEX	23.0	[16]	173.1	166.8
14	4,8,10,12-Tetranitro-2,6-dioxa-4,8,10,12-tetraaza-isowurtzitane	Aurora-5, TNIW-5	12.5	[9]	146.1	165.4
15	4,6,10,12-Tetranitro-2,8-dioxa-4,6,10,12-tetraaza-isowurtzitane	Aurora-6, TNIW-6	12.2		146.8	152.4
16.1	ε -2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane	ε -HNIW	13.4	[17]	148.9**	139.9**
16.2	α -2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane	α -HNIW	10.2		148.9**	139.9**

Note: * according to reference [10], the actual sensitivity should be much lower; ** the DFT methods used are not able to differentiate between the polymorphic modifications in the corresponding BDE values

2.3 X-Ray crystallographic data

The longest N-N bond in each nitramine studied was obtained from the literature and are all collected in Table 2. The unpublished lengths for TTAZ and 1,3-dinitroimidazolidine (CPX) were determined as described below.

2.3.1 X-ray crystallographic study of 1,3,5-trinitro-1,3,5-triazepane and 1,3-dinitroimidazolidine

Full sets of diffraction data for 1,3-dinitroimidazolidine (CPX) and 1,3,5-trinitro-1,3,5-triazepane (TTAZ) were collected at 150(2) K with a Bruker D8-Venture diffractometer equipped with Mo (Mo/K α radiation; $\lambda = 0.71073$ Å) microfocus X-ray ($I\mu$ S) source, Photon CMOS detector. An Oxford Cryosystems cooling device was used for data collection.

The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The data obtained were processed by XT-version 2014/5 and SHELXL-2014/7 software implemented in the APEX3 v2016.5-0 (Bruker AXS) system [18].

Hydrogen atoms were mostly localized on a Fourier difference map. However, in order to ensure uniformity of treatment of the crystals, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$ (pivot atom) or $1.5 U_{\text{eq}}$ (methyl). Hydrogen atoms in the methylene moiety were placed with C–H lengths of 0.97 Å.

Following relations were used:

$$R_{\text{int}} = \sum |F_o^2 - F_{o,\text{mean}}^2| / \sum F_o^2,$$

$$S = [\sum (w(F_o^2 - F_c^2)^2) / (N_{\text{diffrs}} \cdot N_{\text{params}})]^{1/2} \text{ for all data,}$$

$$R(F) = \sum | |F_o| - |F_c| | / \sum |F_o| \text{ for observed data,}$$

$$wR(F^2) = [\sum (w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{1/2} \text{ for all data.}$$

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 1900898-1900899 for CPX and TTAZ, respectively. Copies of this information may be obtained free of charge from reference [19].

Relevant crystallographic data and structural refinement parameters for CPX were:

- $\text{C}_3\text{H}_6\text{N}_4\text{O}_4$, $M = 162.12 \text{ g}\cdot\text{mol}^{-1}$,
- orthorhombic, $P2_12_12_1$, $a = 10.8571(6)$, $b = 10.8793(6)$, $c = 15.7917(8)$ Å, $\beta = 90^\circ$, $Z = 12$, $V = 1865.28(17)$ Å³, $D_c = 1.732 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 0.159 \text{ mm}^{-1}$, $T_{\text{min}}/T_{\text{max}} = 0.4759/0.7456$,
- $(-14) \leq h \leq 14$, $-14 \leq k \leq 14$, $-20 \leq l \leq 20$,

- 21896 reflections measured ($\theta_{\max} = 27.52^\circ$), 4274 independent ($R_{\text{int}} = 0.1075$), 3192 with $I > 2\sigma(I)$, 298 parameters, $S = 1.037$, $RI(\text{obs. data}) = 0.0564$, $wR2(\text{all data}) = 0.1295$;
- max., min. residual electron density = $0.390, -0.369 \text{ e} \cdot \text{\AA}^{-3}$.

Crystallographic data and structural refinement parameters for TTAZ were:

- $\text{C}_4\text{H}_8\text{N}_6\text{O}_6$, $M = 236.16 \text{ g} \cdot \text{mol}^{-1}$,
- monoclinic, $P2_1/n$, $a = 6.1092(7)$, $b = 10.0176(10)$, $c = 14.2186(18) \text{ \AA}$, $\beta = 95.902(4)^\circ$, $Z = 4$, $V = 865.56(17) \text{ \AA}^3$, $D_c = 1.812 \text{ g} \cdot \text{cm}^{-3}$, $\mu = 0.168 \text{ mm}^{-1}$, $T_{\text{min}}/T_{\text{max}} = 0.3893/0.7456$,
- $(-7) \leq h \leq 7$, $-13 \leq k \leq 13$, $-18 \leq l \leq 18$,
- 9279 reflections measured ($\theta_{\max} = 27.52^\circ$), 1981 independent ($R_{\text{int}} = 0.0303$), 1876 with $I > 2\sigma(I)$, 146 parameters, $S = 1.069$, $RI(\text{obs. data}) = 0.0332$, $wR2(\text{all data}) = 0.0786$,
- max., min. residual electron density = $0.348, -0.207 \text{ e} \cdot \text{\AA}^{-3}$.

Figures 1 and 2 represent the molecular structures obtained for CPX and TTAZ respectively, Figures 3(a) and 3(b) show the corresponding supramolecular architectures of these two nitramines, respectively.

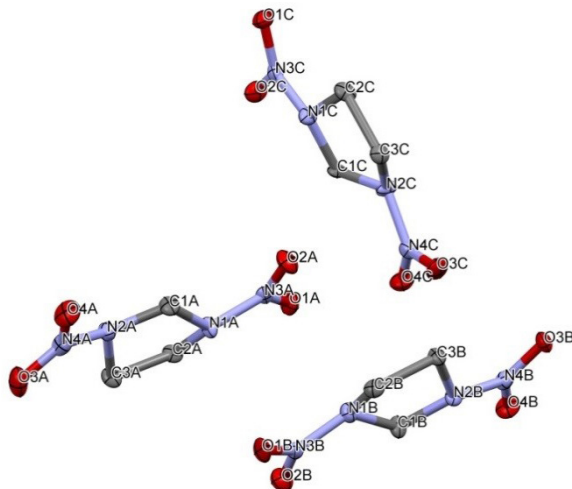


Figure 1. Molecular structure of 1,3-dinitroimidazolidine (CPX) (ORTEP view, 50% probability level); hydrogen atoms are omitted for clarity; selected interatomic distances [\AA]: N2A–N4A 1.350(5), N1A–N3A 1.348(6), N1B–N3B 1.351(6), N2B–N4B 1.347(5), N1C–N3C 1.352(6), N2C–N4C 1.343(5)

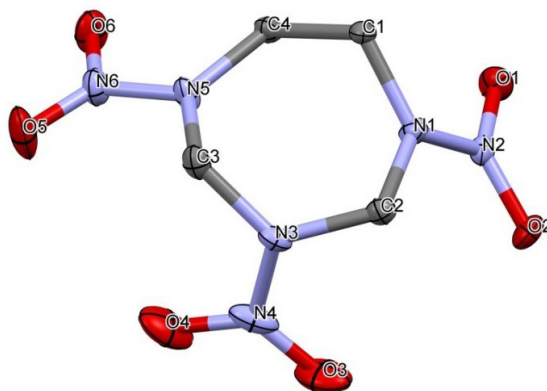


Figure 2. Molecular structure of 1,3,5-trinitro-1,3,5-triazepane (TTAZ) (ORTEP view, 50% probability level); hydrogen atoms are omitted for clarity; selected interatomic distances [Å]: N1–N2 1.3532(14), N3–N4 1.3869(14), N5–N6 1.3562(14)

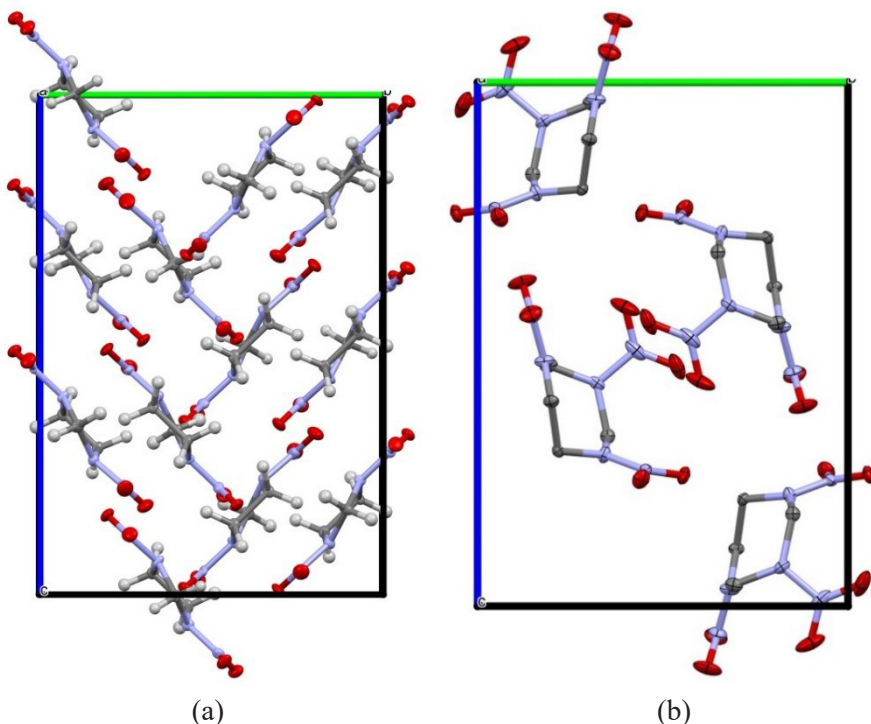


Figure 3. Supramolecular architecture (ORTEP view, 50% probability level) for CPX along a-axis (a) and TTAZ along c-axis (b)

2.4 Impact sensitivity data

The impact sensitivity data in Table 1 (expressed as drop energy, E_{dr} , in J) were taken from the published literature: they were obtained by means of a standard impact tester with an exchangeable anvil (Julius Peters), the detection of the 50% probability of initiation being based on the sound effect (Bruceton method) – see references in Table 1. The most serious data based on sound detection measurements come from the Los Alamos National Laboratory, Naval Surface Weapons Center and/or Lawrence Livermore National Laboratory (see in reference [6] and references therein). In our laboratory, we selected the published impact sensitivity results and those obtained by us and other groups on the basis of their correlation with the NMR chemical shifts of those atoms bearing the most reactive nitro group in the molecule [6, 20].

2.5 Thermoanalytical data

The thermoanalytical data used for the study of the individual nitramines were taken from published literature and are collected in Table 2 for the two Arrhenius parameters for mono-molecular decomposition. The majority of the data was obtained by the Russian isothermal manometric (RMM) method, making use of Bourdon's glass compensation manometer [21]. These data are known to correspond to the primary non-autocatalyzed stage of thermal decomposition of the energetic materials (references [20-22] and references therein). This table also includes collected published values of the enthalpies of formation in the condensed state.

3 Results and Discussion

3.1 Energy content of molecules

It is well-known that increasing the explosive strength of a molecule is usually accompanied by an increase in its sensitivity and therefore an insensitive explosive will not exhibit the greatest explosive strength [4]. It is possible to demonstrate this with PBXs filled with technically attractive cyclic nitramines [5, 6]. The sensitivity of any given Energetic Material (EM) should be directly proportional to the length of the weakest bond in its molecule; applying this to nitramines means the length of the N–N bond. On the basis of this, it should be valid that an increase in the length of the trigger N–N bond in nitramines should be related to an increase in the energy content of these molecules. The molecular energy content can be represented

by the enthalpy of formation (here in the condensed state). As Figure 4 shows, there exists a semi-logarithmic relationship between this enthalpy and the longest length of the N–N bond. It is interesting that, in the sense of this figure, both the experimental and calculated lengths of the N–N bonds correlate, except in the case of Tetrogen. This relationship thus corresponds to expectations.

The N–N bond lengths at the 2,4,6,8 positions of the ε -HNIW molecule lie in a relatively broad range, from 138.0 to 143.6 pm [49], whereas the maximum length of a single N–N bond should be 142.5 pm [41]. The fact that the data for ε -HNIW lie at the intersection of the partial dependencies in Figure 4, confirms that this substance represents an explosive with the highest energy content of the cyclic nitramines, which corresponds with reality.

3.2 Thermal decomposition

A simple comparison of the activation energies, E_a , with the lengths of the longest N–N bond is shown in Figure 5. Due to the molecular-structural similarity and the various states of thermal decomposition (solid or liquid state, pre-melting or dissolved in intermediates of decomposition, *etc.*), the relationship obtained is not unambiguous. Figure 5 is very strongly reminiscent of a similar relationship between the E_a values and the crystal lattice free volume (ΔV) values [67]. The straight lines **I** and **II** correspond in the present case to the decomposition of nitramines in the solid state. By further comparison with the results of reference [68], the straight lines **III** and **IV** in Figure 5 associated with nitramines in which it is not entirely clear in what physical state they were in (micro-regions in their crystals) during the initial phase of their thermal decomposition (similar to the case in reference [68]), and line **V**, should correspond to molecules decomposed in the gaseous state, even if, for HNIW, a solid state is reported in the literature (see data 16.1 and 16.2 in Table 2); it is well-known that thermolysis of HNIW is certainly influenced by cracking of its crystals during the *epsilon-gamma* polymorphic transition, its level of purity, its sublimation during measurement and flaws in its crystal lattice (see reference [67] and references therein). For the case of thermal decomposition in the gas phase, the lengths of the optimized N–N bonds for isolated HNIW molecules are also assigned to this straight line. When experimental X-ray data were unavailable, the optimized length of the N–N bond was used, as also for DNDC (see Table 2). In addition, comparison with the relationships mentioned in reference [67], group **VI** in Figure 5 corresponds to decomposition in the gas phase; data for TNAZ are presented here twice, once for the length of the N–N bond in the crystal, and secondly with an optimized length for possible gas phase decomposition (due to the high volatility of this nitramine

Table 2. List of the Arrhenius parameters (E_a and $\log A$) of the unimolecular thermal decomposition, the longest N–N bond lengths in molecules of the nitramines studied and their enthalpies of formation in the condensed state

Data No.	Code designation	Arrhenius parameters of thermolysis					The longest N–N bond			Enthalpy of formation		
		Resulted from	For the state	Temperature region [K]	E_a [kJ·mol ⁻¹]	$\log A$ [s ⁻¹]	Ref.	Length [pm]	Note	Ref.	ΔH_f [kJ mol ⁻¹]	Ref.
1	DMNA	IR	solid	298	192.5	14.2	[17]	133.2	–	[40]	-71.54	[52]
		NMR	liquid	–	159.8	14.7	[23]					
2	OHMX	NMR	solid	–	202.2	17.6	[24]	135.8	position 2 in molecule	[41]	19.66	[52]
		NMR	liquid	–	180.6	16.4						
3	TETROGEN	calcd.	–	–	153.1	14.1	[25]	135.5	HF/6-31G*	[25]	217.47	[25]
								141.2	extrapolated	[25] ^a		
4	TNAZ	DSC	liquid	400-510	161.6	15.7	[26]	135.1	crystal	[42]	26.82	[57]
								139.3	B3LYP/6-31G(d,p)	[64]		
5	CPX	RMIM	liquid	423-473	155.2	13.5	[27]	134.3	3-21G optimization	[41]	-5.94	[55]
								135.0	X-ray	[41] ^b		
6	DNDC	RMIM	liquid	489-507	198.4	17.3	[27]	137.3	isolated molecule, 3-21G optimization	[43]	-53.1	[57]
7	RDX	manom	solid	423-476	217.6	19.1	[32]				66.2	[58]
7.1		RMIM	gas	443-473	146.4	13.5	[31]	141.4	gas phase	[65]		
7.2		RMIM	DNB ^c sol	433-473	166.1	14.3	[3]	–	–	–		
8	TTAZ	RMIM	DCP ^d sol	474-553	173.7	15.4	[36]	138.7	–	this paper ^b		
								137.7	extrapolated	[1]	22.44	–

9	β -HMX	manom.	solid	544-587	220.5	19.5	[34]	equatorial N-N bond of δ -polymorph	[40]	77.3	[58]	
		MS	solid	534-549	209.0	17.8	[37]		[64]			
		DSC	^c	544-558	214.6	18.8	[38]					
10	α -HMX	RMM	gas	478-553	165.3	14.2	[31]	averaged optimized by B3LYP/6-31G(d)	[40]	-	-	
		RMM	solid	423-443	171.5	12.6	[39]	equatorial	[52]			
		manom	solid	453-473	210.2	18.0	[20]	position 1	[52]			236.5
10.1	BCHMX	RMM	DNB sol	418-463	170.0	15.8	[3]	-	-	-	-	
10.2		RMM	DBP ^e sol	413-458	165.0	15.0						
11	DINGU	RMM	solid	458-473	203.0	18.5	[44]	138.6	[29]	-343.7	[59]	
12	TNAD	DSC	solid	477-507	209.0	18.8	[45]	141.7	[54]	73.22	[15]	
13	TEX	RMM	"solid" ^f	483-498	196.8	15.4	[46]	141.4 140.0 ^f	[46]	-540.87	[60]	
		NMR	solid	-	213.9	-	[36]					
		RMM	gas	512-523	163.3	14.1	[46]					
13.1	TEX	RMM	DBP sol	483-523	158.1	13.2	[3]	141.4	[53]	-	-	
14.1	α -Aurora 5	RMM	solid	463-483	188.4	16.7	[47]	143.8	[47]	211.3	[61]	
14.2		RMM	DBP sol	423-453	162.9	15.2						
14.3	β -Aurora 5	RMM	solid	423-463	188.8	16.8	-	139.6	-	-	-	
15	Aurora 6	-	-	-	-	-	-	142.1	-	-	-	
16.1	ε -HNIW	TGA	solid	433-453	172.0	13.8	[26]	143.0	B3LYP/6-31G(d,p)	[63]	397.8	[58]
16.2		DSC	solid	483-533	176.0	15.1	[48]					
16.3		manom	solid	443-473	216.9	19.8	[49]					
16.4		iso-TGA	solid	446-484	223.4	20.5	[50]					
16.5		RMM	DNB sol	423-468	189.6	18.6	[3]					
16.6	γ -HNIW	iso-TGA	DBP sol	433-463	183.6	18.0	-	-	-	-	-	
16.6		iso-TGA	solid	445-467	196.0	17.7	[51]	144.0	position 2 in its molecule	[39]	338.99	[62]

Note: ^a estimated in this paper by means of a partial relationship between the logarithm of the length of the longest N-N bond and the enthalpy of formation in Figure 4; ^b determined in this paper, see Figure 1; ^c DNB means 1,3-dinitrobenzene; ^d DCP means dicyclohexyl phthalate; ^e DBP means dibutyl phthalate; ^f since the longest bonds in the optimized states for sterically crowded molecules are somewhat shorter (see the case of HNIW) we estimated a similar shortening for TEX

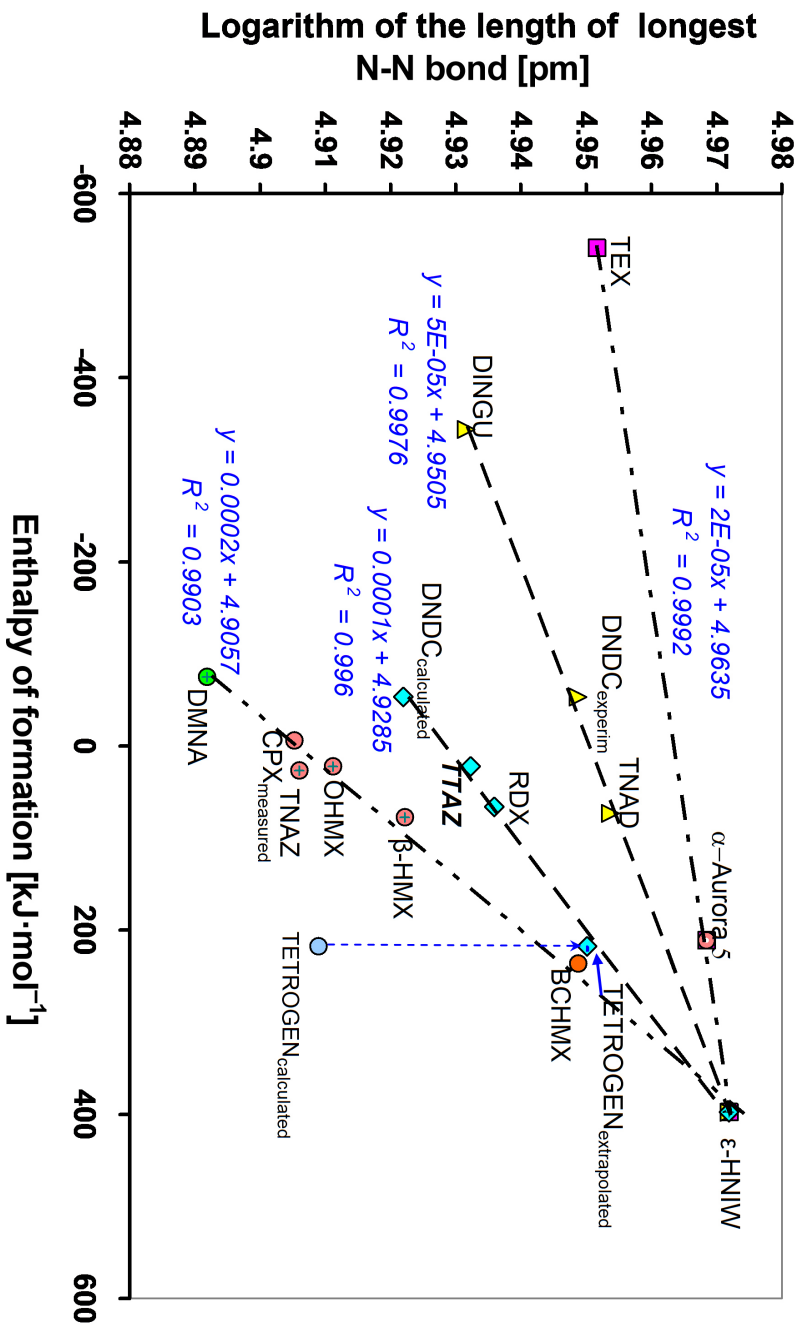


Figure 4. Semi-logarithmic comparison of lengths of the longest N-N bond with enthalpy of formation (as representative of the energy content of the molecule) of the nitramines studied; for TETROGEN the length of the N-N bond was found by extrapolation of the straight line HNIW-RDX-TTAZ-DNDNC_{calculated}

at temperatures around its melting point). In both kinds of dependency discussed here (*i.e.* Figure 5 and the one from reference [68]) it is important to notice that the nitramines appear as if divided into two groups, one derived from dimethylnitramine (DMNA) and one related to ε -2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (ε -HNIW).

The two dependencies mentioned here are quite similar to the older relationship between the E_a values and the sum of the negative and positive extremes of the molecular surface electrostatic potentials ($V_{s,\Sigma}$), of the nitramines studied [6, 69], but with a difference – instead of the two lines **I** and **II**, in the case referenced here, there is only one line which corresponds to nitramines decomposed in the solid state [6, 69].

In all three of the cases mentioned, increasing the $V_{s,\Sigma}$ [6, 69], ΔV [67] or the longest length of the N–N bond values, corresponds unequivocally to an increase in the activation energy of thermal decomposition. Particularly in the last case, this fact clearly highlights the opposite trend, contrary to logical expectations (including decomposition of nitramines in the gaseous state as Figure 5 indicates). In a similar (opposite) relationship, these lengths also correlate with the logarithm of the energies of the electric spark needed for initiation of the studied nitramines [70].

However, the relationship between the logarithm of the reaction rate constants (calculated from the Arrhenius parameters in Table 2 at 230 °C [65]) and the lengths of the longest N–N bond, as Figure 6 shows (thermal reactivity decreases with an increase in this length), exhibits an opposite trend, with one exception. An analogous relationship with the $V_{s,\Sigma}$ values [69] also exists, and a similar relationship with the ΔV variable, but the latter is fully unequivocal [67]. The mentioned exception (the straight line with positive slope) includes data for DMNA, RDX, HMX, TNAD, and HNIW, *i.e.* mostly nitramines which are a part of an exception also in the relations between logarithm of impact sensitivity and volumetric heat of explosion [6] and between impact sensitivity and free volume, ΔV [71]. Data around this “exceptional line” in Figure 6 could perhaps be connected with intramolecular influences on the reaction center in the molecule (the inductive effects) and relations with a negative slope might represent a dominant intermolecular influence on this centre (the influence of intermolecular forces). These facts and assumptions require examination by methods other than those within Physical Organic Chemistry (*i.e.* by Quantum Chemistry approaches, for example).

However, Nazin *et al.* [3] and Stepanov *et al.* [72] have found inverse proportional relationships between the E_a values of the thermal decomposition of nitramines in solution and the corresponding lengths of the longest N–N bond

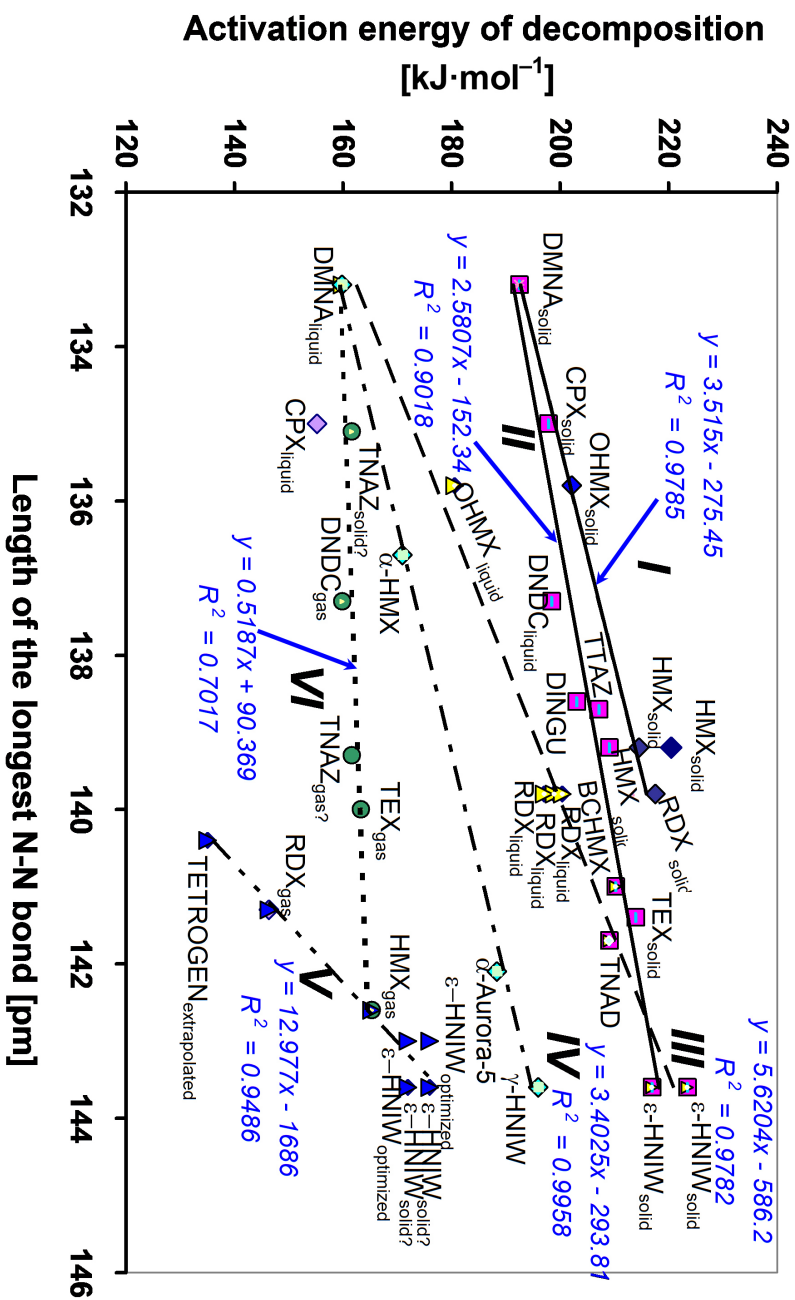


Figure 5. Simple comparison of the activation energies of thermal decomposition and the lengths of the longest N-N bond of the nitramines studied

in these molecules [3]. This is to be expected. Similarly, both Goncharov *et al.* [2] and Stepanov *et al.* [47, 72] have described directly proportional relationships between the logarithms of reaction constants of unimolecular decomposition in solvents (mainly phthalates, and di- and tri-nitrobenzenes) and such lengths in nitramines. It would seem that a basic difference between these various results and facts, represented by Figures 5 and 6, resides in the influence exercised by the nitramine molecule's closest neighbour in the solution (a solvation effect) on their thermal decomposition. For completeness, it should be added that a directly proportional dependence has been described between the $\log A$ values for thermal decomposition of nitramines in di- and tri-nitrobenzene solutions and the lengths of the N–N bonds [72].

3.3. Impact sensitivity

No unambiguous relationship exists between impact sensitivity, expressed as the drop energy (E_{dr}), and the lengths of the longest N–N bond in nitramines, as demonstrated by Figure 7. The expected dependencies are here created by the data files “CPX – DNDC – β -HMX – RDX – BCHMX”, “OHMX – β -HMX – RDX”, and also “DINGU – ε -HNIW – γ -HNIW”. Furthermore, a relationship between the E_{dr} values and the crystal lattice free volume values, ΔV , has been found to be equivocal [71]. An approach to an explanation of the dependencies with the mutually different slopes might be similar, as it is in the case of Figure 6, meaning on the basis of the dominance of induction effects (intramolecular factors) or the action of intermolecular forces (intermolecular factors) on the impact reactivity. It seems that for the interdependencies with negative slopes, there might be dominating intermolecular effects (nitramines with the more different molecular structures are associated here – in comparison with the relatively closely related structures of the nitraminic groups, enumerated above). However, for the attribution of individual types of dependence to the individually mentioned effects, approaches other than those provided by Physical Organic Chemistry should be used.

As the TTAZ case shows, the length of the longest N–N bond may not be related to the increased initiating reactivity of this particular nitramine; in the TTAZ molecule the most reactive nitramine grouping should be in position 1 [20, 22], which has been found from correlations of the ^{15}N NMR chemical shifts of the aza-atoms with impact sensitivity [6, 73], and with the kinetic parameters of thermal decomposition [20], or on the basis of the charges on nitro group correlations with thermal reactivity [20] or with electric spark sensitivity [74]. However, the longest N–N bond in the TTAZ molecule is at position 3 (bond N3–N4 in Figure 2).

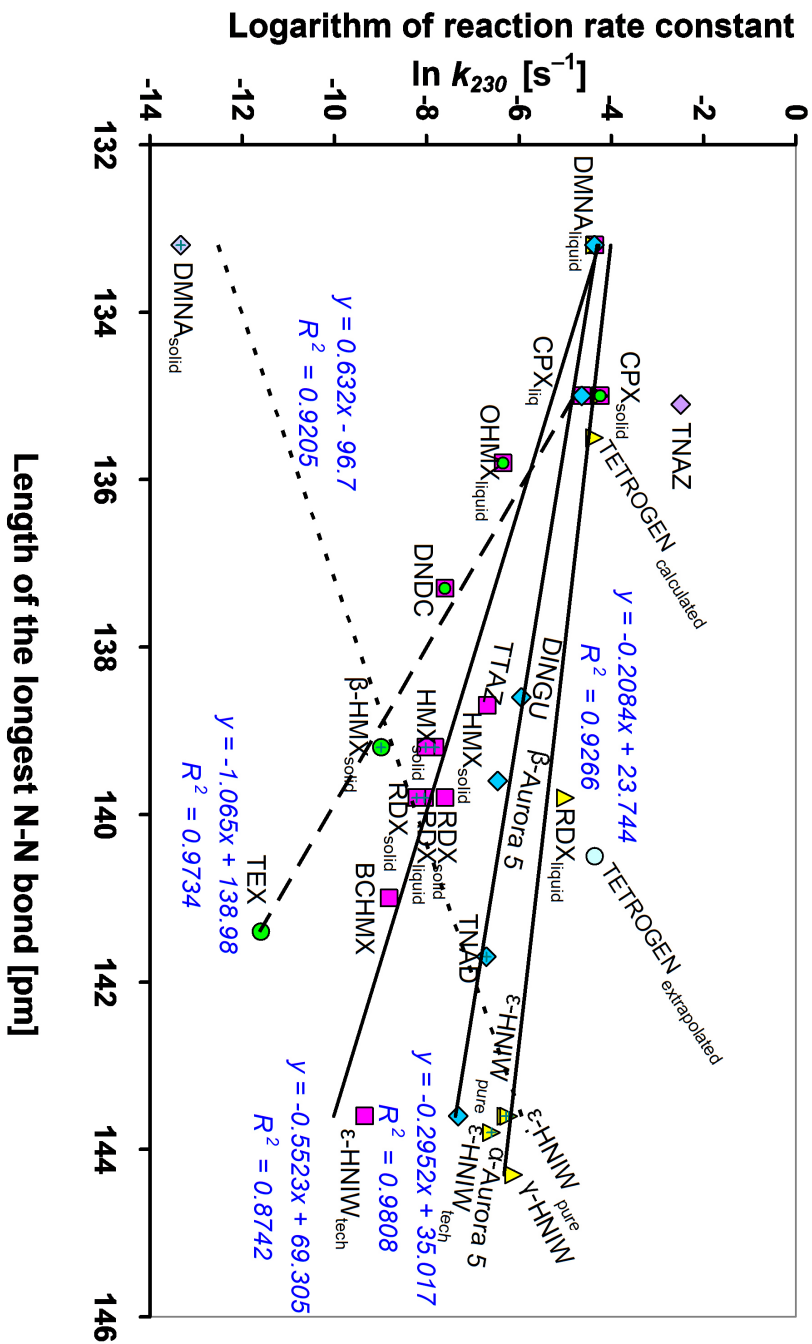


Figure 6. Semi-logarithmic relationship between the reaction rate constants for unimolecular thermal decomposition at 230 °C and the lengths of the longest N–N bond of the nitramines studied

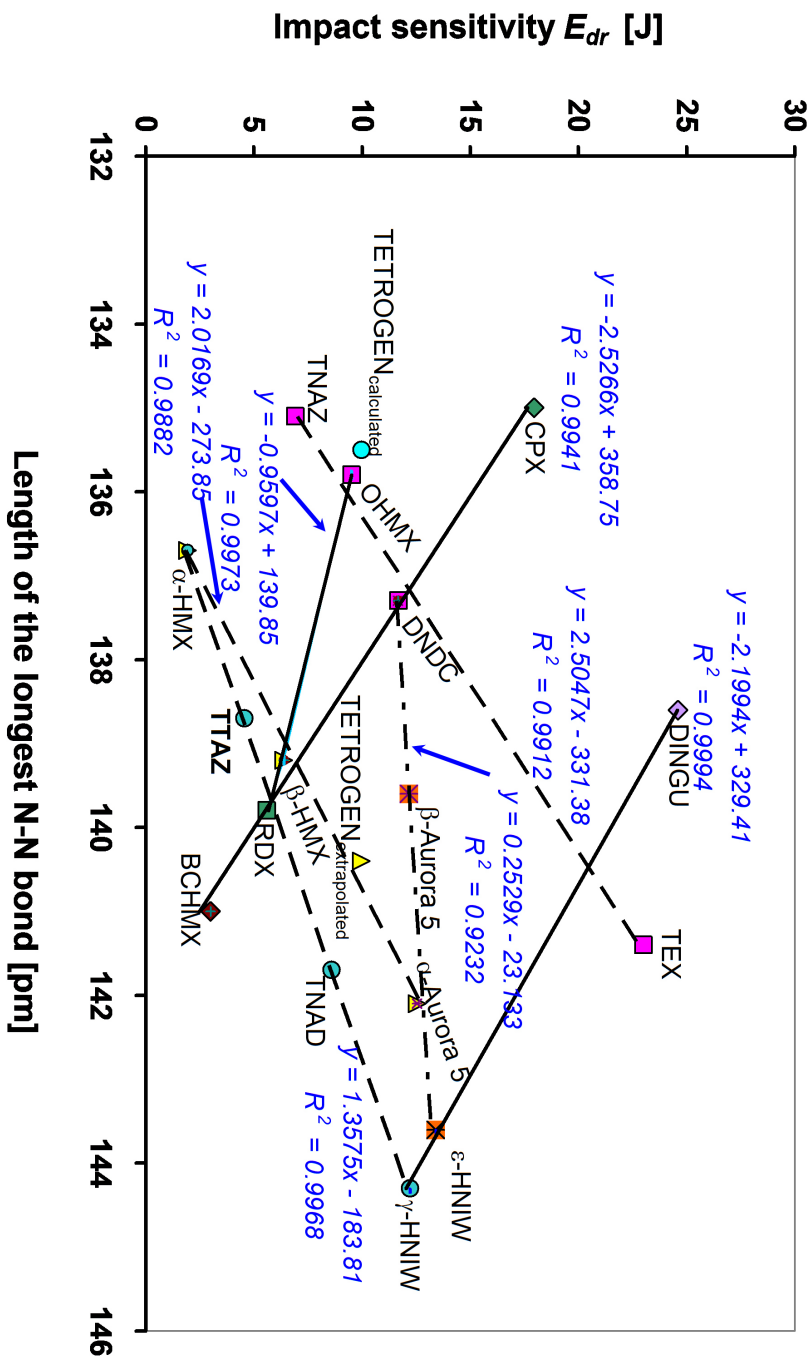


Figure 7. Simple comparison of impact sensitivity (expressed as drop energy, E_{dr} , in J) and the longest N-N bond of the nitramines studied

3.4 Bond dissociation energies

The semi-logarithmic relationship of the E_{dr} values on both bond dissociation energies (BDE^a and BDE^b) [9] has basically the generally expected form, *i.e.* an increase in impact sensitivity with a decrease in the BDE , but there is a group of nitramines (CPX, ε - and α -HNIW, RDX, TTAZ) for which this relationship exhibits the opposite trend. A simple comparison of these BDE values with the lengths of the longest N–N bonds gives Figures 8 and 9. Here, unexpectedly, partial relationships exist which have the opposite trend.

As expected, the BDE^a values provide a more logical dependency, as shown in Figure 8 (a longer length of the N–N bond in most cases corresponds to a decrease in BDE). On the other hand, a group of nitramines in Figure 9 appears as if divided into two groups, one derived from 1,4-dinitropiperazine (DNDC) and one related to 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW). At the same time the DNDC molecular skeleton forms a part of the global molecular skeleton of HNIW (and Aurora too). The trends of partial dependencies in Figure 9 are mostly within the bounds of expectation. A comparison with practice shows that the opposite trends in these Figures are not very far removed from the trends in the impact sensitivity of these nitramines (see Table 1); for example in Figure 9, for group “ β -HMX – Aurora 6 – Aurora 5”, their impact sensitivities decrease as follows: 6.4, 12.2 and 12.5 J, respectively [9]. This implies that this phenomenon needs more thorough exploration.

3.5 Peculiarities of the crystallography of CPX and TTAZ

The diffraction data for CPX were already known [3]. Based on the data deposited with the CCDC, we found that the interatomic distances between the nitrogen atoms within the nitramine grouping, N–NO₂, in each of the crystallographically independent molecules in Figure 1 show large differences. The first of these is the shortest to be found within the series of 481 nitramines found in the Cambridge Crystallographic Database, at 1.293 Å. The second moiety in the same molecule was found to be 1.412 Å (this was cited and used in reference [3]). Such a distance is a bit longer than the average calculated from the literature data – 1.35 Å, but shorter than the longest one – 1.476 Å [75]. In the second and the third molecules in this Figure, the discrepancies between the separations of the N–NO₂ bonds are not as large, but are still significant. Surprisingly, the structure determined by the new measurement at 150 K, instead of room temperature, revealed nearly equal unit cell parameters, with compression of the unit cell volume by about 2.6%. This particular change of parameters led obviously to a density increase from 1.688 to 1.732 g·cm⁻³.

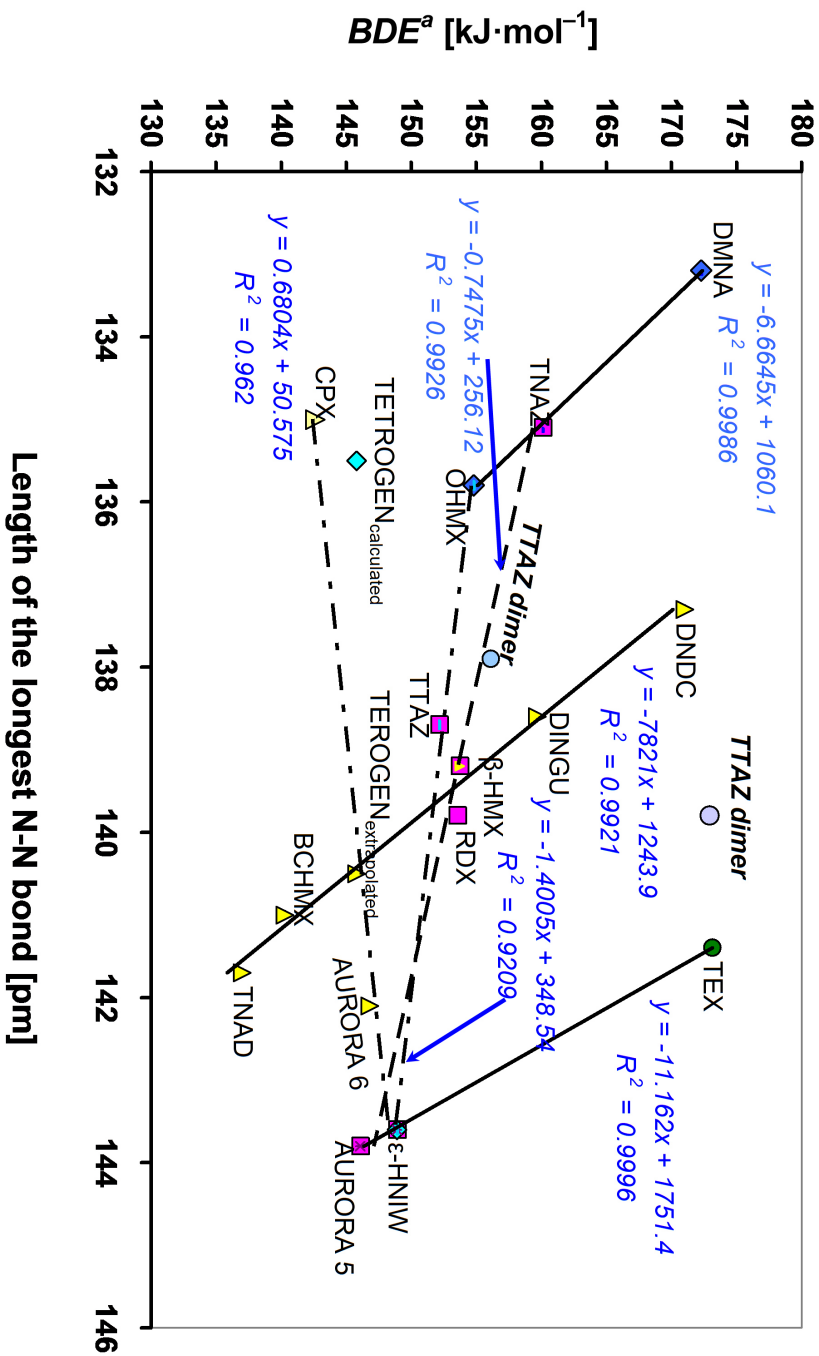


Figure 8. Simple comparison of bond dissociation energies (BDE^a , obtained by the UB3LYP/6-31G* method) and the longest N-N bond of the nitramines studied

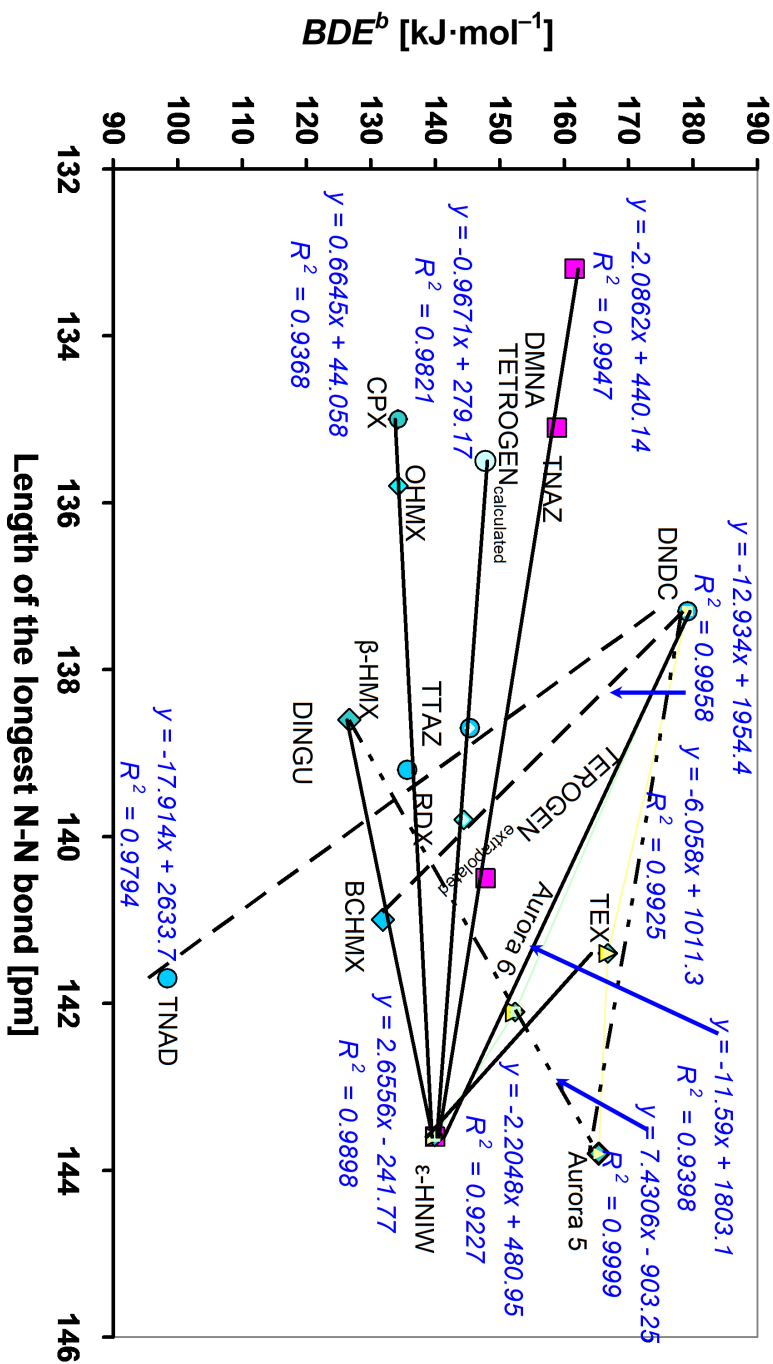


Figure 9. Simple comparison of bond dissociation energies (BDE^b), obtained by the UB3LYP/6-31+G*/PM3 semi-empirical method of optimization) and the longest N-N bond of the nitramines studied

Rather counterintuitively, all three independent molecules in Figure 1 reveal almost the same interatomic distances between nitrogen atoms of all nitramine groupings, N–NO₂, the figure being around 1.35 Å (Figures 1 and 10), which is also in agreement with the calculated data using the simplest split valence basis set, the 3-21G, 1.343 Å [41].

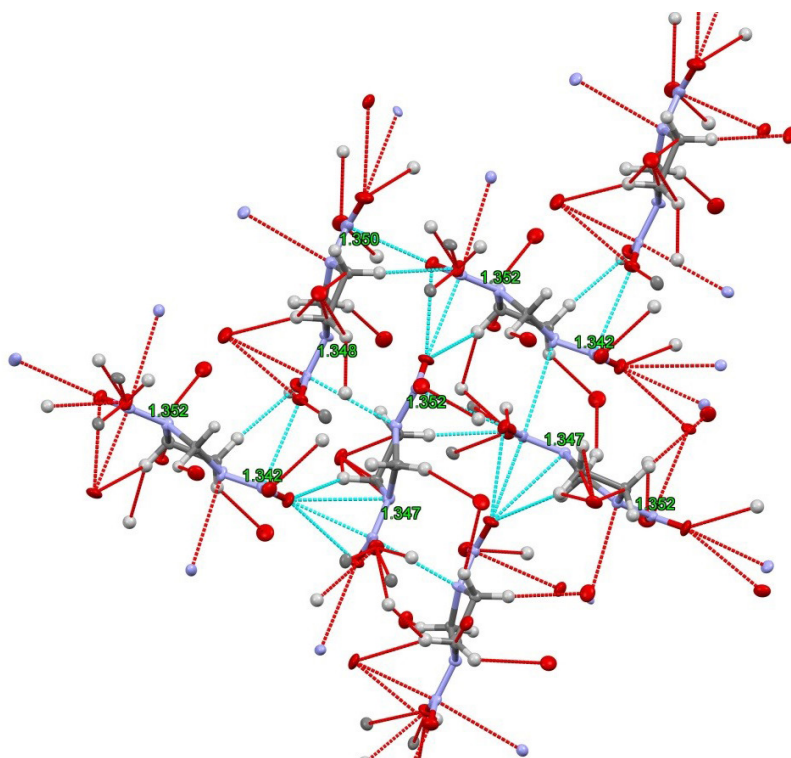


Figure 10. Short contacts within the molecular structure of CPX (ORTEP view, 50% probability level); selected N–N interatomic distances [Å] are shown

In the second crystallographically determined structure, TTAZ (Figure 2), the N–N distance is very close for both nitramine units separated by the ethylene bridge (*i.e.* positions 1 and 5) and for all distances in CPX (1.35 Å), while the third nitramine unit separated by the methylene bridges (position 3) has a distance of 1.387 Å. The crystal packing (Figure 3(b)), in combination with the out of ring conformation of the respective nitramine units and the short contact between the nitro groups of neighbouring molecules (Figure 11), probably cause these differences.

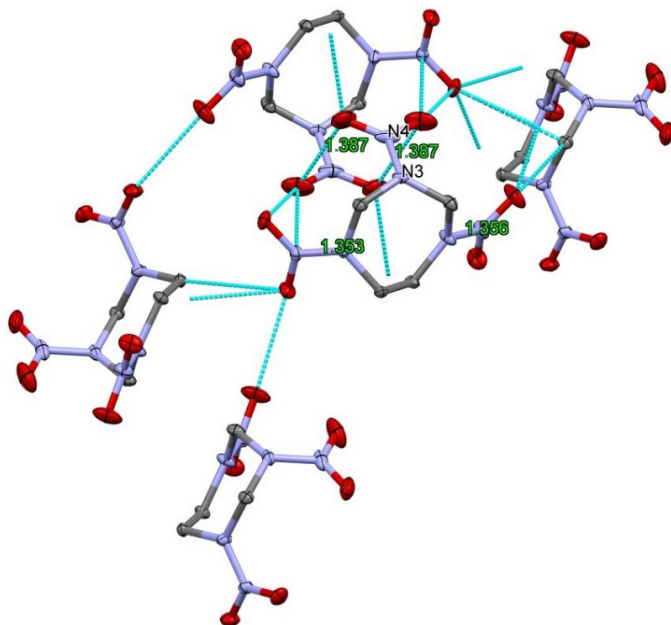


Figure 11. Short contacts in the molecular structure of TTAZ (ORTEP view, 50% probability level); selected N–N interatomic distances [Å] are shown

4 Comments

It follows from Figure 4 that an increase in the energy content of a nitramine molecule should be linked to an increase in the length of its longest N–N bond. This fact should theoretically correspond with the relationship between the energy content and the rate characteristics of thermal decomposition of these compounds. However, this is not found in the case of pure nitramines (see Figures 5 and 6), where the increasing length of the longest N–N bond leads to an increase in the thermal reactivity of nitramines only in solution [2, 3, 47, 72]. The difference mentioned here depends on the solvent's participation in the thermal decomposition of the nitramines, and not only by a solvation effect.

Comparison of the thermodynamic parameters of solvated nitramine decomposition with those of the pure substances (see Table 3) shows that the activation enthalpies (ΔH^\ddagger) of the latter are higher than those for decomposition in solution. This fact indicates, generally [76], that formation of the transition state of this decomposition is more difficult in pure nitramines than it is in solution. This

is logical, because a solvent removes the influence of the stabilizing effect of the crystal lattice. Also, comparing Gibbs free energies (ΔG^\ddagger) mainly for nitramine decomposition in phthalate solutions, shows the same effect (see Table 3 and Figure 12). A concrete conclusion cannot be drawn from just three points for nitramine decomposition in dinitrobenzene (DNB) solution, but their dispersion in Figure 12 may indicate the direct action of poly-nitrobenzenes in their thermal decomposition. For nitramine decomposition in a di- or tri-nitrobenzene medium, a mechanism has been suggested [77, 78], resulting from the termination of the radical polymerization by means of the polynitroarenes [79, 80]. According to this suggestion, the transfer of proton and electron from one aza-radical to another is carried out by direct participation of the nitro groups in the poly-nitrobenzenes, which remain chemically unchanged (they behave simply as catalysts [77, 78]). It is clear that this kind of interaction cannot occur without influencing the Arrhenius parameters of the corresponding decomposition [77, 78]. The difference between the results of thermal decomposition in solvents [2, 3, 47, 72] and in the pure state (Figures 5 and 6) again raises the problem of the “inert solvents” effect in the thermal decomposition of energetic materials [77, 78, 81].

Table 3. Thermodynamic parameters of thermal decomposition of several nitramines, *i.e.* enthalpy of activation (ΔH^\ddagger), entropy of activation (ΔS^\ddagger) and free Gibbs energy (ΔG^\ddagger), all at average temperatures, T_m of the temperature regions for the specification of the corresponding Arrhenius parameters (see Table 2)

Data No. from Table 1	Nitramine	Average temperature, T_m [K]	Thermodynamic parameters of thermal decomposition		
			ΔH^\ddagger [kJ·mol ⁻¹]	ΔS^\ddagger [J(K·mol) ⁻¹]	ΔG^\ddagger [kJ·mol ⁻¹]
7	RDX solid	449.5	213.9	109.0	164.9
7.1	RDX / DNB	453.1	162.3	17.0	154.6
7.2	RDX / DCP	513.6	169.4	37.1	150.4
10	BCHMX solid	463.0	206.3	87.7	165.7
10.1	BCHMX / DNB	440.6	166.3	45.4	146.3
10.2	BCHMX / DBP	435.6	161.4	30.0	148.3
13	TEX solid	440.5	192.7	38.3	175.8
13.1	TEX / DBP	503.1	153.9	-8.8	158.4
14.1	α -Aurora 5 solid	473.0	184.5	59.6	156.2
14.2	Aurora 5 /DBP	438.1	159.3	35.1	143.9
16.2	ϵ -HNIW solid	458.1	213.1	122.1	157.2
16.4	HNIW / DNB	445.6	185.9	99.5	141.6
16.5	HNIW / DBP	448.1	179.9	87.6	140.6

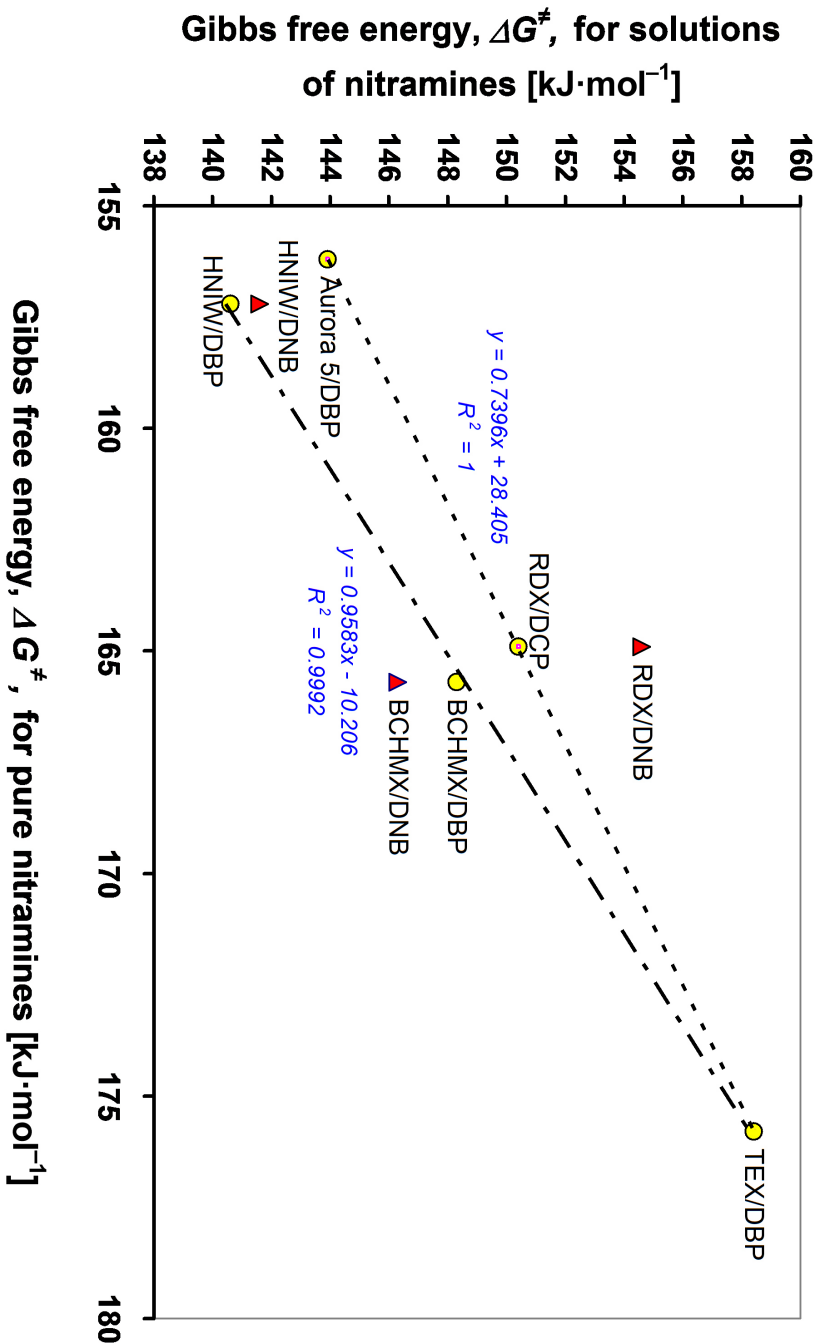


Figure 12. Simple comparison of the Gibbs free energies for nitramine decomposition in solution and in the pure state; here DNB means 1,3-dinitrobenzene, DBP – dibutyl phthalate and DCP – dicyclohexyl phthalate

Concerning the relation of the impact sensitivity to the length of the longest N–N bond (Figure 7), this itself shows that this length need not be a measure of the mentioned sensitivity. It can be documented especially by TTAZ, in whose molecule the longest N–N bond is in position 3 (*i.e.* bond N3–N4 in Figure 1) while its most reactive nitramine grouping is in position 1 (this has been proved many times over by means of ^{15}N NMR chemical shifts [6, 22, 36, 73, 82] and by DFT calculations [10, 11, 83] in studies of the initiation reactivity of nitramines). The mutual orientation and spacing of nitramine groupings in positions 3 of adjacent TTAZ molecules (see in Figures 1, 3(a), and 11) are likely to cause stabilization of the N–N bond in terms of resistance to initiation. Using calculation by the UB3LYP/6-31G* method for the N–N bond length of 139.8 pm in this isolated and optimized “dimeric” TTAZ molecule, we obtained a BDE^a value of $172.9 \text{ kJ}\cdot\text{mol}^{-1}$ in comparison to $152.1 \text{ kJ}\cdot\text{mol}^{-1}$ for the “monomer” (see Table 1). It seems that the presumption of stabilization is thus confirmed. The temperature-dependent crystallographic characteristics of CPX did not manifest themselves as having any influence on its sensitivity within the framework of this paper.

The UB3LYP/6-31G* (Figure 8) approach seems to be a more logical method for using bond dissociation energies in estimating N–N bond strengths (Figures 8 and 9). However, the UB3LYP/6-31+G*//PM3 (UHF) method gave relationships (Figure 9) with better molecular structural interconnection. It is worth mentioning that, concerning the latter approach, the primary step of nitramine decomposition under the influence of thermal and mechanical impulses is homolysis of the weakest N–N bond in their molecules [3, 10, 20, 43, 82], and, therefore, it seems that the optimization of their molecular geometry on the semi-empirical PM3 level has been used correctly.

5 Conclusions

Increasing the energy content (here represented by enthalpies of formation) in nitramine molecules is accompanied by an increase in the lengths of their longest N–N bond, which is described by a relatively tight semi-logarithmic relationship between the two characteristics. These lengths are in a direct proportional relationship with the activation energies of the low-temperature thermal decomposition of pure nitramines in all phases, which suggests that raising the energy content upgrades these energies and suppresses the reaction rate of thermal decomposition. This finding contrasts with the expected negative influence of lengthening these N–N bond lengths on the thermal stability of

these compounds, *i.e.* on an increase in the rate of their thermal decomposition. However, the expected increase in thermal reactivity as a result of increasing of the maximal length of the N–N bond has been described and published for the thermal decomposition of nitramines in solution, mainly in phthalates and di-/tri-nitrobenzenes. This difference in behaviour between pure nitramines and their solutions derives from “inert solvent” participation in the thermal decomposition of nitramines through a solvation effect or a termination of the emerging aza-radicals (for the influence of dinitrobenzene, see explanations in references [77, 78]).

In contrast to the above-mentioned relationships for thermal decomposition of pure nitramines, the calculated dissociation energies of the weakest N–N bonds (*BDE*) yielded a relatively good match with the lengths of the longest N–N bonds in the nitramines studied (decrease of the *BDE* values with an increase in this length). The UB3LYP/6-31G* approach seems to have been the more logical, while the UB3LYP/6-31+G*//PM3 (UHF) method gave relationships with a better molecular-structural interconnection; using molecule optimization at the semi-empirical PM3 level corresponds well with the homolytic scission of the weakest N–N bond during initiation.

The relationship between the impact sensitivity of the nitramines studied with the lengths of their longest N–N bonds is not completely clear. For example, in the 1,3,5-trinitro-1,3,5-triazepane (TTAZ) molecule, the longest N–N bond is in position 3, whereas the most reactive nitramine group is in position 1. The mutual orientation and spacing of the nitramine group in the 3 position of adjacent TTAZ molecules are likely to be the cause of the stabilization of this N–N bond; this particular area of influence of intermolecular interactions on the initiation reactivity requires further study. The length of the longest N–N bond cannot therefore be a measure of impact reactivity (of initiation reactivity in general).

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