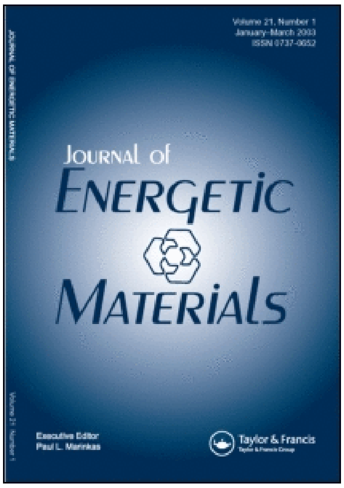

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RELATIONSHIP BETWEEN DETONATION CHARACTERISTICS AND ^{15}N NMR CHEMICAL SHIFTS OF NITRAMINES

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ABSTRACT

The paper presents ^{15}N NMR chemical shifts δ of twenty three nitramines out of which 1-nitro-1-azaethylene (DIGEN), 1,3-dinitro-1,3-diazacyclobutane (TETROGEN) and 1,3,5,7,9-pentanitro-1,3,5,7,9-pentaazacyclodecane (DECAGEN) have not been synthesized yet. The corresponding δ values of these three substances have been predicted. The relationship has been confirmed between squares of detonation velocities or, as the case may be, the detonation heats and δ values of nitrogen atoms in nitro group of the nitramines. This relationship represents a certain form of Evans-Polanyi-Semenov equation and such it directly specifies the most reactive nitro group of nitramine molecule in the detonation and, hence, the $N\text{-}NO_2$ bond primarily split in this process.

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INTRODUCTION

The influence of shock on energetic materials results in adiabatic compression of the molecular layer struck. According to Klimenko and Dremin[1-4], the kinetic energy of the shock in this compression is accumulated through translational-vibrational relaxation processes by translational and vibrational modes of molecular crystals of the material within 10^{-13} to 10^{-12} second. This causes a considerable quasi-overheating (*20000 to 40000 K*[3,4]) especially of vibration modes. A nonequilibrium state is established with concomitant primary splitting of the energetic material into ions and radicals[2-4]. These active particles by chemically interaction with each other evoke a process of spontaneous spreading of the shock front in the starting substance, i. e. evoke of second equilibrium stage of detonation behind the front. This or similar ideas of transformation of low-frequency vibrations of crystal lattice (*acoustic phonons*) into high-frequency vibrations (*vibrons*), with subsequent spontaneous localization of vibrational energy in the explosophore groupings[10,61], have been applied by a number of authors in their studies of shock reactivity of energetic materials (*for representative papers see refs.*[5-10,61]).

Since middle 1970s, the studies of shock reactivity and chemical micromechanism of detonation initiation of organic polynitro compounds have also been adopting the quantum chemistry methods (*see e. g. refs.*[11-22]). From the findings thus obtained it follows that the carrier of this reactivity is nitro group or, more specifically, C-NO_2, N-NO_2 or O-NO_2 bonds[11-22]. There exist direct experimental[23-25] as well as indirect semi-empirical[26-32] pieces of evidence for what has been said.

In the last 10 years, the activities in the area of research of shock reactivity have been more intensive owing to the technical development in picosecond and/or femtosecond spectroscopy, supercomputer simulation of electronic states, and development in molecular dynamics (*see e. g. proceedings*[33]). Nevertheless, no uniform opinion about this problem has been reached yet. This can particularly be due to the standard of formulation of the starting models for simulations and of molecular-dynamics studies, but also by the available level of measuring and computer technique. Beside the above-mentioned methods of ultra-rapid spectroscopy at dynamic experimental conditions, significant findings also result from less complex spectral methods using static conditions of measurement. Sharma et al.[34] using X-ray photoelectron spectroscopy thus obtained very important findings on the relationship between electron structure of molecules of energetic materials and their sensitivity[35,38], on predetonation states of these molecules[37,38], and on their primary splitting by shock wave[24,25,38,39]. Out of other relatively available spectral methods, Owens applied the outputs of ^{1}H NMR spectroscopy in a study of impact sensitivity of trinitroarenes[40]. Owens also described a relationship between ^{1}H NMR chemical shifts and detonation velocities of the said compounds[40]. The application of ^{13}C NMR spectroscopy to determination of detonation velocities and detonation heats of polynitro arenes and nitramines is protected by patents[41,42].

A relation also found[43] between detonation velocities and ^{15}N NMR chemical shifts δ_N of nitrogen atoms in nitro groups of five nitramines with rigid molecules which is described by the following general equation:

$$X = A*\delta_N + B \qquad (1)$$

where X is square of detonation velocity, D^2. No analogous relationship for ^{15}N NMR chemical shifts δ_A of amino nitrogen atoms, carrying nitro groups, could be found[43]. The above relationship (1) is related to the detonation (*shock*) reactivity of nitro groups in nitramines and, therefore, it should be applicable to studies of chemical micromechanism of initiation of detonation of the given substances. The problem is discussed in the present paper.

METHODS AND PROCEDURES

Characteristics of detonation

The values of detonation velocity, D, of nitramines studied were calculated using the known relationships of Kamlet and Jacobs[46] for the maximum theoretical densities of crystals (*i. e. for monocrystal*). When the heat of formation of the substance was not available, the D values were obtained using the relationship of

TABLE 1:

Survey of the nitramines studied, their code designations, velocities of detonation, D, and heats of explosion, Q_P.

	Nitramine		D		Q_P	
No	Chemical name	Code design.	($km.s^{-1}$)	Note	($kJ.g^{-1}$)	Note
1	1-Nitro-1-azaethane	MNA	6.70	a	4002	b
2	1,1-Dinitro-1-azaethane	MDN	9.05	c	5690	d
3	2-Nitro-2-azapropane	DMNA	6.29	a	3817	b
4	1,4-Dinitro-1,4-diazabutane	EDNA	8.42	a	4874	b
5	2,4-Dinitro-2,4-diazapentane	OCPX	7.28	a	4367	b
6	2,4,6-Trinitro-2,4,6-triazaheptane	ORDX	8.04	a	4870	b
7	2,4,6,8-Tetranitro-2,4,6,8-tetraazanonane	OHMX	8.68	c	5404	d
8	2,5-Dinitro-2,5-diazahexane	DMEDNA	6.42	c	3732	d
9	2,4,7,9-Tetranitro-2,4,7,9-tetraazadecane	TNADEC	7.92	c	4827	d
10	1,9-Diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetraazanonane	AcAn	7.18	c	4280	d
11	2,5-Dinitro-2,5-diazahexane-3,4-dione	DMNO	7.20	c	4295	d
12	1-Nitro-1-azaethylene	DIGEN	8.12	c	4978	d
13	1,3-Dinitro-1,3-diaza-cyclobutane	TETROGEN	8.46	a	5236	d
14	1,3-Dinitro-1,3-diaza-cyclopentane	CPX	7.76	c	4708	d
15	1,4-Dinitro-1,4-diaza-cyclohexane	DNDC	6.75	c	3968	d
16	1,3,5-Trinitro-1,3,5-triaza-cyclohexane	RDX	8.89	a	5481	b

	Nitramine		D		Q_P	
No	Chemical name	Code design.	($km.s^{-1}$)	Note	($kJ.g^{-1}$)	Note
17	1,3,5-Trinitro-1,3,5-triaza-cycloheptane	HOMO	8.23	a	5005	b
18	1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane	HMX	9.13	a	5530	b
19	1,3,5,7,9-Pentanitro-1,3,5,7,9-pentaazacyclodecane	DECAGEN	8.96	a	5620	d
20	1,5-Endomethylene-3,7-dinitro-1,3,5,7-tetraaza-cyclooctane	DPT	6.30	c	3758	b
21	1,5-Diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane	DADN	5.81	c	3523	e
22	4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diaza-isowurtzitane	TEX	8.47	a	4538	b
23	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaaza-isowurtzitane	HNIW	9.62	a	5956	b

[a] calculated according to Kamlet and Jacobs[46]
[b] calculated according to Pepekin et. al.[48]
[c] calculated according to Rothstein and Petersen[47]
[d] calculated from eqn. (2)
[e] taken from ref.[28]

Rothstein and Petersen[47]. The explosion heats Q_P were calculated for monocrystals by means of semi-empirical relationships devised by Pepekin et al.[48] (*values Q_P correspond to the experimentally determined heat of explosion*[48], *i. e. to real values of this*). When the heat of formation was not available and also in the case of nitramines not yet synthesized, the Q_P values were obtained from a helpful mathematical relationship derived from the corresponding data (*taken from ref.*[31]) of forty polynitro compounds in the form

$$Q_P = 544.28*D + 12.94*D^2 - 295.56 \qquad (2)$$

with the correlation coefficient r = 0.9332. The values D and Q_P obtained by the said methods, together with the chemical names and code designations of the nitramines studied, are summarized in Table 1.

TABLE 2:

Survey of results of the ^{15}N NMR spectroscopy of the nitramines studied

Data	Nitramine	^{15}N NMR Chemical shift (ppm)			
No	code	Position in	Nitrogen atom of group		Ref.
		molecule	nitro	amino	
1.1	MNA	1-	-24.60	-215.89	44
2.1	MDN	1,1-	-38.8	-89.70	44
3.1	DMNA	2-	-25.84	-215.80	44
4.1	EDNA	1,4-	-26.34	-205.47	a
5.1	OCPX	2,4-	-28.36	-202.61	a
6.1	ORDX	2,6-	-28.49	-202.29	a
6.2		4-	-32.02	-189.90	a
7.1	OHMX	2,8-	-28.77	-202.25	a
7.2		4,6-	-34.52	-195.59	a
8.1	DMEDNA	2,5-	-27.83	-209.55	a
9.1	TNADEC	2,9-	-28.44	-202.75	a
9.2		4,7-	-29.43	-196.03	a

Data No	Nitramine code	^{15}N NMR Chemical shift (ppm)			Ref.
		Position in molecule	Nitrogen atom of group		
			nitro	amino	
10.1	AcAn	2,8-	-32.81	-190.52	a
10.2		4,6-	-33.38	-188.06	a
11.1	DMNO	2,5-	-43.07	-166.78	a
12.1	DIGEN	1-	-23.58	-208.52	b
13.1	TETROGEN	1,3-	-27.83	-203.62	b
14.1	CPX	1,3-	-31.21	-209.01	a
15.1	DNDC	1,4-	-26.26	-205.49	a
16.1	RDX	1,3,5-	-32.90	-198.10	44
17.1	HOMO	1,5-	-33.04	-201.28	a
17.2		3-	-34.38	-196.32	a
18.1	HMX	1,3,5,7-	-34.70	-199.10	44
19.1	DECAGEN	1,3,5,7,9-	-33.25	-197.38	b
20.1	DPT	3,7-	-25.30	-203.70	44
21.1	DADN	3,7-	-23.70	-205.10	a
22.1	TEX	4,10-	-33.40	-197.20	a
23.1	HNIW	2,6,8,12-	-40.30	-199.00	58, c
23.2		4,10-	-43.40	-179.50	58, c

[a] results of this paper

[b] nitramine has not been synthesized yet

[c] values obtained from mesasurements in acetone-d_6 solution

NMR Spectroscopy.

The ^{15}N NMR chemical shifts δ of the nitramines studied were obtained with the help of an AMX-360 Bruker apparatus using the INEPT method. The samples were dissolved in hexadeuteriodimethyl sulfoxide at a concentration of 0.2

mol nitramine per 1 dm^3 solution. For some of the substances the values of these shifts were taken from literature[44,58]; those of the substances not yet prepared were predicted. These all δ_A and δ_N values are summarized in Table 2.

Prediction of ^{15}N NMR Chemical Shifts Values

The substance not yet prepared (*i. e. 12, 13 and 19 in Table 1*) are of considerable theoretical interest in the chemistry of nitramines. For the nitramines **13** and **19**, the prediction of ^{15}N NMR chemical shifts δ_A of their amino nitrogen atoms starts from the equation

$$\Sigma\delta_A = -193.23*n - 20.78 \qquad (3)$$

with correlation coefficient r = 0.9999. In this equation $\Sigma\delta_A$ is the sum of ^{15}N NMR chemical shifts δ_A in the molecules of substances **3**, **16** and **18**, i. e. in the nitramines containing $-CH_2N(NO_2)-$ building units in their rigid molecules, and **n** is the number of these units in the molecule. The δ_A value of nitramine **12** was obtained[31] by menas of its predicted heat of fusion[45]: first the drop energy E_{dr} (*impact sensitivity*) of the given substance was calculated from the relationship between these heats and E_{dr} values of nitramines with rigid molecules, and then this value was introduced into relationship between E_{dr} and δ_A values of the same nitramines to give the predicted δ_A value[31]. The prediction of ^{15}N NMR chemical shifts δ_N of nitrogen atoms of nitro groups started from the analysis of the relationship between δ_A and δ_N values of nitramino groups (*made in this work*) which turned out to be describable by the following general form of relationship:

$$\delta_N = a^*\delta_A + b \qquad (4)$$

In the sense of relationship (4), the investigated set of substances falls naturally into several subsets as it is documented in Table 3. Data of caged molecules of nitramines **22** and **23** do not correlate with any forms of this equation . The estimate of δ_N values of all the three so far unknown nitramines was based on a subset *C* of substances in Table 3. The correctness of choice of particular linear dependence was verified[31] by calculation the activation energies E_a of low-temperature thermolysis of nitramines from the predicted δ_N values in the sense of relation[31,43]:

$$E_a = a_1{}^*\delta_N + e \qquad (5)$$

and subsequent evaluation of reality of the E_a values thus obtained by means of modified Evans-Polanyi-Semenov equation[31](*in some cases also by means of QSPR calculation*[31]).

DISCUSSION

In the present paper, the relationship between detonation velocities D and values of ^{15}N NMR chemical shifts of nitrogen atoms of nitro groups of the nitramines studied has been reevaluated to confirm the existence of relation (1), see

Table 4. In contrast to the preliminary information about this relationship in ref.[43], the much broader assortment of substances investigated in the present work (Table 1): the fact that their molecular structures are much more varied (*which is still more important*) enables a reasonable interpretation of physical meaning of the equation discussed.

TABLE 3:

Coefficients of the individual forms of eqn. (4)[a]

Group of nitramines		Coefficients		
No.	Structure of data[b]	a	b	r
A	2.1, 3.1, 5.1, 6.1, 8.1, 9.2	-0.095	-47.478	0.9914
B	1.1, 5.1, 6.1, 6.2, 7.1, 9.1, 10.1, 10.2, 11.1	-0.374	-104.380	0.9899
C	4.1, 5.1, 7.2, 15.1, 16.1, 17.2	-0.869	-204.740	0.9978
D	6.1, 9.1, 18.1, 20.1, 21.1	-1.883	-409.710	0.9928
E	14.1, 17.1, 17.2	-0.248	-83.157	0.9993

[a] with exception of a line for group E of nitramines the remain lines have a common intersection characterized by $\delta_A = -202.4$ ppm and $\delta_N = -28.7$ ppm.
[b] data are numbered as in Table 2.

Generally, the square of detonation velocity (D^2) and explosion heat (Q) in the Chapman-Jouget plane are interrelated by definiendum[49,50]:

$$Q = D^2 * \{2 * (\gamma^2 + 1)\}^{-1} \qquad (6)$$

where γ is the polytropy coefficient whose value for high explosives ranges from 2.79 to 3.48[49]. Hence it is possible to introduce Q for X in equation (1) - see Table 4: for this case it can be combined with equation (5) to give:

$$E_a = C \pm \alpha * Q \qquad (7)$$

which – in general sense – is a form of Evans-Polanyi-Semenov equation[51,52] (*the heat of reaction ΔH is instead of Q in the original relationships*) which was originally derived for radical substitution reactions. This relationship is valid for narrow sets of substance structures and it documents that the strength of bond being split is a decisive factor in the given reaction[51,52]. It was proved that equation (7) also holds for the detonation transformation of energetic materials[29,31,53,54]; in this case then E_a means activation energy of low-temperature thermolysis and Q may be substituted by real explosion heat Q_P. The relationship (7) thus modified not only documents the importance of the bond primarily splitting in detonation of individual energetic materials, but also signals the identity of chemical mechanism of primary splitting in low-temperature thermolysis and detonation reactions[29,31,32]. These statements fully agree with the outputs of quantum-chemical studies of impact and shock reactivities of organic polynitro compounds[11-20], with experimental results of studies of their primary fragmentation by shock wave[23-25], as well as with the findings concerning their low-temperature thermolysis (*for a survey see e. g. ref.*[55]). In comparison the modified relationship (7), equation (1) makes it possible in a simpler and more concrete way to specify the nitro group primarily reacting in detonation, i. e. the $N-NO_2$ bond primarily split in the molecules of nitramines exposed to shock.

As can be seen from Table 4 and Figure 1 the nitramine set studied falls into four subsets in the sense of equation (1). This falling for $X = D^2$ is the same as for $X = Q_P$: with exception of subset *IV* of nitramines the relationships for D^2 possess more close correlation as for Q_P.

The subset ***I*** involves nitramine **12** and its cyclic polymers (*i. e. substances **13**, **16**, **18** and **19***) with rigid molecules and with isochronous nitrogen atoms. From the point of view of electronic densities distribution in their molecules this subset, with exception of "monomer" **12**, represents nitramines with the most symmetrical molecules from the all substances studied.

The subset ***II*** includes the substances which – from the point of view of molecular structure – cannot be considered integer multiples of a substance **12** molecule although they mostly contain the methylenenitramine grouping in their flexible (*linear nitramines*) or rigid molecules (*cyclic nitramines*). The flexible molecules containing more than two nitramino groups (*i. e. substances **6**, **7** and **9***) correlate with the both linear dependencies of subset ***II*** through their δ_N values of nitrogen atoms in "inner" nitramino groups (*i. e. by data 6.2, 7.2 and 9.2 in Table 2*). This fact agrees with the results of study of initial decomposition process of N-N bond in nitramines which is induced by impact.

TABLE 4

Coefficients of the individual forms of eqn. (1)

Group of nitramines		**Coefficients**					
No.	Structure of the group[a]	for $X = D^2$			for $X = Q_P$		
		A	B	r	A	B	r
I	12.1, 3.1, 16.1, 18.1, 19.1	-1.52	29.66	0.996	-54.63	3705.5	0.971
II	2.1, 3.1, 5.1, 6.2, 7.2, 9.2, 14.1, 15.1, 17,1, 20.1, 21.1, 22.1, 23.1	-3.40	-44.66	0.983	-142.59	237.14	0.964
III	3.1, 8.1, 11.1	-0.71	21.37	0.999	-31.22	2941.0	0.969
IV	7.2, 10.2, 18.1	-15.66	-462.45	0.987	-659.75	-17367.0	0.999

[a] data are numbered as in Table 2.

The study was carried out by Kohno et al. on the basis of quantum chemistry and molecular dynamics[56] with special reference to nitramines 7 and **18**: in connection with action of impact on a crystal, the intramolecular vibration energy is transferred into nitramino groups. The linear molecule 7 shows only little probability of transfer of surplus energy from "inner" to "outer" nitramino groups[56]. In the cyclic structure of nitramine **18** this transfer between nitramino groups is possible although it is 2.5 to 3.5 times slower as compared with linear analogues[56].

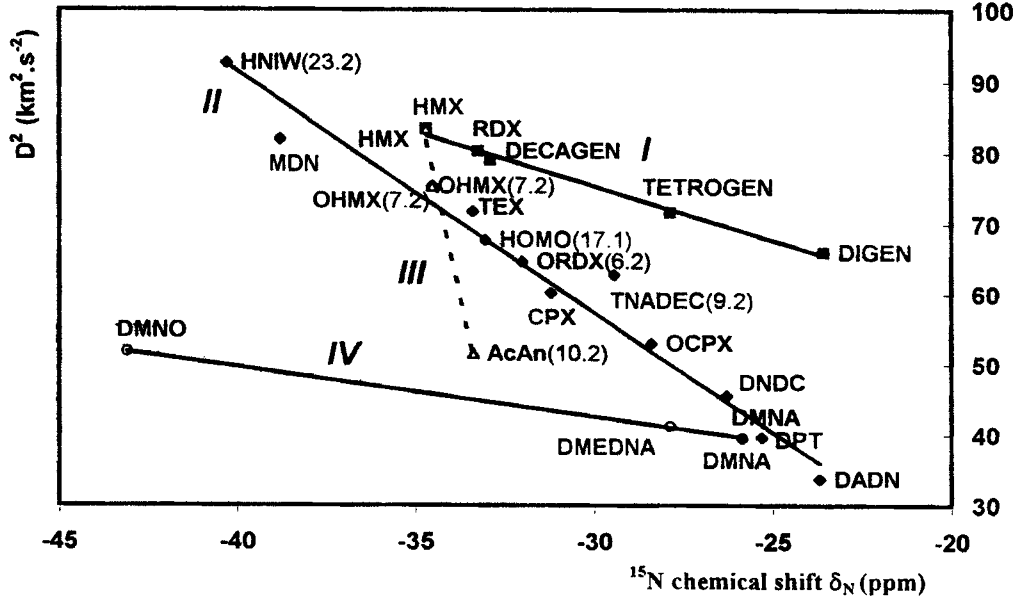
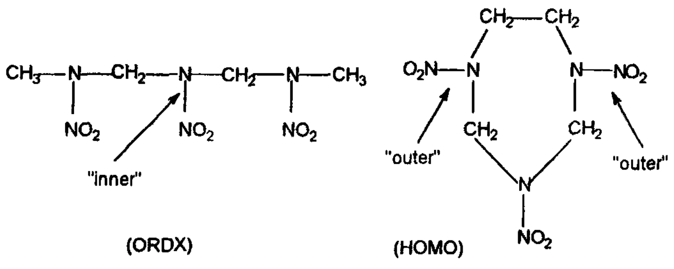


FIGURE 1: Graphic representation of relationship (1) for $X = D^2$



(ORDX) (HOMO)

FIGURE 2: Illustration of the primary splitting of linear (*ORDX – "inner" nitraminogroup*) and non-symmetrical cyclic (*HOMO – "outer" nitraminogroup*) nitramines by impact or shock.

Nonsymmetrical cyclic nitramines with triazacycloheptane skeleton in their molecules (*i. e. substances 17 and 23*) correlate in the sense of relationship (1) for subset *II* by their δ_N values of "outer" nitramino groups, i. e. by corresponding part of data 17.1 and 23.1 (Table 2). This reciprocity (*see Figure 2*) as compared with linear nitramines is in accordance with the results of studies of impact sensitivity of the nitro compounds mentioned[31,57]: in this case the dependence of drop energies E_{dr} on heats of fusion, or on ^{15}N NMR chemical shifts of amino nitrogen atoms in reaction centres of their molecules, or on activation energies E_a of their low-temperature thermolysis have an opposite course for rigid molecules as compared with the course for flexible molecules of the nitramines studied in refs.[31,57]. Combined influence of the electronic configuration of reaction centre and conformational stability of the molecules might be a reason of this finding[31,57].

The subset *III* involves substances with methylnitramine grouping which is bonded to "unexplosive" rest of their molecules (*i. e. to methyl group in substance 3, ethylene bridge in substance 8 and oxaldiyl bridge in substance 11*).

The substance subset *IV* consists of nitramine **12** tetramers, i. e. cyclic substance **18** and linear analogues **7** and **10**. The existence of the subset is again in accordance with the findings by Kohno et al.[56]: in this case both the linear nitramines participate in the correlations by their δ_N values of "inner" nitramino groups (see *data 7.2 and 10.2 from Table 2*).

Data of nitramines **1** and **4** do not correlate with any forms of equation (1). Unlike to other nitramines studied these two substances primarily thermolyze by a bimolecular mechanism[55,59] (*due to an association of their molecules by hydrogen bonds*[60]). This basic difference and findings of paper[43] signal an existence of separate forms of the equation for primary nitramines.

CONCLUSION

The relationship between the square of detonation velocities and ^{15}N NMR chemical shifts of nitrogen atoms of nitro groups in nitramines represented in this paper by equation (1)[43] can be considered an analogue of Evans-Polanyi-Semenov equation[51,52] in its modified form, i. e. as a relationship between activation energies of low-temperature thermolysis and detonation heats of energetic materials[29,31,53,54]. These relationships show that the strength of bond primarily homolyzed is a decisive factor in detonation of energetic materials inclusive of nitramines. Relationship (1) directly specifies the most reactive nitro group of nitramine molecule in the detonation and, hence, the N-NO_2 bond primarily split in this process. In linear polynitramines the shock or impact reactivities are connected with primary splitting of "inner" N-NO_2 bonds in their molecules. These statements perfectly agree with theoretical[12-20,27-31,56] as well as experimental findings[23,24] concerning shock and impact reactivity of this class of polynitro compounds.

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