Recent Advances in the Study of the Initiation of Nitramines by Impact Using Their ^{15}N NMR Chemical Shifts

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Abstract: The relationship between the ^{15}N NMR chemical shifts of aza nitrogen atoms in twelve nitramines and the impact sensitivity of these compounds, expressed as the drop energy, E_{dr}, has been analyzed from the point of view of recently published findings. This relationship appears to be the best method for identifying the key atoms at the reaction centre of a given molecule. These atoms might be taken as "chemical hot spots". The absence of any solid state influence on the chemical shifts, which were here determined in solution, does not have a fundamental influence on the reaction centre identification. The relationship discussed here confirms the close molecular structural dependence for drop energies (impact sensitivities) obtained for individual energetic materials (EMs) by means of a standard impact tester (Julius Peters) with the detection of the 50% probability of initiation based on acoustic detection. The dependence of impact sensitivity on specific crystal surfaces, using samples of individual EMs obtained by screening, should be investigated more extensively.

Keywords: impact sensitivity, initiation, ^{15}N NMR chemical shifts

1 Introduction

In one of the first papers concerning the relationship between low-temperature thermal decomposition and detonation characteristics, it was postulated [1] that the electronic configuration and steric effects play a decisive role at the reaction centre of the molecule during the primary fission of detonation initiation. At the same time, these facts represent one of the basic approaches in organic chemistry for dealing with reactivity problems in general. The electronic configuration and

steric conditions within the reaction centre of the molecule can be represented by the NMR chemical shifts of the key atoms at the centre. It is well known that the use of ^{13}C, and particularly ^{15}N NMR chemical shifts, in the study of the initiation of polynitro compounds by shock [2-6], impact [2, 3, 5-7,], friction [7], electric spark [2, 3, 6, 8] or heat [2, 3, 5, 9] can give very valuable results. Several papers [2-5, 8, 9] have shown that the centre should be the same in all of the above-mentioned types of initiation.

Concerning impact sensitivity, relatively detailed attention has been paid to its evaluation as the "first reaction" (*i.e.* sensitivity detected by the first chemical change, not acoustically) [2, 3, 5, 10, 11]. A relationship between the impact sensitivity, expressed as the drop energy, E_{dr}, and the chemical shift, δ of a key atom of the reaction centre, has been found of the general form [2, 3, 5, 10, 11]:

$$E_{dr} = a \cdot \delta + c \qquad (1)$$

In the case of nitramines, the ^{15}N NMR chemical shift used, δ_A, was that of the aza nitrogen atom carrying the nitro groups that are cleaved first during the initiation (*i.e.* the most reactive nitro groups) [2, 3, 5, 10, 11]. For impact sensitivity, detected acoustically, the semi-logarithmic version of Equation (1) has been derived for the initiation of polynitro compounds [2, 3, 6, 7, 10, 11]:

$$\ln E_{dr} = a \cdot \delta + b \qquad (2)$$

For nitramines, the δ_A values were used again in Equation (2). The difference between these two equations concerns the different ways in which the impact impulse transfers into the reaction centre of the molecule [2, 3] in the different kinds of sensitivity.

Acoustically-detected impact sensitivity of nitramines has not been studied in as much detail as has the case of their "first reaction" [2, 3], since only partial results and incomplete conclusions have been published so far [3, 6, 7, 10]. The current paper, therefore, shows some new conclusions concerning the impact sensitivity of attractive nitramines from the point of view of Equation (2).

2   Materials

The following nitramines have been studied during the work for this paper (see also Figure 1): 1,4-dinitro-1,4-diazabutane (EDNA), 2,5-dinitro-2,5-diazahexane (DMEDNA), 1,3-dinitro-1,3-diazetidine (TETROGEN), 1,4-dinitropiperazine

(DNDC), 1,3,5-trinitro-1,3,5-triazinane (RDX), 1,3,5-trinitro-1,3,5-triazepane (HOMO), 1,3,5,7-tetranitro-1,3,5,7-tetraazocane (HMX), *cis*-1,3,4,6-tetranitrooctahydroimidazo-[4,5-d]imidazole (BCHMX), 1,3,5,7,9-pentanitro-1,3,5,7,9-pentaazecane (DECAGEN), 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane (TEX) and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW). Table 1 contains the ^{15}N NMR chemical shifts taken from previously published work [4, 6, 17, 18]; the conditions for these shift determinations are presented in the cited papers [4, 6, 17, 18] − here we mention only that they were recorded in DMSO-d_6 and referred to external neat nitromethane in a co-axial capillary. The impact sensitivity data of the nitramines studied, shown in Table 1, have also been taken from published literature [12-16, 19-21]: they were obtained by means of a standard impact tester with an exchangeable anvil (Julius Peters), detection of the 50% probability of initiation being based on acoustic detection (Bruceton method) [5, 12-16, 19-21]. This approach was also used in the work for this paper to determine the impact sensitivity for α-HMX. TETROGEN and DECAGEN have not been synthesized yet – their data have been predicted [4, 5].
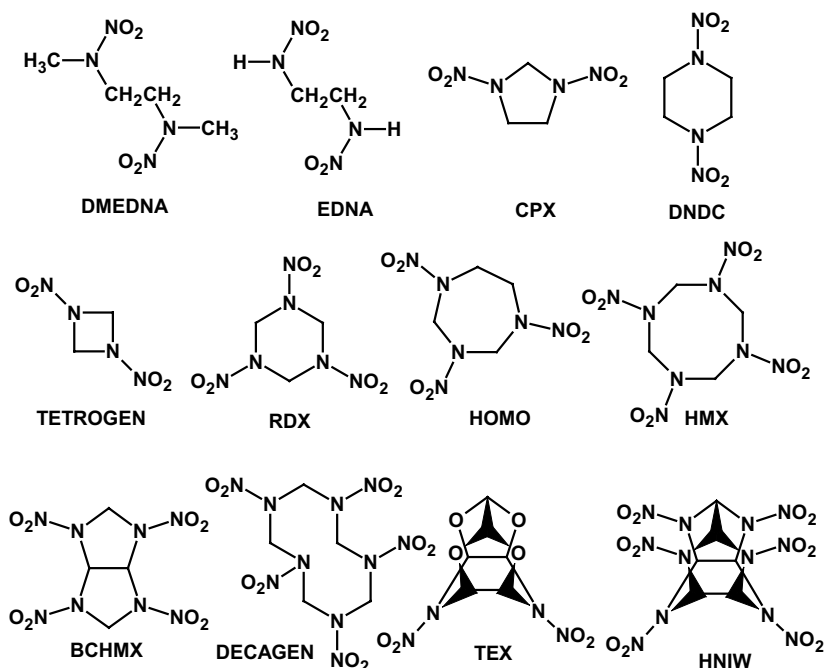
Figure 1.   Chemical formulae of the nitramines studied.

Table 1.   Survey of the ^{15}N NMR chemical shifts and impact sensitivities, expressed as the drop energy, E_{dr}, of the nitramines studied

| Data No.	Nitramine code	^{15}N NMR Chemical shift [ppm]			Ref.	Impact sensitivity [J]	
		Position in molecule	Nitrogen atom of group				
			nitro	amino		E_{dr}	Ref.
1	EDNA	1,4-	-26.34	-205.47	4	8.33	14
2	DMEDNA	2,5-	-27.83	-209.55	4	21.04	16
3	TETROGEN[b]	1,3-	-27.83	-203.62	4	9.97	15
4	CPX	1,3-	-31.21	-209.01	4	17.96	13
5	DNDC	1,4-	-26.26	-205.49	4	11.67	13
6	RDX	1,3,5-	-32.90	-198.10	17	5.58	14
7	HOMO	1,5-	-33.04	-201.28	4	4.55	13
		3-	-34.38	-196.32			
8	BCHMX	2,4,6,8-	-35.2	-190.1	6	2.98	6
9.1	β-HMX	1,3,5,7-	-34.70	-199.10	17	6.37	14
9.2	α-HMX					3.20	a
10	DECAGEN[b]	1,3,5,7,9-	-33.25	-197.38	4	4.90	15
11	TEX	4,10-	-33.40	-197.20	4	23.00	19
						24.25	20
12.1	ε-HNIW	2,6,8,12-	-40.30	-199.00	18	13.20	21
		4,10-	-43.40	-179.50			
12.2	ε-HNIW "normal"					4.10	12
12.3	α-HNIW					10.10	21
12.4	β-HNIW					11.90	21
12.5	γ-HNIW					12.20	21

Note: [a] result in this paper;
        [b] nitramine not yet synthesized.

3   Results and Discussion

The aza (amino) nitrogen chemical shifts, δ_A, in the nitramino groups are expected to be influenced by the nitrogen hybridization, the size and conformation of the molecule, and the extent to which the nitrogen lone pair is involved in π-bonding with the NO₂ group [17]. As both the conformation and the size of the molecule play a dominant role in the intermolecular interactions in the corresponding crystal, these interactions should have a significant influence on the impact

sensitivity [3, 15]. Therefore, the extent to which the nitro groups participate in the primary initiation processes differ depending on the particular nitramine being considered [2-5, 7-10].

Against this, it can be argued that NMR studies in solution overlook important crystal lattice effects that are vital in the determination of explosive properties [22]. From our recent papers [2-10] it can be seen that this has no fundamental significance for studies of the chemical micro-mechanism concerning initiation of energetic materials. This can be shown by Figure 2, especially by the positioning of the data for BCHMX and HNIW in this figure.
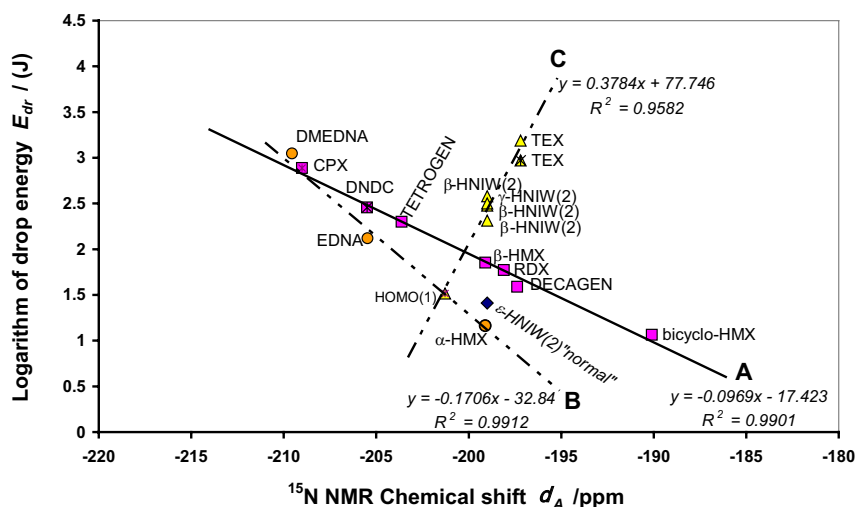
Figure 2. Semi-logarithmic relationship (2) between the drop energy, E_{dr}, and ^{15}N NMR chemical shifts, δ_A, of the aza nitrogen atoms carrying the nitro groups that are cleaved first in the initiation reaction (their positions in the molecule are given in parenthsis) – completed and revised figure from Reference 10.

BCHMX is an angular, rigid molecule with one N–N bond being markedly longer than the remaining three N–N bonds (see Figure 3, bond N3–N7). This fact, together with the absence of polymorphic forms of this nitramine, is a reason for the relatively high impact sensitivity of BCHMX. It is clear that, in solution, the BCHMX molecule is in conformational equilibrium, which means that this molecule is here spectroscopically isochronous. Nevertheless, this fact should not lead to any marked error in the ^{15}N NMR chemical shifts of the aza nitrogen atoms, as is documented by the very good correlation of the BCHMX data with line *A* in Figure 2.
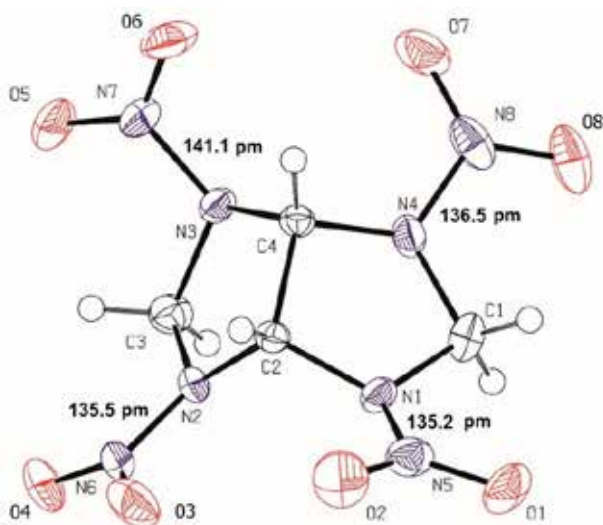
Figure 3. Drawing of the BCHMX molecule taken from paper [6], with the lengths of N–N bonds.

The same can be said about the N–N bonds in the 2,4,6,8-positions of the HNIW molecule; here the longest bond in position 2 (143.6 nm [23]) is a "carrier" of initiation reactivity for this nitramine. Also in this case, Figure 2 shows that the HNIW data correlate relatively well with line *C*: the influence of the different conformations of the HNIW polymorphic forms is reflected in their impact sensitivities, while the aza nitrogen atoms in the above mentioned positions are isochronous for the HNIW molecules in solution.

The impact sensitivity of HNIW strongly depends on crystal quality. In the case of its ε-form the literature still presents this as a highly sensitive nitramine. Impact sensitivities of the pure HNIW polymorphic forms are presented in Table 1. Together with the Crystal Engineering development a new technical product has appeared on the market, described as "Reduced sensitivity ε-HNIW" (RS-CL20) [12, 24-27] with an impact sensitivity of 8-12.6 J. A possible difference between the "normal" and RS-qualities of ε-HNIW can be seen in Figure 4 and also in Figure 2. Data for the ε-HNIW "normal" grade naturally do not correlate with any lines in Figure 2.

The higher initiation reactivity of the nitramino grouping in position 2 of the HNIW molecule correlates well with the higher reactivity of the nitramino grouping in position 1 of 1,3,5-trinitro-1,3,5-triazepane (HOMO); this fact has also been confirmed by use of the Mulliken population analysis of electron densities, q_N, obtained *ab initio* by DFT B3LYP/6-31G**, and its use in the study

of the initiation reactivities of nitramines [3, 5, 13]. It is appropriate to mention that the 1,3,5-triazepane skeleton forms part of the global hexaazaisowurtzitane skeleton; similarly a part of the global molecule TEX is the skeleton of 1,5-dioxa-3-nitroazepane, which should be spatially similar to its 1,3,5-triaza analogue. These facts are part of the reasons for the existence of line *C* in Figure 2.
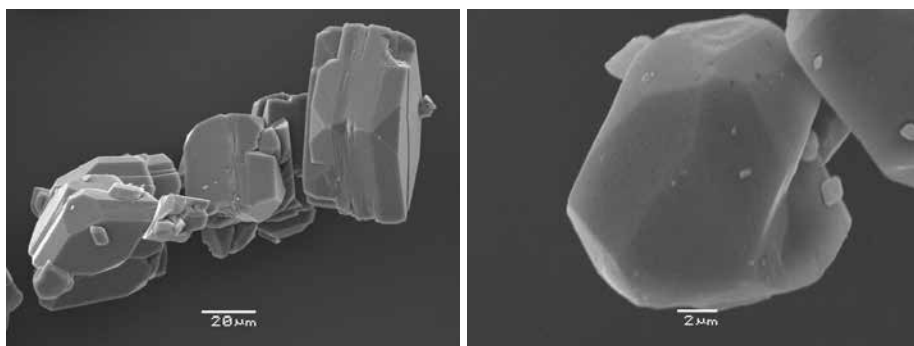
ε-HNIW "normal", purified and re-crystallized several times, purity 99%, impact sensitivity 4.2-4.4 J [12] – cracked surface of the crystals.

RS-ε-HNIW, purity 99%, impact sensitivity 10.8 J [12] – good quality of the crystal surface with rounded edges.

Figure 4.   Difference between the "normal" and RS qualities of ε-HNIW.

Relationship (2), represented in Figure 2 by both lines *A* and *B*, encompasses nitramines which may be generated notionally from the CPX molecule. In the case of the *B* group of nitramines, the presence of the ethylene dinitramine skeleton in them is evident; however, the α-HMX data also correlate with this line, something that might be caused by a similarity in the conformation of a part of its molecule (1,3,5-triazapentane-1,5-di-yl fragment) with parts of the HOMO molecule.

The differences in the slopes of lines *A* and *B*, on the one hand, and line *C* on the other, might be due to differences in intermolecular interaction in the crystals with non-global and global molecules of the nitramines studied. A similar difference between cyclic and linear nitramines was found in the case of impact sensitivity as "the first reaction" [3, 5]. It was already mentioned here that conformation and size of a given molecule play a dominant role in intermolecular interactions [3, 5]. This interaction might be characterized, to a certain extent, by the heat of fusion, $\Delta H_{m,tr}$. While the $\Delta H_{m,tr}$ values for nitramines with non-global molecules in this paper are in the range of 23.2-32.1 kJ mol^{-1} [16, 28, 29], for HNIW and TEX these values are 43.03 and 36.10 kJ mol^{-1} [16, 29], respectively.

The shape of the molecule also plays an important role in the transfer of the impact impulse into the reaction centre of the molecule [30].

It is well-known that the impact sensitivity of energetic materials depends on the general quality and granularity of the crystals. This is clearly demonstrated by HNIW, for which special conditions for obtaining its RS-grade are required, for perfect placing of the molecules into the crystal lattice during crystallization [24-27]. However, most nitramines (for example) when crystallized from a simple "beaker" in the laboratory give products whose impact sensitivity corresponds to the published data. How is it then that the published data for impact sensitivity [14] correlate well with the characteristics of the molecular structures of the given energetic materials [2, 3, 10, 13, 15, 16]? A similar problem has already been encountered in the study of the friction sensitivity of nitramines [16]. In this connection, HMX, crystallized in a "beaker" under ordinary laboratory conditions was screened [16], and the fractions obtained were tested for friction and impact sensitivities – Figure 5 was constructed from the latest sensitivity data [16].
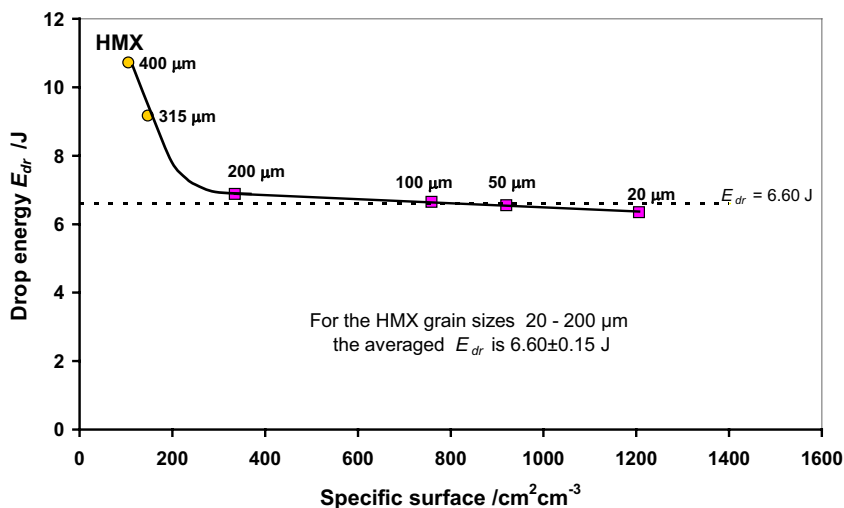
Figure 5.   Comparison of impact sensitivity, expressed as drop energy, with the specific surface area of the HMX fractions studied − constructed from data published in paper [16]; numbering of the points indicates the mesh size on which the given HMX fraction was retained.

The averaged drop energy for the HMX fractions with specific surface area from 588 to 1499 $cm^2 \cdot cm^{-3}$ in Figure 5 is close to the published value [14] in Table 1. A dependence similar to Figure 5 is also valid for friction sensitivity [16].

An interpretation of Figure 5 might be as follows: decreasing HMX granule

size corresponds to an increase in the number of hot spots on the surface (this may be documented by the trend in the specific surface area) which should lead to increasing sensitivity during uniaxial compression, while in the case of shear slide, with a fixed volume, the same trend leads to a loss of shear modulus (the resultant dust behaves as a liquid) – here for a specific surface area greater than 1200 cm$^2 \cdot$cm^{-3}. The problem of the very low dependence of impact sensitivity on the HMX grain size found in a certain range of specific surface area values needs further study, extending it to a wider range of individual energetic materials.

The results in this paper again confirm the close molecular structural dependence for drop energies (impact sensitivities) obtained by means of a standard impact tester (Julius Peters) with detection as the 50% probability of initiation based on acoustic detection (Bruceton method); output using this method can be found in the base data of the Los Alamos National Laboratory and/or the Naval Surface Weapons Center [14, 31, 32].

4   Conclusions

So far, the ^{15}N NMR chemical shifts of aza nitrogen atoms in nitramines appear to correspond best to the real electron configuration and the steric conditions of the key atoms at the reaction centre of a given molecule. From the point of view of the physics of explosion, these atoms might be taken as "chemical hot spots". The absence of any solid state influence on these chemical shifts, which were determined here in solution, does not have a fundamental influence on the above mentioned conclusion. The relationships presented here confirm the close molecular structural dependence of drop energies (impact sensitivities) obtained by means of a standard impact tester (Julius Peters) with detection as the 50% probability of initiation, on the basis of acoustic detection. Attention should be paid to the dependence of impact sensitivity on the specific surface area of the crystals obtained from a sample of an individual energetic material by screening.

5   References

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