

Heats of fusion of polynitro derivatives of polyazaisowurtzitane

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Abstract

Relationships were found between the heats of fusion $\Delta H_{m,tr}$ of 12 nitramines with rigid molecules, on one hand, and their molecular weights or their lengths of the longest N–N bonds or ^{15}N NMR chemical shifts of their amine and/or nitro group nitrogen atoms, on the other hand. On the basis of these relationships, the $\Delta H_{m,tr}$ values have been predicted for 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW, $\Delta H_{m,tr} = 42.70 \text{ kJ mol}^{-1}$) and 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane (TEX, $\Delta H_{m,tr} = 36.10 \text{ kJ mol}^{-1}$). It was stated that the HNIW molecule contributes to the intermolecular potential in its molecular crystals mainly by its nitro groups at 2, 6, 8, and 12 positions. The N–N bond length of 0.1377 nm was also predicted for nitramino groupings in 1 and 5 positions of the 1,3,5-trinitro-1,3,5-triazacycloheptane molecule. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Heat of fusion; ^{15}N NMR; HNIW; TEX

1. Introduction

The nitramines continue to be a source of new explosives characterized by high energy content [1–4]. An important point in selection and exploitation of explosives of this kind is, inter alia, studies of their physical stability [5]. A significant characteristics affecting this stability is the heat of fusion, which to a certain extent represents intermolecular interactions in nitramine crystals. In order to determine this quantity, one can apply differential scanning calorimetry (DSC) as a convenient method [5]. However, for the nitramines, which are thermolysed in solid, phase the heat of fusion $\Delta H_{m,tr}$ is only accessible by means of prediction methods. At present, the said type of attractive nitramines involves derivatives of poly-

azaisowurtzitane, particularly 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW) and 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane (TEX), the prediction of which was the topic of a preliminary study [6]. Results of this study were reinvestigated including a largest number of nitramines.

2. Substances and data sources

Table 1 presents a set of the nitramines whose data were used to predict the $\Delta H_{m,tr}$ values of HNIW and TEX. The heat of fusion $\Delta H_{m,tr}$ defined as a sum of all heats of the polymorphous transitions and of the heat of melting [7] was determined with a DSC-7 apparatus of Perkin-Elmer [5] or predicted in the sense of [5]: the $\Delta H_{m,tr}$ values given in Table 1 are the average of at least three measurements from [5]. The ^{15}N NMR

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Table 1
A survey of the nitramines studied and their molecular characteristics

Nitramine		Molecular weight	The longest N–N bond			¹⁵ N NMR chemical shift in ppm			Heat of fusion	
Chemical name	Code design		Length in nm	Note	Ref.	Position in molecule	Nitrogen atom nitro amino	Ref.	in kJ mol ⁻¹	Ref.
2-Nitro-2-azapropene	DMNA	90.08	0.1332	In the crystal	[14]	2	–25.84 –215.80	[9]	17.26	[5]
1-Nitro-1-azaethylene	DIGEN	74.04	0.1417	Obtained by HF/6-31G* optimization in the original paper	[15]	1	–23.58 –208.52	[7,8]	23.45	[5]
1,3-Dinitro-1,3-diazacyclobutane	TETROGEN	148.08	0.1355	Obtained by HF/6-31G* optimization in the original paper	[15]	1,3	–27.83 –203.62	[7,8]	26.32	[5]
1,3-Dinitro-1,3-diazacyclopentane	CPX	162.11	0.1346	Obtained by 3-21G optimiz.	[13]	1,3	–31.21 –209.01	[7,8]	22.57	[5]
			0.1410	Experimental value						
1,4-Dinitro-1,4-diazacyclohexane	DNDC	168.17	0.1373	Obtained by 3-21G optimization in the original paper	[13]	1,4	–26.26 –205.49	[7,8]	33.82	[5]
1,3,5-Trinitro-1,3,5-triazacyclohexane	RDX	222.12	0.1398	Axial N–N bond	[14]	1,3,5	–32.90 –198.10	[9]	33.01	[5]
1,3,5-Trinitro-1,3,5-triazacycloheptane	HOMO	236.15	0.1377	In 1 and 5 positions–predicted by means of relation E in Fig. 2	This paper	1,5	–33.04 –201.28	[7,8]	27.74	[5]
1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane	β-HMX	296.16	0.1368	Axial N–N bond	[14]	1,3,5,7	–34.38 –196.32	[9]	32.10	[5]
1,3,5,7,9-Pentanitro-1,3,5,7,9-pentaazacyclo-decane	δ-HMX DECAGEN	370.02	0.1392	Equatorial N–N bond		1,3,5,7,9	–34.70 –199.10	[9]	32.10	[5]
1,5-Endomethylene-3,7-dinitro-1,3,5,7-tetraaza-cyclooctane	DPT	218.18	0.1386	Experimental value	[20]	3,7	–33.25 –197.38	[7,8]	34.93	[5]
1,5-Diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclo-octane	DADN	290.24	0.1352	Experimental value	[21]	3,7	–25.30 –203.70	[9]	28.16	[24]
1,4,5,8-Tetranitro-1,4,5,8-tetraazadecaline	TNAD	322.20	0.1417	Experimental value	[13]		–23.70 –205.10	[7,8]	26.26	[25]
2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaaza-isowurtzitane	ε-HNIW	438.20	0.1436	Position 2 in the molecule	[16]	2,6,8,12	–40.30 –199.00	[10]	42.70	This paper
4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaiso-wurtzitane	TEX	262.14	0.1414	Position 4 in the molecule	[11]	4,10	–43.40 –179.50	[7,8]	36.10	This paper
						4,10	–33.40 –197.20	[7,8]	36.10	This paper

chemical shifts of nitrogen atoms of nitramine groupings were mostly measured with an AMX-360 Bruker apparatus using the INEPT method [8,9], whereas a part of them were taken from literature [10,11], and those of the nitramines not yet described were predicted [8,9]. The data about the longest N–N bonds in molecular crystals of nitramines were taken from refs [12–18,20,21].

3. Results and discussion

Physical properties of polyfunctional molecules are influenced by the character and intensity of local interactions, i.e. by magnitude, number, distances and orientation of group dipoles within a molecule. The factors mentioned are directly connected with the size of a molecule, its conformation, symmetry and with the quality and quantity of the substituents present [7,22].

3.1. Heats of fusion versus molecular weights

In crystals of the polynitramines listed in Table 1, the dominant interactions are the direct electrostatic

ones (also named orientation interactions [7]). The dependence of their intensity on the magnitude of molecule weight is depicted in Fig. 1 presenting the relationship between $\Delta H_{m,tr}$ values and molecular weight. In this sense, the set of nitramines with rigid molecular structure is divided into the following subsets:

- Nitramines with four and six-membered rings in their molecules (due to distinct symmetry, DNDC shows a higher $\Delta H_{m,tr}$ value than expected [5]) which can be derived from DMNA,
- The nitramines whose molecules forms four, eight and 10-membered rings which are multiples of DIGEN building units,
- The nitramines which can be derived from DMNA and which are related to the 1,3-dinitro-1,3-diazacyclopentane and 1,3,5-trinitro-1,3,5-triazacycloheptane sections of the HNIW molecule.

Data of DADN do not correlate with any of the above-mentioned subsets due to the presence of two acetyls in its molecule; from the point of view of the electrostatic intermolecular interactions acetyl groups cannot be taken equivalent to nitro

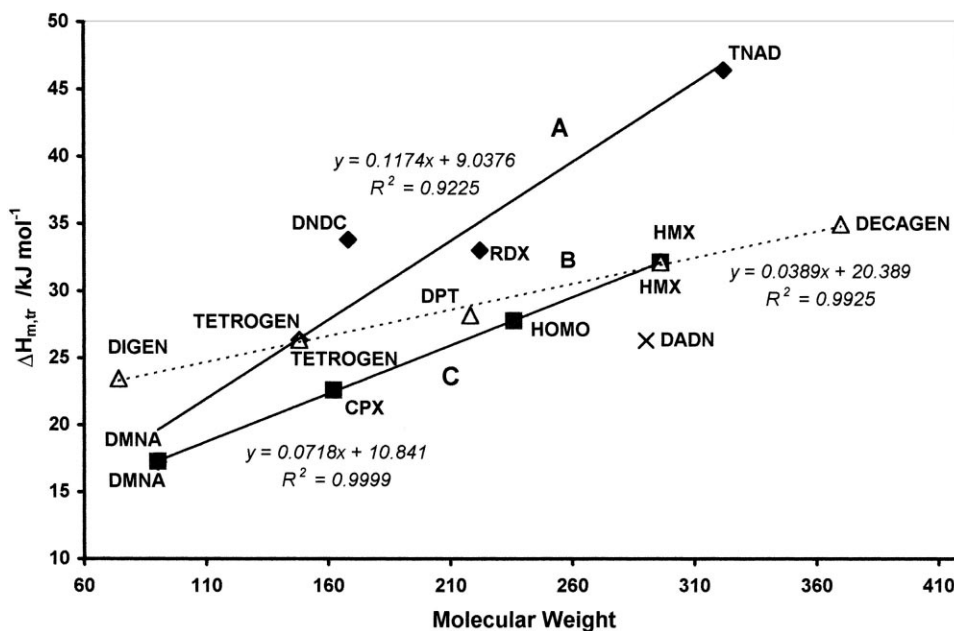


Fig. 1. Relationship between the heats of fusion $\Delta H_{m,tr}$ and molecular weights of the nitramines studied.

groups. Application of the relationship A gave the $\Delta H_{m,tr}$ values $39.81 \text{ kJ mol}^{-1}$ for TEX, while the relationship C resulted in $\Delta H_{m,tr} = 42.30 \text{ kJ mol}^{-1}$ for HNIW.

3.2. Heats of fusion versus N–N bond lengths

It is well known that intra- and intermolecular interactions in crystals affect the conformation of molecules as compared with the conformation of the same isolated molecules or in solution [27] or melt (some N–N bonds in crystals of nitramines can be compressed [15]). Thus, changes in bond lengths can be encountered even in apparently symmetrical molecules (see corresponding data in [15,26]). In the case of nitramine grouping acting as a carrier of orientation interaction in nitramine crystals, one of the N–N bonds is usually the longest one (see e.g. [15,17]). The relation between this distinct manifestation of force factors within the crystal and the $\Delta H_{m,tr}$ values is presented in Fig. 2. In the sense of this relationship the set of nitramines is divided into the following subsets, derived in all cases from DMNA:

- D. Nitramines inclusive of CPX with calculated N–N bond lengths; it must be stated that the 1,4-dinitro-1,4-diazacyclohexane (DNDC) molecule has a chair structure [18], probably about the 2,5-axis [19] and is not centrosymmetric in the crystal lattice [19],
- E. Nitramines in whose molecules all nitro groups have in *cis*-conformation ('crown' conformation—see [15,26] for δ -HMX, [15,27] for RDX and [20] for DPT),
- F. Nitramines including CPX with experimental N–N bond length given here for illustration of possible differences between calculated and real values of N–N bond lengths which can lead, however, to logic relationships.

As the space orientations of the nitro groups of the 1,3-diazacyclopentane skeleton in ϵ -HNIW (see [17]) and of the 1,4-diazacyclohexane skeleton in TEX molecules (see below and [12]) are like to those in nitramines of the E subset, the $\Delta H_{m,tr}$ values of $41.12 \text{ kJ mol}^{-1}$ and of $36.18 \text{ kJ mol}^{-1}$ were obtained for HNIW and TEX, respectively, on the basis of the corresponding relationship.

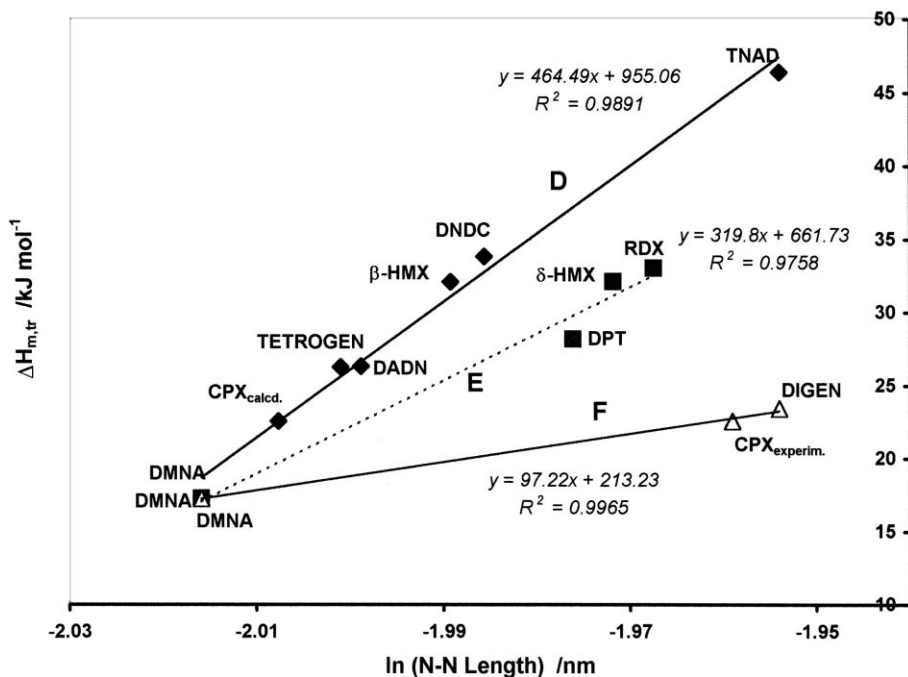


Fig. 2. Relationship between the heats of fusion $\Delta H_{m,tr}$ and lengths of the longest N–N bonds in the nitramines studied.

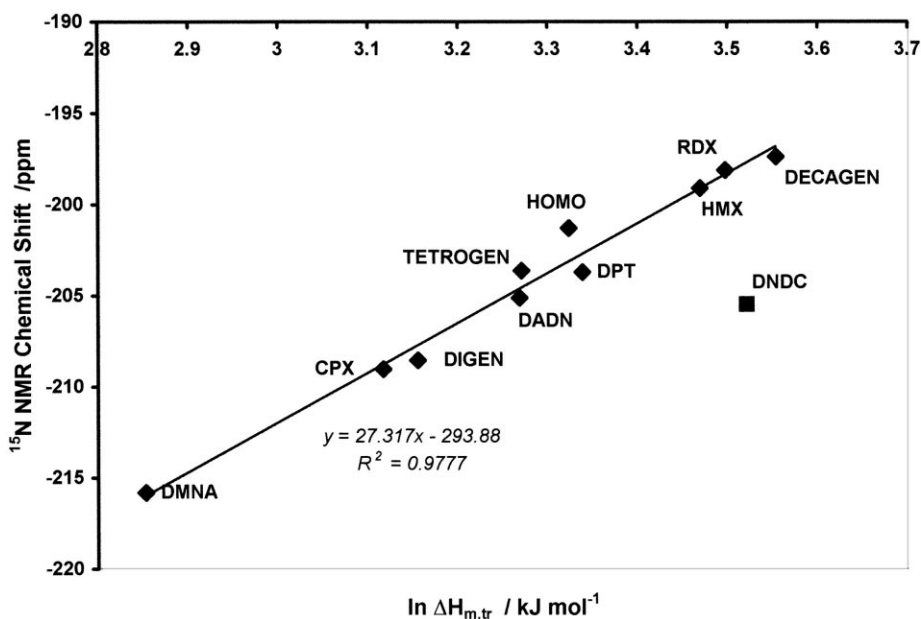


Fig. 3. Relationship between the ^{15}N NMR chemical shifts of aza atoms in nitramine groupings and heats of fusion $\Delta H_{m,tr}$ of the nitramines studied.

3.3. Heats of fusion versus ^{15}N NMR chemical shifts of aza atoms

The conformation of nitramine molecules is connected with the ^{15}N NMR chemical shifts δ_A of amine nitrogen (aza) atoms in their nitramine groupings [10]. With regard to the above-mentioned role played by conformation in intermolecular relations in crystals, Fig. 3 presents the dependence between the δ_A shifts and $\Delta H_{m,tr}$ values of substances of Table 1. In the case of 1,3,5-trinitro-1,3,5-triazacycloheptane (HOMO), this relationship is better obeyed by the chemical shifts of aza nitrogen atoms at 1 and 5 positions than by those at 3-nitrogen atom: in other words, the nitramine groupings at 1 and 5 positions of HOMO molecule play the decisive role in intermolecular effects within its crystal.

Application of the dependence given in Fig. 3 to the case of HNIW gave the value of $\Delta H_{m,tr} = 31.98 \text{ kJ mol}^{-1}$ when using the δ_A values at 2, 6, 8, and 12 positions. Analogous calculations carried out for TEX gave $\Delta H_{m,tr} = 34.15 \text{ kJ mol}^{-1}$. The $\Delta H_{m,tr}$ value of HNIW is too low due to a solvating effect during the NMR measurement: while the N–N bond lengths at 2,6,8, and 12-positions of the ϵ -HNIW molecule in the

crystalline state are different [17], geometrical constraints in the molecule are averaged in acetone- d_6 solution and nitramino groupings at these positions appear equivalent in the ^{15}N NMR chemical shifts (see Table 1), i.e. the shifts appear quasi-equivalence of the above-mentioned lengths of N–N bond.

3.4. Heats of fusion versus ^{15}N NMR chemical shifts of nitrogens in the nitro groups

The values of ^{15}N NMR chemical shifts δ_N of nitrogen atoms of nitro groups are not closely related to the conformation of nitramines [10]. As nitro groups are the main cause of orientation interaction in nitramine crystals, these shifts should be related to the respective $\Delta H_{m,tr}$ values, which is documented in Fig. 4. In the sense of the dependences presented in this picture, the set of nitramines of Table 1 is divided into two subsets:

- G. The nitramines whose molecules are integer multiples of DIGEN building units,
- H. The nitramines derived from DMNA which correspond to the 1,3-dinitro-1,3-diazacyclopentane and 1,3,5-trinitro-1,3,5-triazacycloheptane sections of the HNIW molecule,

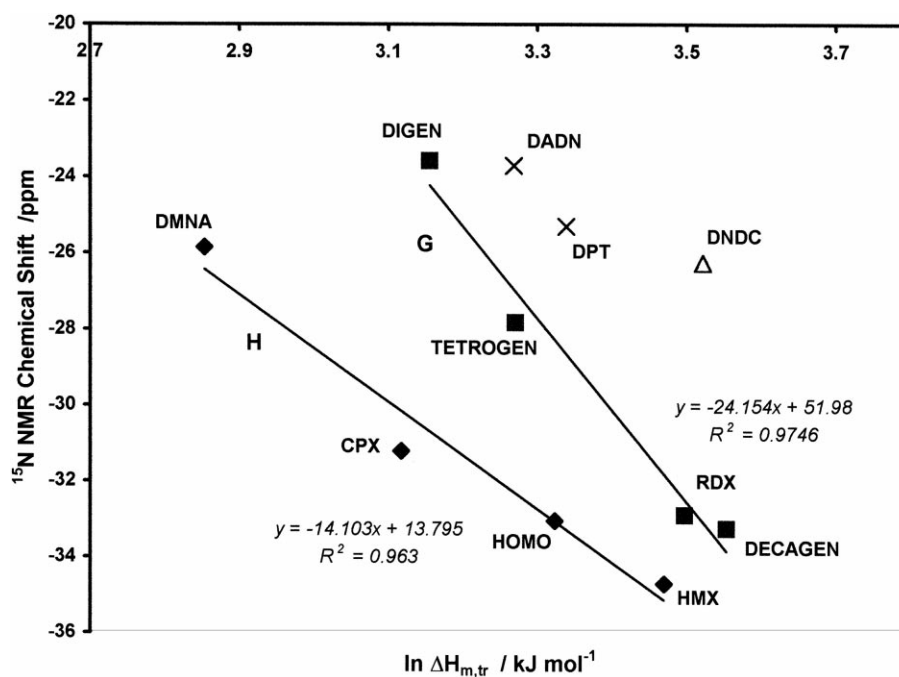


Fig. 4. Relationship between the ^{15}N NMR chemical shifts of nitro nitrogens in nitramine groupings and heats of fusion $\Delta H_{m,tr}$ of the nitramines studied.

Due to the lower portion of nitro groups in DADN and DPT, data of these nitramines do not correlate with any from of the above-mentioned subsets. DNDC data do not correlate probably due to a higher $\Delta H_{m,tr}$ value than expected [5].

The dependences G and H intersect at a point corresponding to the values of $\delta_{\text{N}} = -39.8$ ppm and $\Delta H_{m,tr} = 44.68$ kJ mol $^{-1}$. The δ_{N} value mentioned is practically identical with those at the 2, 6, 8, and 12 positions of NHIW molecules (see Table 1)—in other words: the δ_{N} value measured at these positions correlates well with both the dependences in Fig. 4, and the corresponding value of $\Delta H_{m,tr}$ reflects the real heat of fusion of HNIW.

As far as TEX (whose molecular crystal is dominated by orientation interactions of its nitramine groupings) is concerned, the 1,4-diazacyclohexane part of its skeleton has a boat structure [12]. Negative induction effects of acetal oxygen atoms in its molecule can influence the electronic density of aza atoms. This assumption of steric effects in its molecule and corresponding shielding lead to ^{15}N NMR chemical

shifts, whose values are very close to those of RDX (see Table 1). Therefore, dependence G was applied for the $\Delta H_{m,tr}$ prediction of TEX and value of 34.29 kJ mol $^{-1}$ was thus obtained.

3.5. Discussion of predicted $\Delta H_{m,tr}$ values

The predicted values of $\Delta H_{m,tr}$ (see Table 2) do not exceed the expected limits. In the case of HNIW the said fact can be documented by the trend of these values exhibited when going from linear via cyclic to globular molecules (generally see [22])—in our case nitramines. For an example we can mention polynitramines having the same nitramine groupings in their molecules and similar molecular weights whose $\Delta H_{m,tr}$ are as follows:

2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatridecane	109.07 kJ mol $^{-1}$ [5]
1,3,5,7,9,11-hexanitro-1,3,5,7,9,11-hexaazacyclododecane	37.80 kJ mol $^{-1}$ [23]
2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane	42.70 kJ mol $^{-1}$ (this paper).

Table 2
A survey of predicted $\Delta H_{m,tr}$ values

Nitramine	Prediction of $\Delta H_{m,tr}$ in kJ mol ⁻¹ , by means of			$\Delta H_{m,tr}$ value	Averaged $\Delta H_{m,tr}$ value in kJ mol ⁻¹
	Fig.	and	dependence		
HNIW	1		C	42.30	42.70 ± 1.32
	2		E	41.12	
	4		H-G	44.68	
TEX	1		A	39.81	36.10 ± 1.41
	2		E	36.18	
	3			34.15	
	4		G	34.29	

Linear polynitramines with three and more methylenenitramine groupings in their molecules have higher $\Delta H_{m,tr}$ values than their cyclic analogues [5]. The difference between the $\Delta H_{m,tr}$ values of the first two substances is due mainly to rigidity differences between their molecules [5] and to different N–N bond lengths in linear and cyclic nitramines (see below). As documented by the results of this communication the globular HNIW molecule contributes to the intermolecular potential in its molecular crystals mainly by its nitro groups at 2, 6, 8, and 12 positions (there is the longest N–N bond in 2 position of molecule of its ϵ -polymorph [17]). The N–N bond lengths at these positions in the ϵ -HNIW molecule range in a relatively broad interval from 0.1380 to 0.1436 nm [17] (the length of N–N single bond should be 0.1425 nm [13]). The broad interval of these bond lengths is also characteristic of cyclic nitramine molecules, viz from 0.1346 to 0.1410 nm [14,15], whereas for linear nitramines it varies from 0.132 to 0.136 nm [13,15]. The decisive participation of only some nitro groups in the intermolecular potential, the long N–NO₂ bonds, and the rigid globular structure of HNIW molecule results in its $\Delta H_{m,tr}$ value close to that of 1,3,5,7,9,11-hexanitro-1,3,5,7,9,11-hexaazacyclododecane.

The relationships derived in this communication can also be applied in the reciprocal sense. Thus taking the significance of the nitramine groupings at 1 and 5 positions of HOMO in intermolecular effects within its crystal and by means of relationship for E subsets (from Fig. 2) a length of 0.1377 nm results for the corresponding N–N bonds.

The nitramine groupings in HOMO, HNIW and TEX molecules, which play the decisive role in orientation interaction in their molecular crystals,

are the first to undergo homolysis during both the thermolysis [9] and the initiation of detonation [8] of these substances.

4. Conclusions

The results presented show that we can obtain real heat of fusion ($\Delta H_{m,tr}$) values for 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW) by applying the prediction relationships involving, first of all, the 1,3-diazacyclopentane and 1,3,5-triazacycloheptane structures (i.e. the dependence C and the point of intersection of the dependences G and H) or the comparable effect of intermolecular interactions on the length and *cis*-orientation in space of N–N bonds in molecular crystals (the dependence E). Amongst the measurable characteristics of HNIW molecules the most favorable for application to prediction relationships seem to be the values of ¹⁵N NMR chemical shifts δ_N of nitrogen atoms of nitro groups. On the other hand, the ¹⁵N NMR chemical shifts δ_A of aza atoms lead to unreal $\Delta H_{m,tr}$ values due perhaps to the significant difference between the conformation of HNIW skeleton in solution (during the measurements of NMR spectra) and that in HNIW crystal. The results obtained by these ways show that the globular HNIW molecule contributes to the intermolecular potential in its molecular crystals mainly by its nitro groups at 2, 6, 8, and 12 positions

From the point of view of molecular structure, the predictions of the above-mentioned type are simpler for 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane (TEX): in this case real $\Delta H_{m,tr}$ values result from the application of the dependences A, E, and G.

In contrast to the case of HNIW ^{15}N NMR chemical shifts of aza atoms are also favorable for the said prediction (Fig. 3).

The predicted $\Delta H_{m,tr}$ values of the two nitramines characterize intermolecular force interactions in their crystals and can thus be considered representatives of such interactions.

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