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# Some predictions in the field of the physical thermal stability of nitramines

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**Abstract**

Eight linear and seven cyclic nitramines predominantly with methylenenitramine grouping were studied by means of the differential scanning calorimetry (DSC). For eleven of them the characteristics of fusion were specified. Linear relationships were found between the onset or peak temperatures of melting of these compounds and the melting points of their aliphatic structural analogues (i.e. homomorphs). A similar relationship between the corresponding heats of fusion $\Delta H_{m,\,tr}$ was specified. On the basis of these facts the melting points (in K) and the $\Delta H_{m,\,tr}$ values (in kJ mol$^{-1}$) were predicted for N-nitromethyleneimine, DIGEN (368.5–371.5 and 23.45), 2,4-dinitro-2,4-diazacyclobutane, TETROGEN (433.8–436.1 and 26.33), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane, OCTOGEN (463.4–465.2 and 32.10), 1,3,5,7,9-pentanitro-1,3,5,7,9-pentaazacyclodecane, DECAGEN (600.3 and 34.93) and trans-1,4,5,8-tetranitro-1,4,5,8-tetraazadecaline, TNTAD (555.6–556.1 and 46.40). © 1997 Elsevier Science B.V.

*Keywords:* Heat of fusion; Melting point; Nitramines; Thermal stability

## 1. Introduction

Nitramines have long been important in technological applications. This group is still a source of explosives that possess predominantly a high energy content [1–3]. The important starting point for selection and exploitation of these nitro compounds is the study of both their physical and chemical thermostabilities.

With respect to the physical thermostability of nitramines, the temperatures of the polymorph transitions of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (OCTOGEN) are not clearly defined [4–9] yet and some uncertainty also exists in the case of its melting point as may be shown, for example, by a part of [10]. A prediction of the physical thermostability characteristics has also a certain significance in the field of research and development of new energetic cyclic nitramines. Therefore, these problems have been dealt with in the present study.

Analogous problems have been solved in the [11], where the melting point of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) was predicted on the basis of comparing the melting points of sym-trinitrobenzene and its aminoderivatives with those of sym-triazine structural analogues. Hence the paraffinic structural analogues of the nitramines studied are taken as reference substances (i.e. homomorphs) in the present study.

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## 2. Experimental

The characteristics of fusion, i.e. onset and peak temperatures of melting and values of corresponding heats $\Delta H_{\mathrm{m,\ tr}}$ (according to the monograph [12] defined as the sum of heat of melting and heats of all polymorph transitions) were determined in the thermoanalytical laboratory of CHEMKO Special Production Plant (Strážske, The Slovak Republic) by means of a Perkin–Elmer differential scanning calorimeter DSC-7. The apparatus was calibrated for indium and lead. During the measurement, nitrogen was introduced into the furnace of the DSC and the heating rate of 20° $\mathrm{min}^{-1}$ was used. Weighed amounts (0.978–2.075 mg) of crystalline nitramines were placed in aluminium pans (Perkin–Elmer, Part No. BO14-3016) fitted with covers (Perkin–Elmer, Part No. BO14-3040). The resulting DSC records were analyzed by means of the DSC-7 Standard Program, which is licensed by Perkin–Elmer [13]. The survey of the codes of the nitramines studied and the results obtained are presented in Table 1. Homomorphs fusion data in the Table 1 are taken from Chapter 14 of the monograph [12]. To be specific, the following nitramines were involved (nitramine No, its code designation):

| | |
|---|---|
| 2-nitro-2-azapropane | (1, DMNA) |
| 2,4-dinitro-2,4-diazapentane | (2, DNAPTN) |
| 2,5-dinitro-2,5-diazahexane | (3, DMEDNA) |
| 2,4,6-trinitro-2,4,6-triazaheptane | (4, TNAHP) |
| 2,4,7,9-tetranitro-2,4,7,9-tetraazadecane | (5, TNADEC) |
| 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatridecane | (6, HNATDEC) |
| 1,3-dinitro-1,3-diazacyclopentane | (7, CPX) |
| 1,4-dinitro-1,4-diazacyclohexane | (8, 1,4-DNDC) |
| 1,3,5-trinitro-1,3,5-triazacyclohexane | (9, RDX) |
| 1,3,5-trinitro-1,3,5-triazacycloheptane | (10, TNACHP) |
| $\beta$-1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane | (11, $\beta$-HMX) |
| $\alpha$-1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane | (12, $\alpha$-HMX) |
| trans-1,4,5,8-tetranitro-1,4,5,8-tetraazadecaline | (13, TNTAD) |
| 1,4-dinitro-1,4-diazabutane | (14, EDNA) |
| 2,5-dinitro-2,5-diazahexan-3,4-dione | (15, DMDNO) |

Predictions were made also for N-nitromethylimine (DIGEN), 2,4-dinitro-2,4-diazacyclobutane (TETROGEN) and 1,3,5,7,9-pentanitro-1,3,5,7,9-pentaazacyclodecane (DECAGEN), i.e. for substances which have not been synthesized yet (see Table 4).

## 3. Results and discussion

When studying the interrelations heats of fusion ($\Delta H_{\mathrm{m,\ tr}}$) of nitramines (designated as $\Delta H_{\mathrm{NA}}$) and the heats of corresponding homomorphs (designated as $\Delta H_{\mathrm{HMP}}$) we can find a relationship of the general form

$$\Delta H_{\mathrm{NA}} = a_1 \Delta H_{\mathrm{HMP}} + b_1 \tag{1}$$

Similarly, a relationship can be found between melting characteristics of the nitramines (designated as $\mathrm{Mp}_{\mathrm{NA}}$) and of their homomorphs (designated as $\mathrm{Mp}_{\mathrm{HMP}}$) in the general form

$$\ln \mathrm{Mp}_{\mathrm{NA}} = a_2 \ln \mathrm{Mp}_{\mathrm{HMP}} + b_2 \tag{2}$$

In terms of these equations whose coefficients are presented in Table 2 (Eq. (1)) and in Table 3 (Eq. (2)), the set of substances studied is divided into two groups: linear nitramines 2–6 (flexible molecules); and cyclic nitramines 7–13 (rigid molecules).

The data of nitramine 1 only correlate well with relationships for cyclic analogues; the nitramine has a relatively simple molecular structure (i.e. it exhibits the lowest number of space arrangements) and therefore behaves as a substance with a rigid molecule. The data of cyclic nitramine 8, on the other hand, very poorly correlate with the said relationships due to the high space symmetry of its molecule. The presence of another polar group in nitramine 14 (i.e. N–H with hydrogen bonding) and also in nitramine 15 (i.e. CO) is the reason of incompatibility (in terms of Eqs. (1) and (2)) of the data of substances with those of the other nitramines studied.

By means the fusion data of the homomorphs and Eqs. (1) and (3), the corresponding fusion characteristics of nitramines 6, 11, 12, 13, DIGEN, TETROGEN and DECAGEN were predicted (Table 4).

Table 1
Survey of nitramines studied, their fusion parameters from DSC and of their homomorphs fusion data

| Nitramine | | Polymorph transition | | Melting | | Heat of fusion | Homomorph | | |
|---|---|---|---|---|---|---|---|---|---|
| No. | Code | onset (K) | peak (K) | onset (K) | peak (K) | $\Delta H_{m,\ tr}$ (kJ mol$^{-1}$) | Substance | Mp (K) | Heat of fusion (kJ mol$^{-1}$) |
| 1 | DMNA | | | 328.3 | 330.9 | 17.244 | n-Propane | 86 | 3.51 |
| | | | | 328.8 | 331.3 | 17.111 | | | |
| | | | | 329.3 | 332.4 | 17.442 | | | |
| 2 | DNAPTN | | | 327.9 | 330.2 | 16.481 | n-Pentane | 143 | 8.41 |
| | | | | 328.5 | 330.3 | 16.225 | | | |
| | | | | 327.8 | 330.0 | 16.367 | | | |
| 3 | DMEDNA | | | 406.6 | 409.1 | 29.433 | n-Hexane | 178 | 13.01 |
| | | | | 408.1 | 410.7 | 29.373 | | | |
| | | | | 407.8 | 409.7 | 29.420 | | | |
| 4 | TNAHP | 429.0 | 431.2 | 438.2 | 440.83 | 3.566 | n-Heptane | 183 | 14.10 |
| | | 429.6 | 431.6 | 439.7 | 442.3 | 34.011 | | | |
| | | 429.1 | 431.2 | 440.2 | 442.4 | 34.016 | | | |
| 5 | TNADEC | 473.2 | 475.2 | 485.4 | 488.3 | 67.857 | n-Decane | 243 | 28.70 |
| | | 473.8 | 475.2 | 485.7 | 488.7 | 68.448 | | | |
| | | 473.6 | 475.1 | 484.6 | 487.4 | 67.975 | | | |
| 6 | HNATDEC | 464.6 | 465.6 | decomposition in solid state above 460 K | | | n-Tridecane | 267 [a] | 44.83 [b] |
| 7 | CPX | | | 403.5 | 407.6 | 22.610 | Cyclopentane | 122 | 5.81 |
| | | | | 403.5 | 407.5 | 22.522 | | | |
| | | | | 403.5 | 407.5 | 22.579 | | | |
| | | | | 403 [c] | | 25.104 [c] | | | |
| 8 | 1,4-DNDC | | | 487.3 | 490.0 | 34.569 | Cyclohexane | 186 | 9.29 |
| | | | | 486.2 | 489.1 | 33.294 | | | |
| | | | | 487.0 | 489.8 | 33.608 | | | |
| 9 | RDX | | | 476.7 | 477.8 | 32.141 | Cyclohexane | 186 | 9.29 |
| | | | | 476.4 | 477.4 | 33.598 | | | |
| | | | | 476.5 | 477.4 | 32.963 | | | |
| | | | | | 478.5 [c] | 35.647 [c] | | | |
| | | | | | 477.4 [d] | 30.710 [d] | | | |
| 10 | TNACHP | 424.8 | 428.1 | 433.5 | 435.7 | 27.816 | Cycloheptane | 134 | 7.57 |
| | | 425.4 | 428.8 | 433.9 | 436.1 | 27.609 | | | |
| | | 425.2 | 428.6 | 433.7 | 435.9 | 27.790 | | | |
| 11 | $\beta$-HMX | 457.4 | 462.0 | decomposition in solid state above 530 K | | | Cyclooctane | 166 | 9.12 |
| 12 | $\alpha$ -HMX | 466.2 | 470.7 | decomposition in solid state above 490 K | | | Cyclooctane | 166 | 9.12 |
| 13 | TNTAD | | | decomposition in solid state above 470 K | | | trans-Decaline | 241 | 14.39 |
| 14 | EDNA | | | 451.4 | 455.2 | 23.455 | n-Butane | 107 | 6.74 |
| | | | | 450.9 | 455.9 | 23.032 | | | |
| 15 | DMDNO | | | 395.0 | 397.1 | 22.887 | n-Hexan-3,4-dione | 304 | |
| | | | | 395.4 | 397.0 | 23.910 | | | |

[a] The value taken from [16].
[b] Calculated from Eq. (5).
[c] The values taken from [14].
[d] The values taken from [15].

Table 2
Coefficients of Eq. (1) – relationship between the heats of fusion nitramines and of their homomorphs

| Structure of nitramines groups [a] | Coefficient | | |
|---|---|---|---|
| | $a_1$ | $b_1$ | correlation |
| Linear nitramines 2–5 | 2.5071 | −3.3197 | 0.9980 |
| Cyclic nitramines 7, 9, 10 and linear nitramine 1 | 2.7130 | 7.3639 | 0.9964 |

[a] Nitramines are numbered as in Table 1.

Table 3
Coefficients of Eq. (2) – relationship between the melting characteristics of nitramines and of their homomorphs

| Structure of nitramines groups [a] | Coefficient | | |
|---|---|---|---|
| | $a_2$ | $b_2$ | correlation |
| Linear nitramines 2–5 | | | |
| –for onsets of melting | 0.7248 | 2.2408 | 0.9486 |
| –for peaks of melting | 0.7241 | 2.2503 | 0.9490 |
| Cyclic nitramines 7, 9, 10 and linear nitramine 1 | | | |
| –for onsets of melting | 0.4871 | 3.6485 | 0.9806 |
| –for peaks of melting | 0.4785 | 3.6965 | 0.9789 |

[a] Nitramines are numbered as in Table 1.

The predicted values for TETROGEN are in accordance with the expectation. By the 'Quantitative Structure-Property Relationship' calculation (see on example [22,23]) the value 440.8 K of its melting point was obtained [18]. The value may also be confirmed by comparison with the melting point of 1,3,3-trinitroazetidine (i.e. 370 K [3]), which has similar structure of the molecule basic skeleton; the higher value of melting point of TETROGEN corresponds to the higher space symmetry of its molecule.

Most authors set the visual melting point of OCTOGEN (i.e. nitramine 11 and 12) $\sim 553$ K; Maycock and Pai Verneker have noted [4] an occurrence of melting endotherm in the differential thermal analysis (DTA) of the OCTOGEN only at higher heating rates. A strong and sharp endothermic peak at 558 K in DSC of the nitramine was also recorded by Hussain and Rees [19], who used the heating rate of 20 K $\text{min}^{-1}$. No endotherm of melting is detectable, however, in the current DTA or DSC investigation of the OCTOGEN. With respect to the polymorph transitions of this substance the values of the corresponding temperatures depend not only on the method and techniques of their determination [8], but also on the OCTOGEN grain size [20,21] and the pressure applied [21]. As shown in Table 4, the predicted melting characteristics of OCTOGEN are in a good agreement with the temperature of its $\beta \rightarrow \delta$ polymorph transition determined by Hall [13] and Cetner et al. [7] on the basis of DSC-measurements at atmospheric pressure. Two values of the heat of this transition were published: 9.09 kJ $\text{mol}^{-1}$ [7]; and 9.79 kJ $\text{mol}^{-1}$ [9]. The remaining part of predicted $\Delta H_{\text{m, tr}}$ value of this nitramine participates in its $\delta$ polymorph stabilisation at temperatures above 460 K, inhibiting thus its thermal decomposition.

When taking the HEXOGEN homologues as cyclic polymers of N-nitromethylimine (i.e. DIGEN), and taking also the corresponding characteristics of fusion from Tables 1 and 4, one can obtain interesting results. Thus a relationship exists between the heats of fusion and number ($n$) of DIGEN units in molecule of TETROGEN, OCTOGEN and DECAGEN in the form

$$\Delta H_{\text{m,tr}} = 2.87n + 20.58 \quad (3)$$

with the correlation coefficient $r = 0.9999$. By means of this equation the heat of fusion of DIGEN can be predicted (see Table 4). Another relationship results from the comparison of melting onset values of DIGEN, TETROGEN, HEXOGEN and DECAGEN

Table 4
Survey of the predicted values of fusion characteristics

| Nitramine | Melting onset K | Melting peak K | Heat of fusion kJ mol$^{-1}$ | Note |
|---|---|---|---|---|
| 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazatridecane (HNATDEC) | 539.4 | 542.4 | 109.07 | Experimental melting point of 550 K with decomposition [a] |
| N-Nitromethylimine [b] (DIGEN) | 368.5 [c] | 371.5 [c] | 23.45 [d] | It has not been synthesized yet |
| 2,4-Dinitro-2,4-diazacyclobutane [e] (TETROGEN) | 433.8 | 436.1 | 26.32 | It has not been synthesized yet |
| 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (OCTOGEN, HMX) | 463.4 | 465.2 | 32.10 | Polymorph transition $\alpha \rightarrow \delta$ in the range of 420–458 K [f] or by DSC 471 K [g]<br>Polymorph transition $\beta \rightarrow \delta$ in the range of 415–448 K [f] or by DSC 460±3 K [g] |
| 1,3,5,7,9-Pentanitro-1,3,5,7,9-pentaazacyclodecane [i] (DECAGEN) | 600.3 | 600.3 | 34.93 [h] | It has not been synthesized yet |
| trans-1,4,5,8-Tetranitro-1,4,5,8-tetraazadecaline (TNTAD) | 555.6 | 556.1 | 46.40 | |

[a] The uncorrected value which was determined by means of the Kofler micro-heating table equipped with a microscope (after [24]).

[b] Melting point of ethylene was taken as 103.7 K for calculation.

[c] Calculated from Eq. (2) for cyclic nitramines.

[d] Calculated from Eq. (3).

[e] For cyclobutane [12] a melting point of 145 K and $\Delta H_{m,\,tr}$=6.99 kJ mol$^{-1}$ was taken.

[f] The values taken from [6,8].

[g] The values taken from [14].

[h] Predicted on the basis of the relationship 'impact sensitivity–heat of fusion' [17].

[i] For melting characteristics calculation, a cyclodecane melting point of 282.6 K was taken.

and the corresponding numbers of DIGEN units in their molecules. The relationship is described by the equation

$$\mathrm{Mp}_{\mathrm{NA}} = 57.09n + 312.77 \qquad (4)$$

with the correlation coefficient $r = 0.9980$. The value of melting onset of OCTOGEN calculated by means of Eq. (3) (i.e. 541.1 K) does not correspond to reality.

As for the n-aliphatic homomorphs, a relationship exists between their heats of fusion and the number of carbon atoms ($n_C$) in their chains. Taking the data of homomorphs 1–5 from Table 1 the relationship can be expressed by the equation

$$\ln\Delta H_{\mathrm{HMP}} = 1.732\ln n_C - 0.639 \qquad (5)$$

with the correlation coefficient $r = 0.9962$. A similar relationship can be found for linear nitramines 2–6: in this case it has the form

$$\ln\Delta H_{\mathrm{NA}} = 1.903\ln n_{\mathrm{NC}} - 0.167 \qquad (6)$$

with the correlation coefficient $r = 0.9931$; $n_{\mathrm{NC}}$ is a sum of numbers of nitrogen and carbon atoms in the chain of corresponding nitramine. The similarity between Eqs. (5) and (6) exists due to a similarity in space arrangement of both the flexible chains of n-alkyl homomorphs and linear nitramines (with exception of nitramine 1).

A comparison of the values of melting onsets of linear nitramines 2–6 with the numbers of their chain members ($n_{\mathrm{NC}}$) leads to an equation in the form

$$\mathrm{Mp}_{\mathrm{NA}} = 200.52\ln n_{\mathrm{NC}} + 30.26 \qquad (7)$$

with the correlation coefficient $r = 0.9727$.

## 4. Conclusion

There exist relationships between the fusion characteristics of nitramines with methylenenitramine grouping and those of their aliphatic structural analogues (i.e. homomorphs). The relationships derived in this way also include the influence of molecular space arrangement on physical stability of the corresponding nitramine. Therefore the predictions based on them give real results. In the case of melting point predictions, however, the corresponding results are limited by the chemical thermal stability of the given nitramine. This means that the predicted melting point values of HNATDEC, DECAGEN and TNTAD (see Table 4) are hypothetical. The predicted values of heats of fusion, on the other hand, to a certain extent characterize the intermolecular interactions in the corresponding crystals and they may be applied as a representative of these interactions [17].

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