Thermal deformation and polymorphic transitions of 1,1-diamino-2,2-dinitroethylene in the temperature range from 145 to 475 K

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Abstract. Under atmospheric pressure conditions, direct polymorphic transitions $\alpha \rightarrow \beta$, $\beta \rightarrow \gamma$ and reverse $\gamma \rightarrow \alpha$ were studied, as well as certain phase equilibrium points for 1,1-diamino-2,2-dinitroethylene (DADNE) were determined in the temperature range from 145 to 475 K. The anisotropic characteristics of the thermal deformation of DADNE crystals are determined by powder thermal x-ray diffraction of an internal standard. The points of structural changes were recorded in increments of 20, 10, and 2 K. The calculations of x-ray powder diffraction data were carried out using full-profile analysis methods with the integrated cycle of molecular modeling of the structure of molecules integrated into the algorithm.

1. Introduction
Under normal conditions, 1,1-diamino-2,2-dinitroethylene (DADNE, FOX-7, aprol) is a crystal with a predominantly stable monoclinic structure [1]. Also known is the orthorhombic structure of DADNE [2], which exists in the temperature range from 390 to 443 K. For the last twenty years, DADNE has been regarded as a powerful and insensitive energetic material [3–5]. However, relatively complex synthesis [6, 7] and low physical stability prevent it from being widely used. Similar to the structure of 2,4,6-triamino-1,3,5-trinitrobenzene (TATB) [8, 9], the monoclinic modification of DADNE has a relatively strong network of hydrogen bonds that keep it in a stable state with significant external influences. Unlike TATB, it has less physical stability, which manifests itself as a polymorphism of a molecular crystal. Today, it is known about the existence of four DADNE modifications at a pressure of 0.1–0.2 GPa: monoclinic ($\alpha$ ($P2_1/n$)), orthorhombic ($\beta$ ($P2_12_12_1$)) [1, 2], presumably monoclinic ($\gamma$ ($P2_1/n$)) [10] and the other ($\delta$), little studied, found in [11]. Each of them is determined by a certain set of symmetry elements and anisotropy. In addition, phase diagrams constructed in the range of 0–10 GPa; 298–630 K based on the data of Raman spectroscopy [12, 13] show the existence of at least five phase transitions: three under thermal effects $\alpha \rightarrow \beta$ (more then 380 K), $\beta \rightarrow \gamma$ (more then 430 K), $\gamma \rightarrow \delta$ (more then 470 K) and two at elevated pressure $\alpha \rightarrow \alpha'$ (more then 1.8 GPa), $\alpha' \rightarrow \varepsilon$ (more then 4.0 GPa). Moreover, the temperature of phase transitions depends on the grain size and powder particles. Even without pretending to complete the review of the information provided, it is not difficult to notice that the work on the study of the physical properties of DADNE is more fundamental than the applied one.
Table 1. Parameters of the crystal structure of DADNE (C₂H₄N₄O₄), where Z is the number of formal gross units; R is the R-factor of model is a measure of the agreement between the crystallographic model and the experimental x-ray diffraction (XRD) data; T is a temperature; a, b, c, α, β, γ and V are the unit cell (UC) parameters.

| Phase name   | Crystallographic system | Symmetry group | Parameter name | Parameter value |
|--------------|--------------------------|----------------|----------------|----------------|
| β [2] (at T = 393 K) | orthorhombic | P2₁2₁2₁ | a              | 6.9738(7) Å     |
|              |                          |                | b              | 6.6350(10) Å    |
|              |                          |                | c              | 11.6475(16) Å   |
|              |                          |                | α = β = γ      | 90°            |
|              |                          |                | V              | 538.943 Å³      |
|              |                          |                | Z              | 4              |
|              |                          |                | R              | 3.59           |
| α [1] (at T = 294 K) | monoclinic | P2₁/n        | a              | 6.9396(7) Å     |
|              |                          |                | b              | 6.6374(10) Å    |
|              |                          |                | c              | 11.3406(14) Å   |
|              |                          |                | α = γ          | 90°            |
|              |                          |                | β              | 90.611(9)°      |
|              |                          |                | V              | 522.329 Å³      |
|              |                          |                | Z              | 4              |
|              |                          |                | R              | 3.02           |

As is known, from the physics of a condensed state, most of the fundamental properties of a solid material depend on its structure: the type of atoms, their packaging (ordered or not) and the bonds between them. Most individual energetic materials are highly anisotropic crystalline substances and are characterized by metastability of states.

In the general case, the property of a material can be represented as its ability to respond to external influence by changing its parameters, for example, the parameters of the packing of crystals. From the point of view of the physics of the process the material property is characterized by the relation \( t = \frac{r}{q} \), here the parameter \( r \) is the induced response of the body to external influence \( q \), and \( t \) is the quantitative characteristic or coefficient of proportionality (heat capacity, thermal deformation, pyroelectric constants, chemical activity and others) between dependent exposure parameters and object [14]. From a mathematical point of view, the characteristics of materials under study can be presented in tensor form. In this paper, we are interested in the thermal deformation tensor of two modifications of the energy material DADNE. Their structural characteristics are shown in table 1.

In addition, in this paper we will consider not only the thermal deformation of monoclinic (α-phase) and orthorhombic (β-phase) DADNE, but also briefly polymorphic transitions α–β–γ and points of their phase equilibrium.

2. Basics of thermal strain tensor representation
The thermal deformation of crystalline materials can be written in the form of a second-rank tensor \( \alpha_{ij} \) which is usually represented in the orthogonal coordinate system \( \{e₁, e₂, e₃\} \). In this paper, this coordinate system is represented as a transformation of the base coordinate system (or crystallographic basis vectors \( \{a, b, c\} \)) by means of mathematical transformations \( e₃ \parallel c; \)
$\mathbf{e}_2 \parallel \mathbf{b^*}; \, \mathbf{e}_1 = \mathbf{e}_2 \times \mathbf{e}_3$, otherwise one can write [14–20]
\[
\begin{pmatrix}
  a \\
  b \\
  c \\
\end{pmatrix} = \begin{pmatrix}
  \sin(\beta) & 0 & \cos(\beta) \\
  -b \sin(\alpha) \cos(\gamma^*) & b \sin(\alpha) \sin(\gamma^*) & b \cos(\alpha) \\
  0 & 0 & c
\end{pmatrix} \begin{pmatrix}
  \mathbf{e}_1 \\
  \mathbf{e}_2 \\
  \mathbf{e}_3
\end{pmatrix}, \tag{1}
\]
where $\gamma^*$ is a parameter of reciprocal lattice.

In order to determine components of the thermal deformation tensor of crystalline materials, at the initial stage, it is necessary to register and mathematically describe the experimental data as an anisotropic change in the UC parameters of the substance ($a$, $b$, $c$, $\alpha$, $\beta$, $\gamma$, $V$), for example, using powder x-ray methods [21]. To simplify the procedure, it is customary to use a polynomial not higher than the third order as a support function. In this work, the third order polynomial was used:
\[
S = k_0 + k_1 T + k_2 T^2 + k_3 T^3, \tag{2}
\]
where $T$ is a temperature (K); $S$ is one of the UC parameters: $a$, $b$, $c$, $\alpha$, $\beta$, $\gamma$, and $V$; $k_0$, $k_1$, $k_2$ and $k_3$ are the coefficients of the equation.

The thermal deformation coefficients were anisotropically estimated by the formula:
\[
S' = 1/S \times (\partial S/\partial T)_P \approx (S_1 - S_0)/[(T_1 - T_0)S_0], \tag{3}
\]
where $S'$ is one of the thermal deformation coefficients: $\alpha_{aP}$, $\alpha_{bP}$, $\alpha_{cP}$, $\alpha_{aP}$, $\alpha_{bP}$, $\alpha_{cP}$, and $\beta_P$ associated with the corresponding UC parameter ($S$). Index 0 is the initial state, 1 is the final state.

The equation for thermal deformation coefficients can also be represented as a polynomial:
\[
S' = k_1' + 2k_2' T + 3k_3' T^2, \tag{4}
\]
where $k_1'$, $k_2'$ and $k_3'$ are the coefficients of the equation.

Next, the commons of the tensor are recalculated through the UC. For the triclinic cell, the transforming expressions are written as follows:
\[
\begin{align*}
\alpha_{11} & \approx \frac{1}{a} \frac{da}{dT} + \frac{d\beta}{dT} \cot(\beta), \\
\alpha_{22} & \approx \frac{1}{b} \frac{db}{dT} + \frac{d\alpha}{dT} \cot(\alpha) + \frac{d\gamma^*}{dT} \cot(\gamma^*), \\
\alpha_{33} & \approx \frac{1}{c} \frac{dc}{dT}, \tag{5a}
\end{align*}
\]
\[
\begin{align*}
\alpha_{12} & \approx \frac{1}{2} \cot(\gamma^*) \left( \frac{1}{a} \frac{da}{dT} - \frac{1}{b} \frac{db}{dT} - \frac{d\alpha}{dT} \cot(\alpha) + \frac{d\beta}{dT} \cot(\beta) \right) + \frac{1}{2} \frac{d\gamma^*}{dT}, \tag{5b}
\end{align*}
\]
\[
\begin{align*}
\alpha_{13} & \approx \frac{1}{2} \left( \frac{1}{a} \frac{da}{dT} - \frac{1}{c} \frac{dc}{dT} \right) \cot(\beta), \\
\alpha_{23} & \approx \frac{1}{2} \left( \frac{1}{b} \frac{db}{dT} - \frac{1}{c} \frac{dc}{dT} \right) \cot(\gamma^*) \cot(\beta) + \frac{1}{2} \left( \frac{1}{b} \frac{db}{dT} - \frac{1}{c} \frac{dc}{dT} \right) \cot(\gamma^*), \\
& - \frac{1}{2} \frac{1}{\sin(\gamma^*)} \frac{d\alpha}{dT} + \frac{d\beta}{dT} \cot(\gamma^*). \tag{5d}
\end{align*}
\]

Using the calculated tensor components and the properties of its symmetry, the direction cosines ($l_1$, $l_2$, $l_3$) determine the values of thermal deformation coefficients ($\alpha_{iP}$, $i = 1, 2, 3$) in the orthogonalized reference system $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$ according to the following expression:
\[
\alpha_{iP} = \begin{pmatrix} l_1 & l_2 & l_3 \end{pmatrix} \begin{pmatrix}
  \alpha_{11} & \alpha_{12} & \alpha_{13} \\
  \alpha_{12} & \alpha_{22} & \alpha_{23} \\
  \alpha_{13} & \alpha_{23} & \alpha_{33}
\end{pmatrix} \begin{pmatrix} l_1 \\
  l_2 \\
  l_3 \end{pmatrix}, \tag{6}
\]
\[
l_1 = \frac{hc - la \cos(\beta)}{V b^* |\mathbf{r}^*|}, \quad l_2 = \frac{ha^* \cos(\gamma^*) + kb^* + lc^* \cos(\alpha^*)}{|\mathbf{r}^*|}, \quad l_3 = \frac{1}{c |\mathbf{r}^*|}, \tag{7}
\]
where $V$ is the volume of the direct UC; $a^*$, $b^*$, $c^*$, $\alpha^*$, and $\gamma^*$ are the parameters of the inverse UC; $\mathbf{r}^* = ha^* + kb^* + lc^*$ is the reciprocal lattice vector; $h, k, l$ are Miller indices.
At $i = 1$: $h = 1, k = 0, l = 0$; at $i = 2$: $h = 0, k = 1, l = 0$; at $i = 3$: $h = 0, k = 0, l = 1$.

As a result, the main linear coefficients of thermal deformation ($\alpha_1P$, $\alpha_2P$, $\alpha_3P$) for a crystalline material are obtained.

The obtained coefficients are written in the direction of the orthogonal coordinate system $\{e_1,e_2,e_3\}$, and the eigenvector is $E_i = q_1e_1 + q_2e_2 + q_3e_3$, where $i = 1, 2, 3$; $q_1$, $q_2$, $q_3$ are coefficients.

3. Measurement method

A sample of ultrapure 1,1-diamino 2,2-dinitroethylene was prepared by sublimation purification in a vacuum chamber. Further, the obtained flakes of the $\alpha$-phase DADNE were abraded to a powdery state in an agate mortar to a conditionally uniform particle size from 30 to 50 $\mu$m.

The purity of the samples was controlled by nuclear magnetic resonance (NMR), high-performance liquid chromatography and mass-spectrometry (HPLC-MS), x-ray phase analysis, Raman and Fourier-transform infrared (FTIR) spectroscopy. In this paper, these methods are not considered. However, below the results of x-ray diffractometry is not difficult to trace the degree of purity—as a fact the absence of reflexes of any impurities.

Measurements of changes in the structure of the crystals of the studied substances (refinement of the crystal and microstructural UC parameters: microdistortion, microstrain and crystallite size) were carried out on a XRD station in a standard configuration using a parabolic mirror, which allows to obtain a parallel beam of monochromatic x-ray radiation.

To obtain more accurate values of the scattering angles, parameters of the profile and wave functions of the electron density distribution, as well as points of the internuclear and electronic interaction, separately taken ranges of reflections were recorded and refined. In addition, for the formation of a more accurate solution, in some cases, in the present work, duplicate XRD patterns were used in the optics of a diverging and parallel beam. This is necessary to take into account the impact on the results of total thermal deformation, increase the resolution when applying phases in the sample, as well as to reduce the effect of systematic extinctions so that the presence of other, different from the main phases does not interfere with the profile description, indexing and refinement of atomic coordinates.

Samples for measurements were preliminarily ground to a visually uniform dispersion. Then, the obtained powder samples of the studied substances were placed in an even layer in cuvettes with a built-in thermocouple. Next, the cuvettes were installed inside the Anton Paar TTK 450 low-temperature chamber directly onto the platform with the heating element. The chamber was pre-mounted in the center of the goniometer focusing circle. Calibration of the assembly was performed by recording the primary x-ray pattern of the sample under normal conditions and comparing the positions of the main recorded reflexes with the standard and (or) database. Additionally, an internal standard was used, which was stainless steel with a known coefficient of thermal deformation. The sample was exposed to monochromatic x-rays with a quantum energy of 8 keV, and XRD patterns were recorded with a semiconductor detector. In order to reduce the effect of texture (orientation), the sample was exposed to a sliding beam of x-rays.

Parameters of DADNE diffraction data recording under thermal exposure were preliminary analyzed, scanning ranges, magnitude and speed of thermal exposure were selected, equipment was calibrated and crystallographic models were built according to table 1.

Calibration was performed under normal conditions using a standard reference material (SRM) 1976a [22] and LaB$_6$ powder. Next, the initial state of the studied DADNE samples was determined; their crystal structure was refined relative to the single crystal model (unit cell parameters, crystallite size, microdistortion, extinction). Next was performed thermal powder XRD experiment.

The operating parameters of the recording system are as follows:

- heating and cooling rate—10 K/min;
Table 2. Experimental conditions for various modifications of DADNE.

| Phase name | Symmetry group | Temperature (K) | Pressure (atm) | Scanned range of $2\theta$ (degrees) | Holding, recording time (min) |
|------------|----------------|-----------------|----------------|--------------------------------------|-----------------------------|
| $\alpha$   | $P2_1/n$       | 100–384         | 1              | 13–45                                | 3–20                        |
| $\beta$    | $P2_12_12_1$   | 386–473         |                | 13–43                                | 5–25                        |
| $\gamma$   | $P2_1/n$       | 437–485         |                | 10–40                                | 3–20                        |
| $\delta$   | —              | 485–543         |                | 7–42                                 | 5–40                        |

Figure 1. Picture of x-ray powder diffraction when heated DADNE in the range of 145–475 K. Green color corresponds to the least intense reflexes, blue and yellow reflexes of medium intensity, and red the most intense.

- exposure at a given temperature and registration—5 min.

The evaluation of conditions of thermal XRD measurements and the planning of experiments were carried out using theoretical methods of classical electrodynamics [23] and methods of thermal analysis (table 2).

4. Results

In the presented experimental conditions (see table 2), a registration was made and a picture of the change in XRD data on DADNE powder was made (figures 1 and 2).

High-quality visual analysis of radiographs obtained at different temperatures was carried out using a graphical representation of the thermal powder XRD results in the GNU Octave program [24]. In this case, there is an analogy with the recording of diffraction lines on a photographic plate, when the degree of blackening (in our case, color) corresponds to the intensity of the lines; color scaling was performed on both linear and logarithmic scales.
Figure 2. Changes in the diffraction pattern of x-rays reflected from DADNE crystals under cooling within 475–150 K. Green color corresponds to the least intense reflexes, blue and yellow reflexes of medium intensity, and red the most intense.

Figure 3. Full-profile analysis by the Rietveld method of radiographs of $\alpha$-DADNE crystal at $T = 293$ K, $P = 1$ atm. Marked in gray are carbon atoms, light grey hydrogen atoms, blue nitrogen atoms, and red oxygen atoms.

Thermal x-ray data processing with temperature steps of 20, 10 and 2 K was performed for each point using full-profile analysis methods. Table 1 shows the data used to describe the crystallographic models.
Figure 4. Full-profile analysis by the Rietveld method of radiographs of β-DADNE crystal at $T = 393$ K, $P = 1$ atm. Marked in gray are carbon atoms, light grey hydrogen atoms, blue nitrogen atoms, and red oxygen atoms.

Figure 5. Relative anisotropic changes in the structure of α-DADNE crystals upon heating in the range 145–385 K: (a) UC parameters $a/a_{293}$, $b/b_{293}$, $c/c_{293}$ and (b) volume $V/V_{293}$, density $\rho/\rho_{293}$. The prefix 293 corresponds to the parameter at a temperature of 293 K.

At the initial stage, XRD processing was performed by the Le Bail method [25] without taking into account the molecular and atomic structure of the substance. Further, the structure was refined using the Rietveld method [23], then the Whole Powder Pattern Modelling (WPPM) [26]. After identifying the primary signs of a change in the molecular structure, a quantum chemical analysis was performed to optimize the geometry of molecules at specific temperatures. Further,
Figure 6. Relative anisotropic changes in the structure of β-DADNE crystals upon heating in the range 386–448 K: (a) UC parameters $a/a_{293}$, $b/b_{293}$, $c/c_{293}$ and (b) volume $V/V_{293}$, density $\rho/\rho_{293}$. The prefix 293 corresponds to the parameter at a temperature of 293 K.

Table 3. Coefficients of equation (2).

| Phase name  | $T$ (K) | Parameter | $k_0$ | $10^{-4}k_1$ | $10^{-6}k_2$ | $10^{-6}k_3$ |
|-------------|---------|-----------|-------|--------------|--------------|--------------|
| α-DADNE     | 145–387 | $a$ (Å)  | 6.9496 | 0.86025      | 0.025275     |              |
|             |         | $b$ (Å)  | 6.5031 | 3.4967       | 0.64371      |              |
|             |         | $c$ (Å)  | 11.2660| 3.5279       | 0.18591      |              |
|             |         | $\beta$ (°) | 90.386 | 2.8488       | 1.5837       |              |
|             |         | $V$ (Å$^3$) | 509.19 | 489.67       | 64.608       |              |
| β-DADNE     | 393–443 | $a$ (Å)  | 4.4019 | 0.018003     | −41.472      | 0.03191      |
|             |         | $b$ (Å)  | 18.449 | −0.084765    | 200.88       | −0.15637     |
|             |         | $c$ (Å)  | 0.52447| 0.085521     | −199.60      | 0.15582      |
|             |         | $V$ (Å$^3$) | 744.88 | −1.5965      | 4017.9       | −3.1343      |

the algorithm of the Rietveld and WPPM methods introduced a quantum processing cycle and created a script in the GNU Octave program [24], and full analysis of all x-ray patterns by the conjugate method [27, 28] was carried out.

The initial conditions for calculation of the XRD patterns were taken to be the following:

- the crystallographic model is the result of the primary XRD analysis [1, 2];
- the radiation source is the x-ray tube with a copper anode ($K_{\alpha 1} = 1.5406$ Å);
- the semiconductor detector;
- the pseudo-Voigt profile function;
- the simulated range $2\theta$ is 5–60 degree;
- the initial half-width parameter of full width at half maximum (FWHM) is 0.01.
Table 4. Coefficients of equation (4), where $\alpha_{1P}$, $\alpha_{2P}$, $\alpha_{3P}$ are the main linear coefficients of thermal deformation; $\beta_P$ is the volume coefficient of thermal deformation.

| Phase name | Temperature (K) | Parameter (K$^{-1}$) | $10^{-5}k'_1$ | $2 \times 10^{-5}k'_2$ | $3 \times 10^{-10}k'_3$ |
|------------|----------------|----------------------|---------------|--------------------------|--------------------------|
| $\alpha$-DADNE | 145–387 | $\alpha_{1P}$ | 1.25829 | 7.63 $\times$ 10$^{-4}$ | $-0.181$ |
| | | $\alpha_{2P}$ | 5.35268 | 0.01982 | $-0.290$ |
| | | $\alpha_{3P}$ | 3.11117 | 0.00315 | 0.153 |
| | | $\beta_P$ | 9.58415 | 0.02488 | $-0.540$ |
| $\beta$-DADNE | 393–443 | $\alpha_{1P}$ | 256.9138 | $-1.183$ | 137.0 |
| | | $\alpha_{2P}$ | $-1270.01$ | 6.02214 | $-704.0$ |
| | | $\alpha_{3P}$ | 729.9408 | $-3.40713$ | 399.0 |
| | | $\beta_P$ | $-289.449$ | 1.46147 | $-172.0$ |

Figure 7. Change in the coefficients $q_1$ and $q_3$ of the eigenvectors for $\alpha$-DADNE crystal: (a) $E_1$ and (b) $E_3$.

Figures 3 and 4 show an example of full-profile processing of XRD data of the test substances under normal conditions. As a result of processing, the UC parameters ($a$, $b$, $c$ and $V$) and microstructure parameters (crystallite size—$d$ and microdistortion—$s$) were calculated of DADNE at a certain experiment temperature. The curves of relative changes in UC parameters and crystal density with thermal effects are obtained (figures 5 and 6).

As a result of the regression analysis and statistical calculations, the equations of the thermal deformation tensor of the studied substances were obtained. The coefficients of equation (2) are shown in table 3, and the coefficients of equation (4) in table 4.

The vector of cosine guides (Cartesian) for the orthorhombic $\beta$-DADNE structure is a single tensor, and the direction of the main crystallographic axes and the orthogonal coordinate system of the tensor $\{\textbf{e}_1, \textbf{e}_2, \textbf{e}_3\}$ coincides with the direction of the axes of the base system of coordinates in the scalar as expressed by the parameters of the unit cell.

Imagine a Cartesian for $\alpha$-DADNE crystal in the following coordinates: $\textbf{e}_3 \parallel c; \textbf{e}_2 \parallel b^*; \textbf{e}_1 = \textbf{e}_2 \times \textbf{e}_3$, and the eigenvectors are $\{\textbf{E}_1, \textbf{E}_3\}$. Depending on the temperature, the values of the coefficients $q_1$ and $q_3 = F(T)$ also change; $q_2 = 1$ (figure 7).
Moreover, according to the rules of crystallography, the Cartesian should be calculated in such a way that the condition $\alpha_1 + \alpha_2 + \alpha_3 \approx \beta$ is satisfied.

At the $T = 293$ K we obtain $\alpha_1(293) = 1.3254 \times 10^{-5}$ K$^{-1}$, $\alpha_2(293) = 10.9130 \times 10^{-5}$ K$^{-1}$, $\alpha_3(293) = 4.1668 \times 10^{-5}$ K$^{-1}$, $\beta(293) = 16.411 \times 10^{-5}$ K$^{-1}$ for $\alpha$-DADNE.

At the $T = 393$ K we obtain $\alpha_1(393) = 2.7402 \times 10^{-5}$ K$^{-1}$, $\alpha_2(393) = 10.1000 \times 10^{-5}$ K$^{-1}$, $\alpha_3(393) = 7.1271 \times 10^{-5}$ K$^{-1}$, $\beta(393) = 19.952 \times 10^{-5}$ K$^{-1}$ for $\beta$-DADNE.

The full picture of changes in the main thermal deformation (expansion) coefficients is shown in figure 8. The surfaces of the thermal deformation tensor of the studied $\alpha$- and $\beta$-modifications of DADNE at temperatures of 293 and 393 K, respectively, are presented in figures 9 and 10.

5. Discussion

In order to determine thermal deformation and temperature points of polymorphic transitions, as well as to obtain high-quality XRD data on powder samples, in this work, we planned an x-ray experiment with a preliminary assessment of the operating parameters of the diffractometry station. The optimal signal registration ranges for DADNE crystals of various modifications were selected, which for a wavelength of 1.54 Å fall within the range of 11–45 degrees along the 2 axis. Thermal XRD of the internal standard with a temperature step of 20, 10 and 2 K (near the points of polymorphic transition) with an average recording rate of one point per 11 minutes. DADNE polymorphism in the range of 150–475 K and thermal deformation of two modifications of the DADNE molecular crystal were studied.

It is shown that the full $\alpha-\beta$ polymorphic transition occurs in the range from 384 to 387 K, $\beta-\gamma$ in the range from 437 to 473 K, the reverse $\gamma-\alpha$ transition is not complete. Polymorphic transitions are characterized by a simple phase equilibrium equation. From figure 1, it can be seen that, under the indicated experimental conditions, the full $\alpha-\beta$ phase transition DADNE fits into 2 K, while the $\beta-\gamma$ transition takes 29 K. This is primarily due to minor rebuilding of bonds at the $\alpha-\beta$ transition (rotation of the nitro group), and the long process of rebuilding $\beta-\gamma$ (presumably, stretching and leveling the amino and nitro tails).

In the range of 384–393 K, the substance is a mixture of two modifications $\alpha$-phase and $\beta$-phase, therefore it is necessary to characterize thermal deformation in the vicinity of the 387 K polymorphic transition point in another experiment because of possible oscillations and phase

Figure 8. Change in the main linear thermal deformation coefficients $\alpha_1$, $\alpha_2$, $\alpha_3$ and volume coefficient of thermal deformation $\beta$ for (a) $\alpha$-DADNE and (b) $\beta$-DADNE.
Figure 9. Graphic presentation of the thermal strain tensor for molecular crystals α-DADNE at 293 K.

equilibrium, as was shown in [29]. However, in the present work, the dynamics of the crystal structure in the region of α–β and β–γ polymorphic transitions was noticed.

The anisotropy of thermal deformation was estimated, and the character of changes in the molecular and crystalline structure of α-DADNE (150–384 K) and β-DADNE (386–473 K) was analyzed. The average conditional anisotropy coefficients ($\eta$) for α-DADNE and β-DADNE crystals are 2.69 and 1.13, respectively. The relationship between the thermal strain tensor and the structure of the DADNE crystal is quite obvious and is consistent with the data on intermolecular interactions in the crystal. Large values for relative parameter changes $b/b_{293}$ of α-DADNE crystals, see figure 5(a), indicate weak intermolecular bonds in the [01X] family planes. However, it is not entirely correct to characterize these forces as Van der Waals forces, so additional research in this direction is required. In β-DADNE crystals, weak intermolecular bonds dominate in the direction of the [0X0] and [0X1] family of planes. On average, the shift of the main crystallographic axes relative to the base coordinate system is 10–11 degrees and is carried out by rotation around the b axis. Prevailing thermal deformation is observed in the direction of $E_3$ and $E_2$ vectors.
Figure 10. Graphic presentation of the thermal strain tensor for molecular crystals $\beta$-DADNE at 393 K.

6. Conclusions
The method of determining the thermal strain tensors of crystals based on powder XRD data is applied, and the anisotropic coefficients of thermal deformation $\alpha$ and $\beta$ phases of DADNE are calculated. The calculation of the thermal powder XRD data was performed using the full-profile analysis methods, taking into account the atom–atom force interactions. About 85 radiographs processed in duplicate registration mode.

Polymorphic transitions of DADNE in the temperature range of 150–475 K were studied.

The constructed models of the crystal structure of the modifications under study at various temperatures were presented as files with an extension of the Crystallographic Information File (CIF) standard.

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