



Interplay between composition, structural dynamics and thermodynamic data in amino acid nitrates

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Abstract

A systematic thermodynamic study has been performed for a series of nitrates having cations derived from the α -amino acids glycine (Gly), L-proline (Pro) and L-glutamine (Gln). Combustion and formation enthalpies were for the first time obtained for these amino acid nitrates (AANO₃) by using combustion calorimetry. The thermal behavior in the dynamic regime was investigated by DSC measurements. The values of the formation enthalpies for nitrates were compared with those of the corresponding amino acids and discussed in correlation with structural information obtained from spectral data. FTIR and Raman techniques were used to identify functional groups and hydrogen bonds. Large transmittance in the visible region and the band gap energy value obtained from UV–Vis spectra suggest that these materials are suitable for optoelectronic applications. The band gap values are increasing in the order GlyNO₃ < ProNO₃ < GlnNO₃. Additional polarimetric measurements confirmed the chiral nature of ProNO₃ and GlnNO₃.

Keywords Amino acid nitrates · Formation enthalpy · Calorimetry · FTIR spectroscopy · UV–Vis spectroscopy

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Introduction

The need for materials that combine large nonlinear optical characteristics with resistance to physical and chemical attacks has led to the synthesis and investigation of semi-organic compounds [1, 2].

The advantages of high optical nonlinearity and chemical flexibility of organic materials, on the one hand, and the thermal stability and mechanical robustness of inorganic materials, on the other hand, confer to these compounds' properties which make them suitable for applications in nonlinear optics (NLO) [3, 4]. Amino acids and strong inorganic acids are good raw materials to produce semi-organic crystals [5–11]. Amino acids possess good optical properties as they contain a proton-donor carboxyl ($-\text{COOH}$) group and a proton-acceptor amino ($-\text{NH}_2$) group leading to extensive hydrogen bond networks [12, 13]. Except glycine, all amino acids have chiral symmetry and several compounds crystallize in non-centrosymmetric space groups [11, 12, 14].

Searching for improved properties, a great amount of work was performed involving the synthesis, structural studies and optical properties of organic–inorganic compounds derived directly from natural amino acids or some amino acid salts. However, there is no systematic study allowing to evidence the effect of the different amino acid ligands (anions) on the thermodynamic properties and thermal stability of the complexes formed with a particular inorganic acid. Besides, the information concerning the correlation existing between composition, crystal structure and thermochemical properties of these materials is rather scarce. To experimentally investigate the thermal behavior, differential thermal analysis (DTA), differential scanning calorimetry (DSC) or thermogravimetry (TG) have been generally used. Tao et al. [15] carried out DSC, DTA and TG measurements in order to investigate the thermal behavior of a series of amino acid salts $[\text{AA}]\text{X}$ (X stands for Cl^- , NO_3^- , BF_4^- , PF_6^- , $1/2\text{SO}_4^{2-}$, CF_3COO^-) having amino acid or amino ester acid cations, some of these compounds being considered ionic liquids (ILs) due to their low melting temperatures ($< 373.15\text{ K}$). Thermal properties of diglycine hydrobromide were studied in powder form by recording the TGA/DTA response curve in the temperature range $301.15\text{--}1073.15\text{ K}$ [12]. The thermogravimetric and differential thermal analyses of mono-L-alaninium nitrate (MAN) were performed between 323.15 and 673.15 K by Vimalan et al. [5]. DTA and TG have been also used by Pal et al. [6] for the investigation of mixed crystals of two nonlinear optical materials, L-arginine hydrochloride monohydrate (LAHCl) and L-arginine hydrobromide monohydrate.

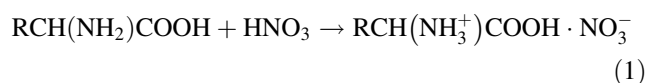
Instead, there are only a few studies reporting information on relevant experimental thermodynamic functions of these compounds, suitable for evaluation of their phase stability. To our best knowledge, except two works (our recent study on the formation and combustion enthalpies of L-alanine nitrate and L-alanine ethyl ester nitrate [16] and the research on the enthalpies of formation of several structurally similar glycine-based sulfate/bisulfate amino acid reported by Zhu [17]), there are no other experimental studies on the thermodynamic data of formation of organic–inorganic compounds having amino acid cation. Particularly, except for our data reported in the above-mentioned paper [16] there are no other experimental values of combustion and formation enthalpies mentioned in the literature for the amino acid nitrates (AANO_3).

Continuing our previous investigations on the thermodynamic properties of the amino acids [18–20] and their derivatives [16] the goal of the present paper is to perform a systematic study of the thermodynamic stability of a series of nitrates (AANO_3) synthesized in our laboratory having cations derived from the α -amino acids glycine (Gly), L-proline (Pro) and L-glutamine (Gln) and to provide new experimental thermodynamic data regarding their enthalpies of combustion and formation. Of particular interest to us is to evidence the strong interplay between thermodynamic behavior, composition and structural dynamics by using techniques such as combustion calorimetry and DSC, as well as FTIR, Raman and UV–Vis spectroscopy.

Experimental

Material synthesis and chemical identification

The nitrates of glycine, L-glutamine and L-proline were prepared starting from the corresponding amino acids: glycine (Merck, assay $> 99.7\%$), L-glutamine (Merck, assay $> 99\%$), L-proline (Merck, assay $> 99\%$) and nitric acid (HNO_3 from Merck, 65% , density 1.4 kg L^{-1}) taken in stoichiometric ratio 1:1. The required amounts were estimated taking into account the following general reaction:



Appropriate amounts of amino acid were first dissolved in deionized water, and then the solutions were slowly added to the solution of nitric acid on stirring. The resulting mixtures were allowed to evaporate at room temperature for 24 h and then were kept in the oven at 333 K for 12 h. Purity of the synthesized salt was further improved by

successive recrystallization processes (see Table 1). GlyNO₃ and GlnNO₃ are solids, and ProNO₃ is gel at room temperature. All samples were dried under vacuum at 333 K before starting the experiments. The water content in the samples was determined by using a Metrohm 848 TitrinoPlus Karl Fischer titrator (Table 1). *Elemental analysis* of AANO₃ was performed using a EuroVector model EA3000 CHNS elemental analyzer, the results being included in Table S1 (Supplementary Material). The elemental analysis indicated that the contents of C, H and N are in good agreement with the values based on the structure formula.

Apparatus and methods

FTIR and Raman spectroscopy

The various functional groups present in the samples were identified and confirmed by recording the FTIR spectra at room temperature, in the 4000–525 cm^{−1} range, using a Thermo Scientific Nicolet iS10 FTIR spectrophotometer with attenuated total reflection (ATR) method. Sixty-four scans were accumulated for each spectrum. All ATR spectra were collected with a spectral resolution of 4 cm^{−1}.

Unpolarized Raman spectra of the glycine, glutamine and proline nitrate materials were recorded by means of a LabRam HR spectrometer (Jobin–Yvon–Horiba) over 50–4000 cm^{−1} range. The 514-nm line of an Ar⁺ laser was used as exciting radiation through a 50 LWD objective of an Olympus microscope in a backscattering geometry and at a confocal hole of 200 μm. The spectral resolution was better than 2 cm^{−1}. Spectra of glycine, L-proline and L-glutamine were collected for comparative purposes. The resulting spectra were background-corrected and curve-fitted by using Igor software, version 6.2 [21]. Fitting residuals were kept below 2%. Incident laser power below 8 mW was used to avoid local heating and graphitization effects.

UV–Vis spectrophotometry

The UV–Vis spectrum of ProNO₃ was recorded with an Ocean Optics High-Resolution Fiber Optic Spectrometer HR 4000 in the range 200–1100 nm. The optical resolution

was ± 0.27 nm. For GlyNO₃ and GlnNO₃ the spectra were obtained with UV–Vis Jasco V 550 spectrophotometer (the resolution of ± 1 nm and wave length accuracy ± 0.3 nm, in a 10-mm quartz cell and 60-mm-diameter integrating sphere) with scanning speed of 1000 nm/min. The optical band gap energy is estimated using the formula $E_g = h \nu$, and the data are also presented in Table 1. The h is the Plank's constant ($h = 6.626 \times 10^{-34}$ J s), and ν is frequency of light ($\nu = c/\lambda$, $c = 3 \times 10^9$ m s^{−1}, and λ is wavelength measured in nm).

Polarimetry

Considering the importance of the chiral properties of molecules in NLO applications, as well as in the field of ionic liquids, polarimetric measurements have to be carried out. The measurements of optical rotation were performed with a 341 PerkinElmer polarimeter using a 1-cm path length glass cell. Determinations were made for solutions of the three nitrates in deionized water, at 25 °C, in D line of sodium. The values of specific rotation $[\alpha]_D^{25}$ are obtained.

Combustion calorimetry

A Parr Instruments model 6200 microprocessor-controlled isoperibol oxygen bomb calorimeter was used. Samples were burned by using the semi-micro-combustion kit of the calorimeter provided with a small bomb, inner volume 22 mL. The bomb was placed into the bucket, which contained 450 mL of water, filled from an automatic pipet. The temperature was measured with a high-precision electronic thermometer using a specially designed thermistor sensor. Measurements were taken with resolution of 0.0001 K. Purity of the oxygen used for combustion was 99.998%.

The energy equivalent of the calorimeter, $\epsilon_{\text{calor}} = (2339.6 \pm 3.6)$ J K^{−1} (twice the standard deviation of the mean), was derived from combustion of the standard benzoic acid (CAS 65-85-0) supplied by Parr Company, from ten calibration experiments, using samples weighing between 0.10 and 0.19 g. The massic energy of combustion under certificate conditions of benzoic acid was $\Delta_{\text{benzoic acid}} u^\circ = -26,434$ J g^{−1}.

Table 1 Sample table

Chemical name	Source	Purification method	Fraction purity/%*	Analysis method
GlyNO ₃	Synthesis	Recrystallization	99.84	Elemental analysis
			99.45	Fractional melting, DSC
ProNO ₃	Synthesis	–	98.98	Elemental analysis
GlnNO ₃	Synthesis	Recrystallization	99.31	Elemental analysis

*The water content < 100 ppm in all compounds was measured by Karl Fischer titration

The samples were weighed using a Mettler Toledo microbalance with an accuracy of $\pm 2 \times 10^{-6}$ g. The water content in the samples measured by Karl Fischer titration was used to make the appropriate corrections for the combustion results. For combustion of proline nitrate we checked if this compound is hygroscopic, by determining the water content (using Karl Fischer titration) before combustion experiment and then after 15 min, period of time when the sample was maintained in the presence of the deionized water from the bomb. No change in the water content in the samples has been registered. The buoyancy effect was taken into account in the experiments, and the masses were corrected using densities listed in Table S4 in Supplementary Material. The water volume added to the bomb for dissolution of combustion gases was 0.5 cm³. The bomb was flushed with purified oxygen for 30 s, then sealed and filled with oxygen. The samples were burned in oxygen at a pressure of 3.04 MPa. The final solution from the bomb was analyzed for the presence of nitric acid (about 20% from the total nitrogen) by titration with 0.0709 N Na₂CO₃ solution. The heat due to nitric acid formation was obtained using the value of the molar internal energy of formation of nitric acid solution (0.1 M), $\Delta_f u^\circ_{\text{HNO}_3, \text{aq}} = -58.8 \text{ kJ mol}^{-1}$ [22].

Auxiliary materials—cotton and Ni–Cr filament—were used in combustion measurements. The corrections for the auxiliary materials, $q_{(\text{cotton})}$ and $q_{(\text{ign})}$, were calculated from the mass of cotton and the mass of the filament, the combustion enthalpy $\Delta_c u^\circ_{(\text{cotton})} = -(16,240 \pm 4.8) \text{ J g}^{-1}$ (determined in our laboratory, the value being in agreement with Ref. [23]) and $\Delta_c u^\circ_{\text{Ni–Cr}} = -5.86 \text{ kJ g}^{-1}$ (certified by the fabricant). The experimental values of massic energy of combustion, $\Delta_c u$, were brought to the standard state ($T = 298.15 \text{ K}$ and $P = 10^5 \text{ Pa}$), the corrections being made following the procedure recommended by Hubbard et al. [24] and using the data from Tables S4a, S4b, S4c from Supplementary Material.

DSC measurements

The thermal behavior of the samples under non-isothermal regime was investigated by scanning calorimetry (DSC) using a computer-controlled PerkinElmer power-compensated DSC (model 8500) calorimeter.

Samples were placed in aluminum sealed pans, while an empty pan was used as reference. Temperature and heat flow rate scale of the DSC was calibrated by measuring high-purity indium ($T_{\text{fus}} = 429.8 \text{ K}$ and $\Delta H_{\text{fus}} = 28.4 \text{ J g}^{-1}$). The DSC curves of the studied compounds were recorded at a heating rate of 10 K min^{-1} under nitrogen of purity $> 99.996\%$ with a flow rate of 20 mL min^{-1} . The Pyris Software for Windows was used

in order to calculate the thermal effects (melting/decomposition enthalpies).

Results and discussion

Vibrational modes

IR and Raman spectroscopies have proved useful in identification of the amino acid and their derivatives, as well as for studying changes in the hydrogen bond lengths, which govern structural properties of these compounds [25, 26]. IR and Raman spectra of the (Gly/Pro/Gln)NO₃ along with the corresponding amino acids Gly, Pro and Gln are illustrated in Fig. 1, while positions and band assignments [25–34] of the bands are listed in Table S2 in Supplementary Material.

Upon HNO₃ reaction with Gly, splitting ($\Delta = \nu_a[\text{CH}_2] - \nu_s[\text{CH}_2]$) between $\nu_a(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$ (see inset of Fig. 1b) increases to 63 cm^{-1} in comparison with Gly where Δ is of 33 cm^{-1} . Smaller splitting value [35] recorded for GlnNO₃ indicates protonation of the terminal amine group and/or variation of the hydrogen bond strength under NO₃[−] influence. This finding is also supported by the lack of the IR and Raman bands at 3400 cm^{-1} due to the $\nu_a(\text{NH}_2)$ for the GlnNO₃.

Evidence beyond doubt of the NH₃⁺ groups consists in their IR finger prints, i.e., deformation, $\delta(\text{NH}_3^+)$, and torsion modes, $\tau(\text{NH}_3^+)$, at 2116 cm^{-1} for Gly and 2038 cm^{-1} for Gln (Fig. 1a). Hydrogen atoms of the NH₃⁺ group, giving rise to three bonds N⁺–H···O, cause different spectral features in the IR spectrum within $2600\text{--}3400 \text{ cm}^{-1}$ of Gly in comparison with the ones of GlyNO₃ (Fig. 1a).

All the solid samples (Gly/Gln)NO₃ and the ionic liquid ProNO₃ [36] investigated here show evidence of the $\nu_1(\text{NO}_3)$ modes at about 1040 cm^{-1} in their IR and Raman spectra.

IR bands at about 1700 cm^{-1} and 1200 cm^{-1} (Fig. 1a and Table S3 in Supplementary Material) indicate C=O and CO_H stretching modes of the COOH groups from (Gly/Pro/Gln)NO₃.

Low vibrational bands ($< 600 \text{ cm}^{-1}$) in the Raman spectra of (Gly/Pro/Gln)NO₃ in Fig. 1b are assignable to skeletal deformations of COOH groups, lattice modes ($< 200 \text{ cm}^{-1}$), vibrational and translational (105 cm^{-1} [31]) motions of NO₃[−] and hydrogen bonds within $50\text{--}300 \text{ cm}^{-1}$ region [31, 37]. Thus, fitting of the Raman band within $450\text{--}540 \text{ cm}^{-1}$ domain reveals that torsional mode $\tau(\text{NH}_3^+)$ at 491 cm^{-1} for Gly undergoes splitting into 494 cm^{-1} and 498 cm^{-1} in case of GlyNO₃ (see Fig. 1b) pointing out the existence of two types of N⁺–H···O bonds due to NH₃⁺ interactions with both COO[−] and NO₃[−]. Moreover, intense Raman band at 122 cm^{-1} , attributed to

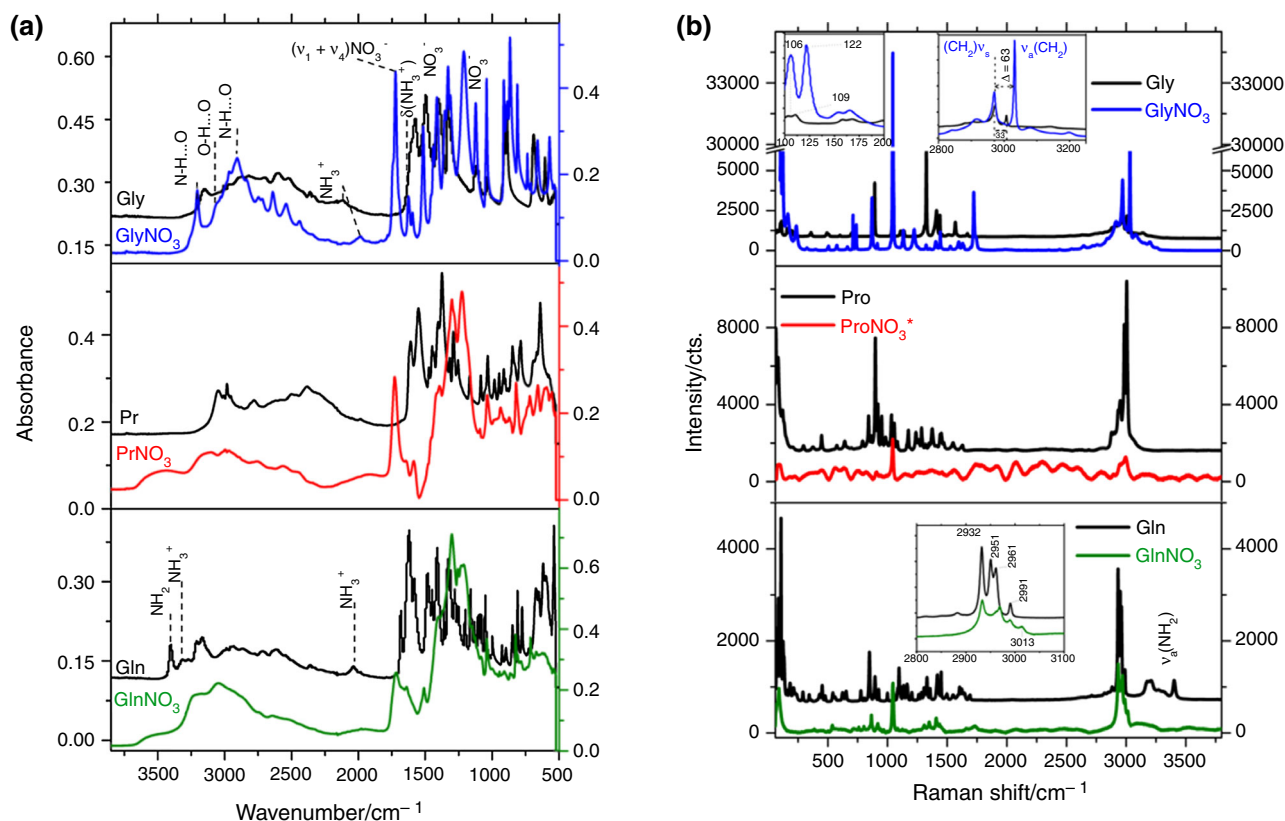


Fig. 1 Vibrational spectra of the (Gly/Pro/Gln)NO₃ and of the corresponding AA: **a** IR and **b** Raman (*liquid phase)

in-phase vibrations of atoms involved in ionic N–H...O hydrogen bonds [37], might indicate the hyperpolarizability of the GlyNO₃ crystals, providing a structure without center of symmetry.

UV–Vis spectra

The UV–Vis spectra for AANO₃ are shown in Fig. 2. These show a wide transparency window as there is no absorption in the region between 350 and 1050 nm. The values of the UV cutoff wavelengths are shown in Table 2.

The smallest value of the cutoff wavelength of 337 nm is recorded for the simplest amino acid nitrate, namely GlyNO₃. The width of the transparency window decreases in succession: ProNO₃ > GlnNO₃ > GlyNO₃. Moreover, wide transparency windows and band gap energy values (E_g) point out suitability of these materials for optoelectronic applications.

Polarimetric measurements

Polarimetry was used for checking chirality of the asymmetrical carbon atom in the nitrates synthesized in the laboratory.

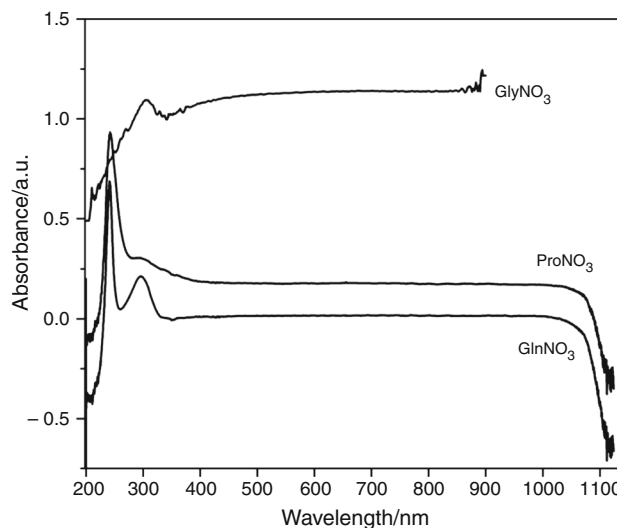


Fig. 2 Absorption spectra of the synthesized AANO₃

The calculated specific rotation values were as follows: $[\alpha]_D^{25} = -39.8^\circ \text{ mol}^{-1}$ for ProNO₃ (solution in water and $c = 1 \text{ g } 100 \text{ mL}^{-1}$) and $[\alpha]_D^{25} = +7.76^\circ \text{ mol}^{-1}$ for GlnNO₃ (solution in water and $c = 2.5 \text{ g } 100 \text{ mL}^{-1}$). The chirality of these compounds is preserved during the processes of preparation and purification. Conversely, the optical rotation value for GlyNO₃ is 0 (solution in water

Table 2 Characteristics of the UV–Vis spectra corresponding to the nitrogen derivatives

Compound	$\lambda_{\text{cutt off}}/\text{nm}$	E_g/eV	Domain of optical transparency
GlyNO ₃	337	3.69	400–850
ProNO ₃	277	4.49	370–1050
GlnNO ₃	259	4.80	340–1010

and $c = 20.4 \text{ g } 100 \text{ mL}^{-1}$) despite the hyperpolarizability of the GlyNO₃ crystals noticed in the low-frequency Raman spectrum in Fig. 1b.

Combustion measurements

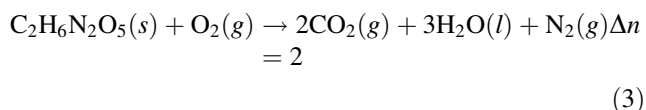
The molar standard combustion enthalpies $\Delta_c H_m^\circ$ of the compounds are calculated from the constant-volume combustion energy $\Delta_c U_m^\circ$:

$$\Delta_c H_m^\circ = \Delta_c U_m^\circ + \Delta n RT \quad (2)$$

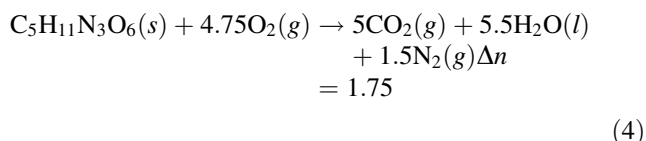
where Δn is the change in gas mole number (products vs. reactants) during the combustion reaction.

The following combustion reactions have been taken into account:

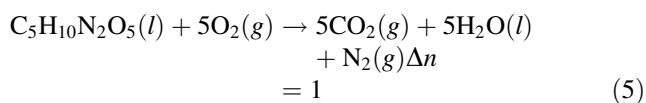
GlyNO₃ combustion:



GlnNO₃ combustion:



ProNO₃ combustion:



Tables S4a, S4b, S4c from Supplementary Material show the individual values of the combustion experiments of AANO₃. A total of over ten runs were performed for every material, but some runs were rejected because of doubt about combustion completeness. In runs used in data calculation, there was no evidence of soot formation in the bomb. Five runs were retained for GlyNO₃, GlnNO₃ and ProNO₃.

In Table 3 are given the derived molar quantities from the mean standard massic energy of combustion for each compound. $\Delta_c U_m^\circ$ and $\Delta_c H_m^\circ$ are the standard molar energy and enthalpy of combustion, respectively, and $\Delta_f H_m^\circ$ is the

Table 3 Thermochemical data at $T = 298.15 \text{ K}$ ($p^\circ = 0.1 \text{ MPa}$) for AANO₃

AANO ₃	$\Delta_c U_m^\circ/\text{kJmol}^{-1}$	$\Delta_c H_m^\circ/\text{kJmol}^{-1\text{a}}$	$\Delta_f H_m^\circ/\text{kJmol}^{-1\text{b}}$
GlyNO ₃	-847.5 ± 2.8	-842.6 ± 2.8	-801.9 ± 2.8
GlnNO ₃	-2532.9 ± 0.7	-2528.6 ± 0.7	-1011.1 ± 1
ProNO ₃	-2634.8 ± 2.3	-2623.8 ± 2.3	-764.4 ± 2.4
AlaNO ₃	-1557.6 ± 1.3	-1552.4 ± 2.8	-771.5 ± 2.8 [16]

^aTotal uncertainties were calculated according to the guidelines presented by Olofsson [39]

^bUncertainty included the uncertainties of the enthalpies of formation of the reaction products H₂O and CO₂

calculated standard molar enthalpy of formation. As recommended [24, 39], the uncertainties associated with these molar quantities are twice the overall standard deviation of the mean, and they include the uncertainties associated with the calibration experiments (uncertainties of massic energy of combustion of benzoic acid and energetic equivalent of the calorimeter) and auxiliary substances.

Enthalpies of formation of the studied nitrates are calculated according to Eq. (6) from the corresponding enthalpies of combustion and taking into account the known enthalpies of formation of CO₂ and H₂O: $\Delta_f H_m^\circ \text{CO}_2(\text{g}) = -393.51 \pm 0.13 \text{ kJ mol}^{-1}$ and $\Delta_f H_m^\circ \text{H}_2\text{O}(\text{l}) = -285.83 \pm 0.042 \text{ kJ mol}^{-1}$ [38].

$$\Delta_f H_m^\circ = n_{\text{CO}_2} \Delta_f H_m^\circ \text{CO}_2(\text{g}) + n_{\text{H}_2\text{O}} \Delta_f H_m^\circ \text{H}_2\text{O}(\text{l}) - \Delta_c H_m^\circ \quad (6)$$

The uncertainty assigned to $\Delta_f H_m^\circ$ includes the uncertainties of the enthalpies of formation of the reaction products H₂O and CO₂.

In Table 3 are also included the thermochemical data of AlaNO₃ previously reported by us [16], for comparison. Among these amino acid nitrates, the highest enthalpy of formation value ($-764.4 \text{ kJ mol}^{-1}$) belongs to ProNO₃ and the lowest one ($-1011.3 \text{ kJ mol}^{-1}$) is the formation enthalpy of GlnNO₃. The influence of the chemical structure of the amino acid cation on the thermochemical properties of the synthesized derivatives has been evidenced. The trend in the variation of the enthalpy of formation in the series of the studied amino acid nitrates is as follows: $\text{GlnNO}_3 > \text{GlyNO}_3 > \text{AlaNO}_3 > \text{ProNO}_3$. Since the cationic form was IR depicted for all the AANO₃ under discussion, the latter succession obeys hydrogen bonds involving N-containing groups, i.e., five different hydrogen bonds of the NH₃⁺ and NH₂ groups from GlnNO₃, three hydrogen bonds of the NH₃⁺ from GlyNO₃ and AlaNO₃ and only two hydrogen bonds of the NH₂⁺ in ProNO₃.

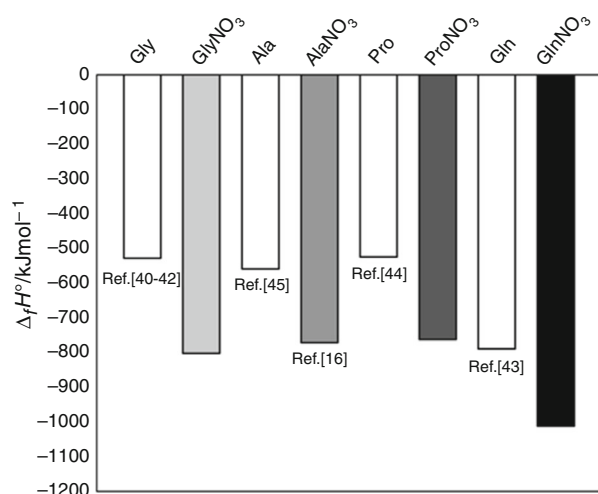


Fig. 3 Enthalpies of formation of the AANO₃ studied in this work (filled bars) and the data of the corresponding AA taken from the literature (white bars)

In Fig. 3 our data for the enthalpies of formation of the AANO₃ are given together with the values of the corresponding amino acids from the literature [40–45].

More negative enthalpies of formation of AANO₃ than those of the corresponding amino acids point out that nitrate compounds are more stable. The contribution of the additional chemical bonds to the energetic parameters affects their enthalpies of formation. The enthalpy of formation of GlyNO₃ is about 273.6 kJ mol⁻¹ lower than that of Gly, the difference being comparable with the difference of about 237.6 kJ mol⁻¹ found between the enthalpies of formation of ProNO₃ and Pro. The GlyNO₃–Gly and ProNO₃–Pro pairs contain N⁺–H...O bonds, in contrast to GlnNO₃–Gln pair which contains also two N–H...O bonds of the amide group [46] with different bond strengths. Hence, in the case of GlnNO₃–Gln pair the difference is smaller, indicating that nitrate formation does not change too much the energetic contribution of the hydrogen bonds.

DSC runs

The DSC curves of all samples have been recorded in the temperature range 200–523 K. Distinct thermal behavior of AANO₃ is illustrated in Fig. 4.

For comparison in Table 4 are also included the T_{onset} values of melting and/or decomposition reported by different authors from DTA or DSC/TG measurements. A very good agreement of the decomposition temperatures of GlyNO₃ and ProNO₃ obtained in our work with the data reported by Tao et al. [15] from TGA measurements could be noticed (Table 4). Concerning the melting point of GlyNO₃, the value of 419 K obtained by us is very near the value of 418.85 K obtained by Dhas [4] from DTA/TG

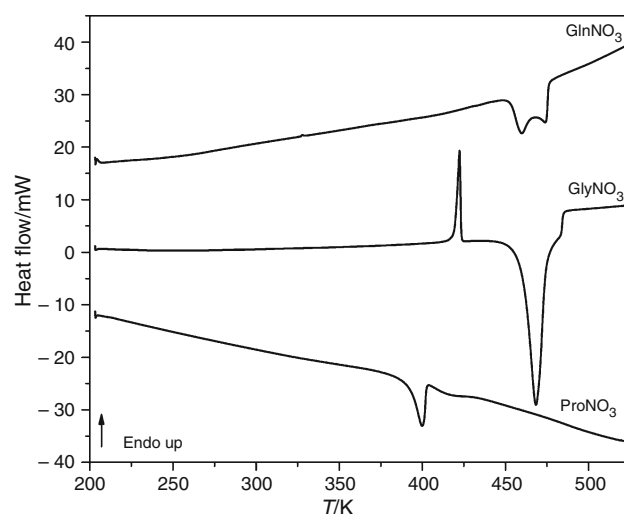


Fig. 4 DSC curves of AANO₃

data when working at a heating rate of 10 K min⁻¹ (like in our conditions of measurements).

The initial temperature of decomposition and the total enthalpy of decomposition are also important parameters when assessing the thermal stability of amino acids and their derivatives. Thermal stability, referring to the initial temperature of decomposition, decreases in succession GlyNO₃ > GlnNO₃ > ProNO₃ due to longer side chains of the L-Gln and L-Pro in comparison with Gly [47]. The same order is recorded in the case of the decomposition enthalpies.

Thermal stability of these compounds is ruled by breaking bonds at different positions in accordance with their side chains. Despite the same number of carbon atoms, the side chain of L-Pro consists in a pyrrolidine ring (C₄H₉N), while an amide (C₄H₉N₂O) represents the side chain of L-Gln. Moreover, the lack of the $\nu_a(\text{NH}_2)$ modes at 3402 cm⁻¹ in the IR and Raman spectra of GlnNO₃ in contrast to L-Gln (Table S2 in Supplementary Material) points out the participation of NH₂ of the amide group in additional N–H...O bonds formation. Tao et al. [36] also reported different thermal stabilities of amino acid derivatives in accordance with the thermal stability of the corresponding amino acids. Hence, the thermal stability scale based on the decomposition parameters could be explained by the fact that the less stable cations presented here are those of Gln and L-Pro. Although AA loss carboxyl group by decomposition, the presence of the heteroatoms in the side chains (here L-Pro and L-Gln) can hinder losing of the carboxyl groups and trigger further cleavage of other bonds from side chains [47].

In Fig. 5, the total heats of decomposition of the GlyNO₃, ProNO₃ and GlnNO₃ are compared with the heats of decomposition values of the corresponding amino acids obtained in our previous works [43, 44, 48] by using the

Table 4 Thermodynamic parameters for melting/decomposition of AANO₃ from DSC measurements

Sample	GlyNO ₃		ProNO ₃		GlnNO ₃	
Sample mass/g	0.001159		0.000763		0.000510	
Process	Decomposition		Decomposition		Decomposition	
	Melting	Decomposition	Stage 1	Stage 2	Stage 1	Stage 2
$T_{\text{onset}}/\text{K}$	419 ± 0.4 [this work] 384.15 [15] 418.85 [4]	460 ± 0.8 [this work] 465.15 [15] 419.15 [4]	394 ± 0.8 [this work]	410 ± 0.8 [this work] 411.15 [15]	453.6 ± 0.5 [this work]	468.7 ± 0.3 [this work]
T_{max}/K	422 ± 0.3 [this work]	469 ± 0.4 [this work]	400 ± 0.8 [this work]	414 ± 0.9 [this work]	460 ± 0.4 [this work]	475 ± 0.3 [this work]
T_{end}/K	424 ± 0.4 [this work]	475 ± 0.8 [this work]	403 ± 0.5 [this work]	417 ± 0.4 [this work]	466 ± 0.8 [this work]	476 ± 0.6 [this work]
$\Delta H/\text{kJmol}^{-1}$	30.0 ± 0.6 [this work]	– 257.5 ± 0.4 [this work]	– 79.8 ± 0.3 [this work]	– 18.1 ± 0.1 [this work]	– 77.3 ± 0.6 [this work]	– 63.1 ± 0.5 [this work]

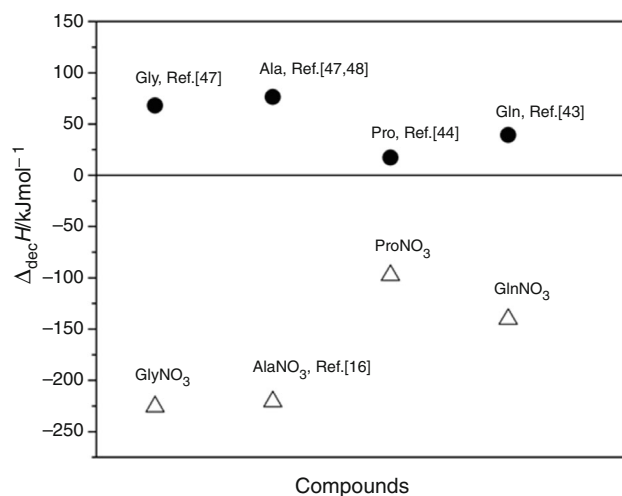
Conclusions

In the present paper a systematic study of the thermodynamic stability of a series of nitrates (AANO₃) synthesized in our laboratory having cations derived from the α -amino acids glycine (Gly), L-proline (Pro) and L-glutamine (Gln) has been performed. The strong interplay between composition, structural dynamics and thermodynamic behavior has been evaluated by using techniques as combustion calorimetry and DSC, as well as FTIR, Raman and UV–Vis spectroscopy.

For the first time the combustion and formation enthalpies of the synthesized nitrates have been measured by combustion calorimetry. A critical comparison of the formation enthalpy of nitrate compounds with that of the corresponding amino acids indicates increased stability of the derivatives. At the same time, the influence of the cation structure (type of the side chain R and number and type of the hydrogen bonds) on the thermochemical stability of the nitrates was emphasized.

The initial temperature of decomposition and the total enthalpy of decomposition obtained from DSC measurements show without exception, a shift to lower values of both these parameters for nitrates, the result being explained by the formation of the N⁺–H···O and N–H···O bonds with NO₃[–]. The exothermic decomposition evidenced by DSC measurements is influenced by the presence of an additional functional group and length side chain that determines the decreasing of the decomposition temperatures and changes in the developed energy.

Large transmittance in the visible region and band gap energy value obtained from UV–Vis spectra suggest that these materials are suitable for optoelectronic applications.

**Fig. 5** Total decomposition enthalpies of the studied AANO₃ (empty triangles) and of the corresponding AA (filled circles)

same experimental conditions. For comparison, the data for AlaNO₃ [16] and Ala [47, 48] are also included in Fig. 5.

One can observe, without exception, a shift to lower values for nitrates, the result being explained by the formation of the N⁺–H···O and N–H···O bonds with NO₃[–]. It should be noted that the exothermic decomposition is influenced by the presence of an additional functional group that determines the decreasing of the decomposition temperatures and changes in the developed energy.

Supplementary material

The elemental analysis of AANO₃, the NMR spectra, IR and Raman data (band position and assignments) of the (Gly/Pro/Gln)NO₃ and of the corresponding amino acids, as well as the combustion experiments results of the amino acid nitrates, are included in Supplementary Material.

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References

- Ramabadran U, Zelmon DE, Kennedy GC. Electro-optic, piezoelectric, and dielectric properties of zinc tris thiourea sulfate. *Appl Phys Lett*. 1992;60:2589–91. <https://doi.org/10.1063/1.106918>.
- Meera K, Muralidharan R, Dhanasekaran R, Prapun M, Ramasamy P. Growth of nonlinear optical material: L-arginine hydrochloride and its characterization. *J Cryst Growth*. 2004;263:510–6. <https://doi.org/10.1016/j.jcrysgro.2003.11.093>.
- Haja Hameed AS, Lan CW. Nucleation, growth and characterization of L-tartaric acid- nicotinamide NLO crystals. *J Cryst Growth*. 2004;270:475–80. <https://doi.org/10.1016/j.jcrysgro.2004.07.001>.
- Martin Britto Dhas SA, Natarajan S. Growth and characterization of a new organic NLO material: Glycine nitrate. *Opt Commun*. 2007;278:434–8. <https://doi.org/10.1016/j.optcom.2007.06.052>.
- Vimalan M, Helan Flora X, Tamilselvan S, Jeyasekaran R, Sagayaraj P, Mahadevan CK. Optical, thermal, mechanical and electrical properties of a new NLO material: mono- L-alaninium nitrate (MAN). *Arch Phys Res*. 2010;1:44–53.
- Pal T, Kar T, Wang XQ, Zhou GY, Wang D, Cheng XF, Yang ZH. Growth and characterization of nonlinear optical material, LAHClBr—a new member of L-arginine halide family. *J Cryst Growth*. 2002;235:523–8. [https://doi.org/10.1016/S0022-0248\(01\)01818-8](https://doi.org/10.1016/S0022-0248(01)01818-8).
- Ittyachan R, Sagayaraj PJ. Growth and characterization of a new promising NLO L-histidine bromide crystal. *J Cryst Growth*. 2003;249:557–60. [https://doi.org/10.1016/S0022-0248\(02\)02116-4](https://doi.org/10.1016/S0022-0248(02)02116-4).
- Rajan Babu D, Jayaraman D, Mohan Kumar R, Jayavel RJ. Growth and characterization of non-linear optical L-alanine tetrafluoroborate (L-AIFB) single crystals. *J Cryst Growth*. 2002;245:121–5. [https://doi.org/10.1016/S0022-0248\(02\)01708-6](https://doi.org/10.1016/S0022-0248(02)01708-6).
- Vimalan M, Ramanand A, Sagayaraj P. Synthesis, growth and characterization of L-alaninium oxalate—a novel organic NLO crystal. *Cryst Res Technol*. 2007;42:1091–6.
- Natarajan S, Martin Britto SA, Ramachandran E. Growth, thermal, spectroscopic, and optical studies of L-alaninium maleate, a new organic nonlinear optical material. *Cryst Growth Des*. 2006;6:137–40. <https://doi.org/10.1021/cg0502439>.
- Razzetti C, Ardoino M, Zanotti L, Zha M, Paorici C. Solution Growth and Characterisation of L-alanine, single crystals. *Cryst Res Technol*. 2002;37:456–65.
- Moolya BN, Dharmaparakash SM. Growth and characterization of nonlinear optical diglycinehydrobromide single crystals. *Mater Lett*. 2007;61:3559–62. <https://doi.org/10.1016/j.matlet.2006.11.117>.
- Hanumantharao R, Kalainathan S. Growth, spectroscopic, dielectric and nonlinear optical studies of semi organic nonlinear optical crystal—L-alanine lithium chloride. *Spectrochim Acta Part A Mol Biomol Spectrosc*. 2012;A86:80–4. <https://doi.org/10.1016/j.saa.2011.10.006>.
- Rubyand A, Alfred Cecil Raj S. Growth, spectral, optical and thermal characterization of NLO organic crystal—glycine thiourea. *Int J ChemTech Res*. 2013;5:482–90.
- Tao GH, He L, Sun N, Kou Y. New generation ionic liquids: cations derived from amino acids. *Chem Commun*. 2005;28:3562–4. <https://doi.org/10.1039/B504256A>.
- Gheorghe D, Neacșu A, Contineanu I, Teodorescu F, Tănăsescu S. Thermochemical properties of L-alanine nitrate and L-alanine ethyl ester nitrate. *J Therm Anal Calorim*. 2014;118(2):731–7. <https://doi.org/10.1007/s10973-014-3996-8>.
- Zhu JF, He L, Zhang L, Huang M, Tao GH. Experimental and theoretical enthalpies of formation of glycine-based sulfate/bisulfate amino acid ionic liquids. *J Phys Chem*. 2012;B116:113–9. <https://doi.org/10.1021/jp209649h>.
- Contineanu I, Neacșu A, Gheorghe D, Tanasescu S, Perisanu S. The thermochemistry of threonine stereoisomers. *Thermochim Acta*. 2013;563:1–5. <https://doi.org/10.1016/j.tca.2013.04.001>.
- Neacșu A, Gheorghe D, Contineanu I, Tanasescu S, Perisanu S. A thermochemical study of serine stereoisomers. *Thermochim Acta*. 2014;595:1–5. <https://doi.org/10.1016/j.tca.2014.08.032>.
- Gheorghe D, Neacșu A, Contineanu I, Tanasescu S, Perisanu S. A calorimetric study of L-, D- and DL-isomers of tryptophan. *J Therm Anal Calorim*. 2017;130(2):1145–52. <https://doi.org/10.1007/s10973-017-6396-z>.
- Anghel EM, Pavel PM, Constantinescu M, Petrescu S, Atkinson I, Buixaderas E. Thermal transfer performance of a spherical encapsulated PEG 6000-based composite for thermal energy storage. *Apply Energy*. 2017;208:1222–31. <https://doi.org/10.1016/j.apenergy.2017.09.031>.
- Jessup RS. Precise measurement of heat of combustion with a bomb calorimeter, National Bureau of Standards Monograph 7. Washington, DC: National Bureau of Standards; 1960.
- Coops J, Jessup RS, van Nes K. Calibration of calorimeters for reactions in a bomb at constant volume. In: Rossini FD, editor. *Experimental thermochemistry* (Chapter 3), vol. 1. New York: Interscience; 1956. p. 27.
- Hubbard WN, Scott DW, Waddington G. In: Rossini FD, editor. *Experimental thermochemistry*, vol. 1. New York: Interscience; 1956. p. 75–128.
- Krishnan RS, Sankaranarayanan VN, Krishnan K. Raman and Infrared spectra of amino acids. *J Indian Inst Sci*. 1973;55:66–116.
- Krishnan RS, Balasubramanian K. Raman spectrum of crystalline & #x03B1;-glycine. *Proc Indian Acad Sci Sect A*. 1958;48:55–61.
- Pandiarajan S, Umadevi M, Sasirekha V, Rajaram RK, Ramakrishnan V. FT-IR and FT-Raman spectral studies of bis(L-proline) hydrogen nitrate and bis(L-proline) hydrogen perchlorate. *J Raman Spectrosc*. 2005;36:950–61. <https://doi.org/10.1002/jrs.1390>.
- Dhamelincoourt P, Ramirez FJ. Polarized micro-Raman and FT-IR spectra of L-glutamine. *Appl Spectrosc*. 1993;47:446–51.
- Rozenberg M, Shoham G, Reva I, Fausto R. A correlation between the proton stretching vibration red shift and the hydrogen

- bond length in polycrystalline amino acids and peptides. *Phys Chem Chem Phys*. 2005;7:2376–83. <https://doi.org/10.1039/B503644E>.
30. Baran JA, Ratajczak H. Polarized vibrational studies of the α -glycine single crystal Part I. Polarized Raman spectra—the problem of effective local Raman tensors for the glycine zwitterions. *Vib Spectrosc*. 2007;43:125–39. <https://doi.org/10.1016/j.vibspec.2006.07.002>.
 31. Baran JA, Drozd MA, Ratajczak H. Polarised IR and Raman spectra of monoglycine nitrate single crystal. *J Mol Struct*. 2010;976:226–42. <https://doi.org/10.1016/j.molstruc.2010.03.055>.
 32. Mary YS, Ushakumari L, Harikumar B, Tresa Varghese H, Yohannan Panicker C. FT-IR, FT-Raman and SERS spectra of L-proline. *J Iran Chem Soc*. 2009;6:138–44.
 33. Nakamoto K. Infrared and raman spectra of inorganic and coordination compounds, part A: theory and applications in inorganic chemistry. Wiley; 2009. p. 279–81.
 34. Pawlukojc A, Holderna-Natkaniec K, Bator G, Natkaniec I. L-glutamine: dynamical properties investigation by means of INS, IR, RAMAN, ^1H NMR and DFT techniques. *Chem Phys*. 2014;443:17–25. <https://doi.org/10.1016/j.chemphys.2014.08.003>.
 35. Bykov SV, Myshakina NS, Asher SA. Dependence of glycine CH_2 stretching frequencies on conformation, ionization state, and hydrogen bonding. *J Phys Chem*. 2008;B112:5803–12. <https://doi.org/10.1021/jp710136c>.
 36. Tao GH, He L, Liu WS, Xu L, Xiong W, Wang T, Kou Y. Preparation, characterization and application of amino acid-based green ionic liquids. *Green Chem*. 2006;8:639–46. <https://doi.org/10.1039/B600813E>.
 37. Vijayakumar T, Hubert Joe I, Reghunadhan Nair CP, Jayakumar VS. Non-bonded interactions and its contribution to the NLO activity of Glycine Sodium Nitrate—a vibrational approach. *J Mol Struct*. 2008;877:20–35. <https://doi.org/10.1016/j.molstruc.2007.07.021>.
 38. CODATA Bulletin nr. 28 (April 1978), Recommended Key Values for Thermodynamics, 1977, Paris, France.
 39. Olofsson G. Assignment of Uncertainties. In: Sunner S, Mansson M, editors. *Combustion calorimetry*. London: Pergamon Press; 1979. p. 137–59.
 40. Vasilév VP, Borodin VA, Kopnyshev SB. Calculation of the standard enthalpies of combustion and of formation of crystalline organic acids and complexones from the energy contributions of atomic groups. *Russ J Phys Chem*. 1991;65:29–32.
 41. Ngauv SN, Sabbah R, Laffitte M. Thermodynamique de composés azotes. III. Etude thermochimique de la glycine et de la L- α -alanine. *Thermochim Acta*. 1977;20:371–80.
 42. Huffman HM, Fox SW, Ellis EL. Thermal data. VII. The heats of combustion of seven amino acids. *J Am Chem Soc*. 1937;59:2144–9.
 43. Contineanu I, Neacsu A, Perisanu S. The standard enthalpies of formation of L-asparagine and L-glutamine. *Thermochim Acta*. 2010;497:96–100. <https://doi.org/10.1016/j.tca.2009.08.017>.
 44. Contineanu I, Neacsu A, Zgiran R, Tanasescu S, Perisanu S. The standard enthalpies of formation of proline stereoisomers. *Thermochim Acta*. 2012;537:31–5. <https://doi.org/10.1016/j.tca.2012.02.035>.
 45. Contineanu I, Marchidan DI. The enthalpies of combustion and formation of D-alanine, L-alanine, DL-alanine, and β -alanine. *Rev Roum Chim*. 1984;29:43–8.
 46. Suresh CG, Vijayan M. Occurrence and geometrical features of head-to-tail sequences involving amino acids in crystal structures. *Int J Pept Prot Res*. 1983;22:129–43. <https://doi.org/10.1111/j.1399-3011.1983.tb02077.x>.
 47. Rodante F, Marrosu G, Catalani G. Thermal analysis of some α -amino acids with similar structures. *Thermochim Acta*. 1992;194:197–213. [https://doi.org/10.1016/0040-6031\(92\)80018-R](https://doi.org/10.1016/0040-6031(92)80018-R).
 48. D. Gheorghe. Ph.D. Thesis, Thermodynamics characterization of some amino acids and their derivatives, Romanian Academy Library. 2015; 129–141.

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