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THE POLYMORPHISM OF GLYCINE
Thermochemical and structural aspects

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Abstract

X-ray, DSC and solution calorimetric investigations were carried out for α-, β- and γ-modifications of glycine. Particular attention was paid to kinetic and thermochemical aspects of γ- → α-phase transition. The temperature of this phase transition turned out to be sensitive to a) conditions under which the crystals of the γ-modification were grown, b) tempering of crystals c) form (geometry) of crystals. Kinetics of this phase transition of single crystals of γ-phase in rhomboedric form can be described by the equation for two-dimension nuclei growth, whereas for crystals of triangle geometry the equation for three dimension growth is valid. On the basis of energy parameters describing growth of α-form in γ- → α-phase transition, the kind of structure defects, which are responsible for this phase transition, was estimated. Taking into account the $\Delta_{sol}H_m$, the absolute values of the lattice energies of the investigated polymorphs in descending order are follows: γ->α->β-modification. The obtained results are discussed with respect to the peculiarity of the crystal lattice structures, particularly the network of hydrogen bonds. The β-modification of glycine is monotropically related to the other forms, whereas γ- and α-polymorphs are enantiotropically-related phases.

Keywords: crystal structure, enthalpies of solution, enthalpy of phase transition, glicine, kinetics of phase transition, monotropic and enantiotropic phases, phase transition, polymorphism, single crystal

Introduction

Three different polymorphic phases of glycine have already been known for a long time: the first attempts to study α-glycine (α-Gly) by means of X-ray diffraction were undertaken by Bernal [1] and by Hengstenberg and Lenel [2] independently. However, accuracy and interpretation of their results left something to be desired. The explicit crystalline structure was refined by Albrecht and Corey [3], and a precise refinement of not only the heavier atoms but also locating of the hydrogen atoms for

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α-modification was carried out by Marsh [4]. In the seventies, Jönsson and Kvick [5] investigated deformation electron density of this modification employing X-ray and neutron diffraction measurements.

β-Glycine (β-Gly) had already been obtained and described by Fischer [6] at the beginning of the century, whereas X-ray examination was performed quite a long time later [1, 7]. It can be suspected that this fact was due to the general low stability of this phase and possibly due to irreversible transformation into α- or γ-Gly forms.

γ-Glycine (γ-Gly) was first revealed and the structure resolved by X-ray diffraction by Iitaka [8–10]. Moreover, he analysed not only the packing of the molecules in the crystal lattice, but also the role of the hydrogen bonds in the formation of the framework and the substructure of the hydrogen bonds. Investigations of γ-glycine at 298 and 83 K were carried out by means of neutron diffraction by Kvick [11] in order to determine electron density changes of the molecules with temperature.

Numerous studies dealing with thermophysical and thermochemical studies of glycine are literally known: as examples may be mentioned determination of combustion enthalpies [12–14], constant pressure heat capacity of the solid [15–17], and sublimation enthalpies [13, 18–20]. Unfortunately, none of these articles take into account the crystal lattice of the studied phases. Furthermore, investigations into the thermodynamics of phase transitions of the considered polymorphs are not practically existent.

In the present study, thermochemical aspects of the phase transition γ- → α-Gly are studied in detail. Furthermore, differences of crystal lattice energies of the polymorphs are investigated.

Material and methods

Glycine (aminoacetic acid, >99%) was from Sigma (Sigma-Aldrich Sweden AB, Stockholm, Sweden). For crystallisation of the polymorphs the following solvents were used: ethanol, extra pure grade (99.6 v/v%, maximum water content 0.4%); acetic acid (analysis grade, 100%), bought from Merck (Merck GmbH, Darmstadt, Germany) and distilled water.

All the polymorphs under examination were grown as described earlier [7, 10]. The obtained crystals were thoroughly dried under vacuum and stored under moisture-free conditions. Details of thermal treatment and preparation of the crystals are described below.

Thermal properties of different modifications of glycine were measured using a Perkin Elmer Pyris 1 DSC differential scanning calorimeter (Perkin Elmer Analytical Instruments, Norwalk, Connecticut, USA). DSC runs were performed in an atmosphere of flowing dry nitrogen gas of high purity (20 ml min^{-1}) using closed standard aluminium sample pans. DSC was calibrated with indium from Perkin Elmer (P/N 0319-0033). The value of the determined enthalpy of fusion corresponded to –28.48 J g^{-1} (reference value –28.45 J g^{-1}). The melting point was 156.5±0.1°C.

Enthalpies of solution ($\Delta_{\mathrm{sol}}H_{\mathrm{m}}$) were measured using a Precision Solution Calorimeter in the 2277 Thermal Activity Monitor Thermostat (both from Thermometric

AB, Järfälla, Sweden). The software SolCal Version 1.2 (Thermometric) was applied to all calculations. The measuring temperature was 25±10^{-4}°C, volume of the vessel 100 ml, stirrer speed 500 rpm and the mass of investigated compounds approximately 63 mg. The accuracy of mass measurements corresponded to ±10^{-6} g. The calorimeter was calibrated using KCl (analysis, grade >99.5%, from Merck) in water in a wide concentration interval with a number of measurements of more than 10. The obtained standard value of solution enthalpy was $\Delta_{sol}H^0$=17 225±50 J mol^{-1}. This is in good agreement with the value recommended by IUPAC of $\Delta_{sol}H^0$=17 217±33 J mol^{-1} [21].

Single-crystal X-ray measurements were carried out using a Nonius CAD-4 diffractometer with graphite-monochromated MoK$_\alpha$ radiation (λ=0.71069). Intensity data were collected at 20°C by means of a ω-2θ scanning procedure up to a 2θ limit of 70°. The crystal structure was resolved using direct methods and refined by means of a full-matrix least-squares procedure. All programs used in the solution (Sheldrick, 1997a [22]), refinement (Sheldrick, 1997b [23]) and display [24] of the structures are included in the OSCALL program package [25].

Results and discussion

Crystal structures of different polymorphic modifications of glycine

The crystal structure of a polymorph determines its lattice energy. Therefore, before discussing experimental results, details of crystal structures of α-, β- and γ-modifications of glycine are discussed. The parameters of the investigated crystal lattices obtained by other and the present authors (in order to characterise the single crystals under investigation) using various X-ray and neutron diffraction methods are presented in Tables 1and 2. Final fractional co-ordinates are listed in Table 3.

All data derived for the three modifications in this study are in good agreement with literature data [1–7, 10, 11].

The dimension of the carboxyl group and the arrangement of oxygen atoms around the nitrogen atom suggest that the molecules in all three (α-, β- and γ-) modifications form zwitter ions. The configuration states of the molecules in the considered polymorphic phases differ from one another only by the angle between C–N and the least-squares plane (a twist around the C_I–C_{II} bond): 18.6° in α-; 24.8° in β-; 12.8° in γ-phases (Fig. 1). This fact is a consequence of the complicated packing of molecules in the crystal lattice and the competition of several kinds of interactions: a) van der Waals, b) electrostatic (particularly dipole-dipole interaction) and c) framework hydrogen bonds.

In order to explain experimental results of different methods (IR, X-ray), particular attention is paid to the structure hydrogen bonds. Therefore, in order to analyse the number and strengths of the hydrogen bonds located between a reference molecule and its nearest neighbours, the scheme proposed by Iitaka is used [10]. The projection of molecule bonds of the modifications is presented in Fig. 2, where the direction along the C–N bond is taken as the polar axis (N–H bond also indicated).

Table 1 The lattice parameters of the α-phase of glycine

	Marsh [4]	Albrech and Corey [3]	Bernal [1]	Jönsson and Kvick [5][b]	Legros and Kvick [36]	This work[c]
a/Å	5.1020(8)	5.10	5.04	5.1054(6)	5.0835(10) 5.0830(8)[b]	5.107(2)
b/Å	11.9709(17)	11.96	12.1	11.9688(19)	11.820(2) 11.816(3)[b]	12.040(2)
c/Å	5.4575(15)	5.45	5.41	5.4645(9)	5.4579(9) 5.4590(10)[b]	5.460(2)
α/deg	90	90	90	90	90	90
β/deg	111.71(2)	111.63	111.63	111.697(11)	111.95(2) 111.93(2)[b]	111.82(2)
γ/deg	90	90	90	90	90	90
Z	4	4	4	4	4	4
$V/\text{Å}^3$	309.69	309.02	306.69	310.25	304.17 304.15[b]	311.67(17)
SG[a]	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
T/K	298	298	298	298	120	298(2)

[a] space group

[b] neutron diffraction

[c] after DSC measurement; number of reflections measured are 544; number of independent reflections are 489; absorption coefficient is $\mu_\alpha = 0.142\ \text{mm}^{-1}$; final *R*-value is 0.059

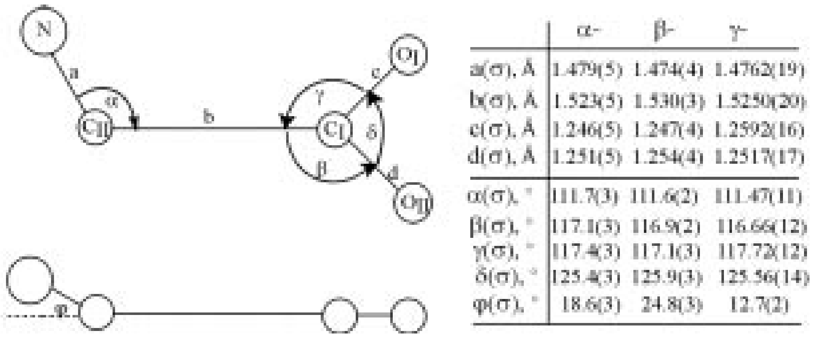
Table 2 The lattice parameters of the β- and γ-phases of glycine

	β-glycine			γ-glycine			
	Bernal [1]	Iitak [7]	This work[c]	Iitaka [10]	Kvick [11][b]	Kvick [11][b]	This work[d]
a/Å	5.18	5.077(4)	5.0943(13)	7.037	7.046(3)	6.975(2)	7.035(2)
b/Å	6.18	6.267(6)	6.286(5)	7.037	7.046(3)	6.975(2)	7.035(2)
c/Å	5.29	5.379(9)	5.3831(15)	5.483	5.491(2)	5.473(2)	5.481(2)
α/deg	90	90	90	90	90	90	90
β/deg	114.33	113.2	113.21(2)	90	90	90	90
γ/deg	90	90	90	120	120	120	120
Z	2	2	2	3	3	3	3
V/Å^3	154.31	157.36	158.44(13)	235.14	236.1(2)	230.6(2)	234.91(13)
SG[a]	$P2_1$	$P2_1$	$P2_1$	$P3_2$	$P3_2$	$P3_2$	$P3_2$
T/K	298	298	298	298	298	83	298(2)

[a] space group
[b] neutron diffraction
[c] number of reflections measured are 374; number of independent reflections are 353; absorption coefficient is $\mu_{\beta\text{-}}$= 0.140 mm^{-1}; final R-value is 0.046
[d] number of reflections measured are 746; number of independent reflections are 741; absorption coefficient is $\mu_{\gamma\text{-}}$= 0.141 mm^{-1}; final R-value is 0.036

Table 3 Final position of atoms in three glycine modifications

	α-phase			β-phase			γ-phase		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
N	–0.3008(8)	0.4104(3)	1.2588(7)	–0.3509(6)	0.0129(5)	1.2623(5)	0.75431(19)	0.78341(19)	0.6222(2)
O_1	–0.3042(6)	0.4055(2)	0.7653(5)	0.0914(4)	0.1405(5)	0.9029(4)	0.76732(18)	0.77862(18)	0.1328(2)
O_2	0.1472(6)	0.3586(3)	0.8954(6)	–0.3780(5)	0.0897(6)	0.7575(4)	0.4570(2)	0.4565(2)	0.1004(2)
C_1	–0.0752(8)	0.3750(3)	0.9341(7)	–0.1122(6)	0.1267(7)	1.2305(5)	0.6070(2)	0.6080(2)	0.2208(2)
C_2	–0.0647(9)	0.3549(3)	1.2130(8)	–0.1337(6)	0.1157(5)	0.9391(5)	0.6014(3)	0.5769(2)	0.4967(3)
H_1	0.101(9)	0.386(3)	1.332(9)	0.051(9)	0.064(8)	1.376(8)	0.665(7)	0.478(7)	0.547(8)
H_2	–0.086(9)	0.271(4)	1.234(9)	–0.112(9)	0.261(10)	1.286(9)	0.455(6)	0.522(7)	0.570(10)
H_3	–0.492(12)	0.387(4)	1.140(11)	–0.313(15)	–0.116(19)	1.210(15)	0.886(4)	0.823(4)	0.576(5)
H_4	–0.303(11)	0.490(5)	1.229(11)	–0.526(10)	0.047(7)	1.159(9)	0.724(4)	0.889(4)	0.589(6)
H_5	–0.295(9)	0.398(4)	1.432(10)	–0.331(10)	0.039(9)	1.412(10)	0.708(7)	0.744(6)	0.806(8)



	α-	β-	γ-
a(σ), Å	1.479(5)	1.474(4)	1.4762(19)
b(σ), Å	1.523(5)	1.530(3)	1.5250(20)
c(σ), Å	1.246(5)	1.247(4)	1.2592(16)
d(σ), Å	1.251(5)	1.254(4)	1.2517(17)
α(σ), °	111.7(3)	111.6(2)	111.47(11)
β(σ), °	117.1(3)	116.9(2)	116.66(12)
γ(σ), °	117.4(3)	117.1(3)	117.72(12)
δ(σ), °	125.4(3)	125.9(3)	125.56(14)
φ(σ), °	18.6(3)	24.8(3)	12.7(2)

Fig 1 Conformation state of molecule in the crystal lattice for the different glycine modifications

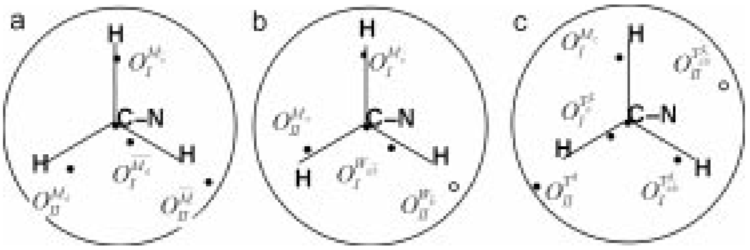
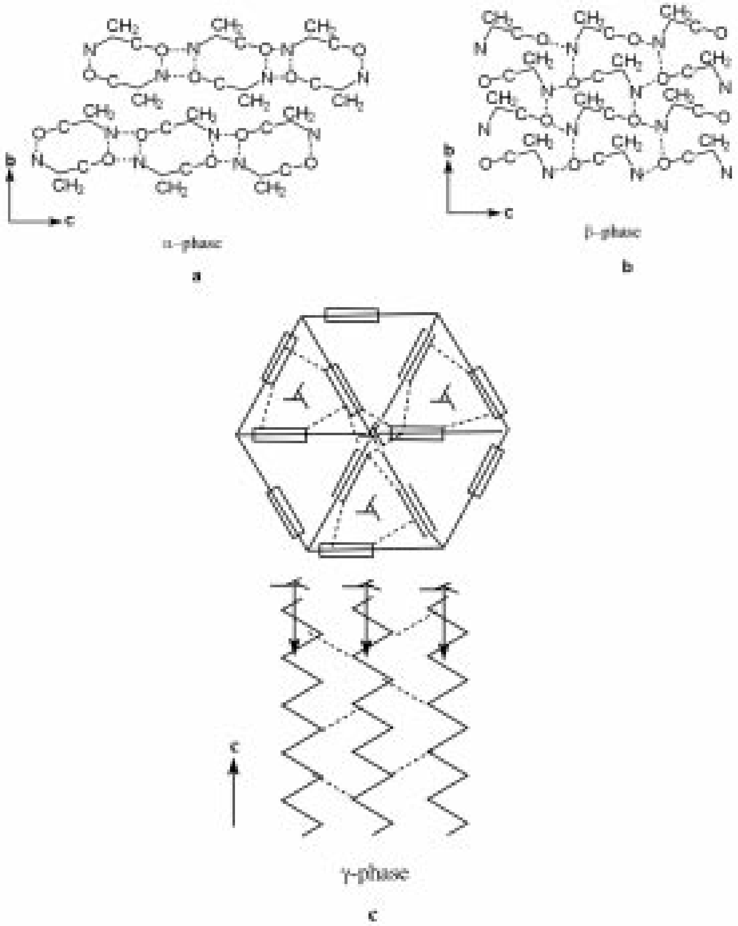


Fig 2 Stereographic projections of NH_3–C_{II} fragment of glycine molecule (along N–C_{II} bond) and nearest oxygen atoms: a – α-, b – β-, c – γ-modifications

The molecules, received by a threefold screw axis of a molecule M, are designated by T^1 and T^2 and other molecules which are related to these three by lattice translations are designated with subscript the translation vector (for example M_a, $T^1_{\overline{ab}}$). In α- and β-glycine two oxygen atoms ($O_I^{M_{\bar{c}}}$ and $O_{II}^{M_a}$) are situated approximately in the tetrahedral directions and are participating in those strong hydrogen bonds which hold the molecules in a sheet. The third hydrogen atom (NH_3^+-group) is situated on a line approximately bisecting the angle $O_I^{M_a}$–N–$O_{II}^{\overline{M}}$ (α-Gly) or $O_I^{W_{a\bar{b}}}$–N–$O_{II}^{W_{\bar{b}}}$ (β-Gly) and forms a bifurcate hydrogen bond, which accounts for the cohesion of the sheets. For the γ-phase the situation is different: five oxygen atoms at short distances surround the nitrogen atom, which implies the presence of hydrogen bonds. The three oxygen atoms $O_I^{M_c}$, $O_{II}^{T^1}$ and $O_I^{T^1_{\overline{ab}}}$ in the γ-modification are arranged approximately in the tetrahedral directions. Therefore, these atoms are taking part in hydrogen bonding and the rest of the oxygen atoms, namely $O_I^{T^2_a}$ and $O_{II}^{T^2_{\overline{ab}}}$, interact with NH_3^+-group by means of electrostatic attraction.

The respective structures of α- and β-Gly are shown in Figs 3a and 3b accordingly. They may be described as structures consisting of molecular layers lying in parallel to the (010) planes. The configuration of the sheets in these two polymorphs is almost the same. In β-Gly, the single sheets are packed together by hydrogen bonds in the b-direction, whereas in α-Gly, pairs of two single sheets are held together by hydrogen bonds to form double sheets, which then are packed together by van der Waals forces.

The framework of hydrogen bonds in the γ-Gly crystal lattice is schematically shown in Fig. 3c. The dominating feature of the intermolecular packing is the hydrogen bonding between amino atoms which links the molecules into helical chains around the threefold screw axes parallel to the *c*-axis. These chains are packed together by lateral hydrogen bonds forming a three-dimensional network of hydrogen bonds. The electrostatic forces between oppositely charged groups would enhance the effect of such bonding. Furthermore, the alignment of the hydrogen bonds seems to be better in this case than with the corresponding hydrogen bonds in the other forms of glycine. As derived from IR-experiments [7, 26], in α- and β-glycine the lateral hydrogen bonds are stronger than the interlayer hydrogen bonds. It is interesting to note that the methylene–methylene or methylene–oxygen distances in the γ-phase are somewhat longer than observed between the double layers of α-Gly, and the



α-phase
a

β-phase
b

γ-phase
c

Fig 3 Schematic illustration crystal structure and network of hydrogen bonds for different polymorphic forms of glycine packing of the molecules within the crystal is less compact compared to the α-form. Presumably, hydrogen bond and electrostatic energies overcome the decrease in van der Waals energies.

Theoretical calculation of values of crystal lattice energies is a rather demanding problem because of the competition of several energetic terms. Moreover, it is difficult to estimate a bifurcate hydrogen bond by means of mathematical procedures.

In the present study, attempts were made to measure the differences of crystal lattice energies of the investigated polymorphs by solution calorimetry as a direct experimental method.

DSC measurements

The γ- → α-phase transition

The first scientist who studied the transition of glycine phases by means of DSC experiments was Iitaka [8, 10]. It should be noted that he emphasised the unusual behaviour of the heat effects he measured. First of all, they were widely spread over a wide temperature range of 165±5°C. Secondly, this phase transition was very sensitive to grinding and other mechanical treatment of the crystals. For example, the phase transition takes place when the crystals of the γ-phase are powdered. As a consequence of this fact, the phase transition (both the transition temperature and the heat effect) is sensitive to the function of distribution of structure defects in the crystal and, consequently, to the procedure of preparation of a crystal. Kvick [11] has shown that the structure of γ-glycine contains mosaic spreads of 17.4″ (83 K) and 20.8″ (298 K). This fact is also an evidence for the relation between growth parameters and perfection of a crystal.

The preparation of single crystals of γ-glycine usually takes place at a temperature around 1°C. However, experimental temperatures (DSC and solution calorimetry) exceed this temperature. Hence the density of different kinds of structure defects does not have the thermodynamical equilibrium value. Taking this into account, an exceeded number of defects will relax during time and at definite environmental conditions the system (crystal+defects) achieves a stage closer to equilibrium. As far as a relaxation process is a kinetic process, the relaxation time depends on the temperature treatment. This can be used for an effective homogenisation of properties in a crystal. Moreover, dislocations and other defects of the crystal structure promote local disorder, even breaking of the network of the hydrogen bonds, particularly those weak bifurcate and lateral hydrogen bonds. Therefore, reproducibility of DSC and solution calorimetry measurements can be widely improved by thermal treatment of the material (tempering) prior to the measurements without changing crystal lattice.

In order to confirm this hypothesis the following experiment was carried out: a perfect γ-glycine single crystal with a cross area of approximately 2 mm^2 (which had three big clear-determinated faces) was carefully divided into several equal pieces. Two pieces were used to examine the γ- → α-phase transition temperature immediately upon breaking by means of DSC at a heating rate of 10 K min^{-1}. The remaining pieces were exposed to thermal treatment at 175°C during 4.5 h under a dry nitrogen atmosphere, prior to DSC measurement. The temperatures of phase transition were essentially different: for the untreated material T_{tr}=189.3°C and for the treated material T_{tr}=200.7°C respectively. Similar dependencies were observed for the crystals of other forms and geometry. For example, the initial (fresh prepared) rhombus-like crystals had T_{tr}=168.4°C, whereas the phase transition temperature of these crystals after thermal treatment at 159°C for 5 h was increased to 181.7°C (Fig. 4). It should be mentioned that the values of enthalpies of phase transition, $\Delta_{tr}H(\gamma\rightarrow\alpha)$, can widely differ for crystals prepared at slightly different conditions. For example, the γ-phase having T_{tr}=165°C corresponds to a heat effect of 1200±80 J mol^{-1}, whereas for T_{tr}=180°C the heat effect was measured to be $\Delta_{tr}H(\gamma\rightarrow\alpha)$=1800±80 J mol^{-1}.

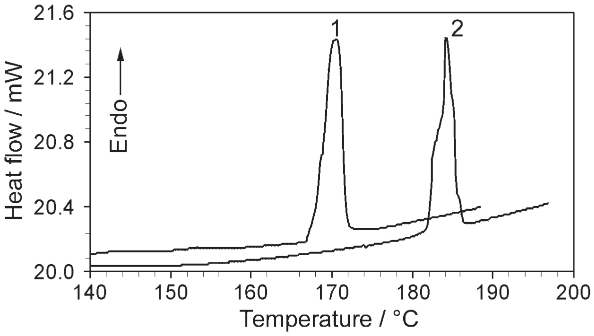


Fig 4 DSC curves of the phase transition γ- →α-modification glycine for rhombus-like crystals: 1 – the initial (fresh prepared) crystals, 2 – the crystals after thermal treatment at 159°C for 5 h

Powder X-ray diffraction is usually used to identify the modification after the phase transition [8]. In this study, identification of the transformed phase was carried out in a different way. The same single crystal before and after DSC measurements was studied by X-ray diffraction with the single crystal method. The results of these investigations are presented in Tables 1, 2 and 3.

γ- → α-phase transition is irreversible and endothermic and can be characterised as an enantiotropic phase transition, which is in accordance with the heat-of-transition rule (HTR) and the infrared rule (IRR) introduced for polymorph transitions by Burger and Ramberger [27]. The Gibbs' free energies of the investigated phases in the transition temperature are equal:

$$\Delta_{tr}H(\gamma\rightarrow\alpha)=\Delta_{tr}G+T_{tr}\Delta_{tr}S=0-T_{tr}\,(\partial\Delta G/\partial T)_p>0 \quad (1)$$

in the point of phase transition $S_\alpha>S_\gamma$. Assuming that volume and density are a measure of entropy, one can compare these values for different phases. The experimentally obtained density of γ-form is higher than of α-modification: $\rho^{25}(\gamma)$=1.63 g cm^{-3} [8] >$\rho^{25}(\alpha)$=1.606 g cm^{-3} [28] or $\rho^{25}(\alpha)$=1.607 g cm^{-3} [29]. However, the values of the molecular volumes, V_{mol}, and the density calculated from X-ray diffraction data, $\rho_{X\text{-ray}}$, just contradict the above relationship: $V_{mol}(\gamma)$=78.30(13) $Å^3$>$V_{mol}(\alpha)$=77.92(17) $Å^3$ and $\rho_{X\text{-ray}}(\gamma)$=1.592 g cm^{-3}>$\rho_{X\text{-ray}}(\alpha)$=1.600 g cm^{-3} [this work]. This fact may be explained by the essential influence of the network hydrogen bonds in the overall organisation of the crystal lattices. Similar contradictions were observed for another molecular crystal with network of hydrogen bonds [30].

As was mentioned before, the temperature of γ- $\rightarrow$ α-Gly phase transition is sensitive to: a) form (geometry) crystals; b) thermal treatments; c) grinding and other mechanical treatment. These facts essentially complicate kinetic and thermodynamic investigations of this process. Taking this into account, in the present study it was attempted to grow small crystals as homogeneously as possible with approximately the same size, geometry and form. Moreover, it was tried to carry out all measurements with the polymorphs under the same experimental conditions. For this goal, relatively bigger crystals with different geometry (form) were grown: a) small rhombus; b) small triangles; c) small pyramids; d) big pyramids, which were then carefully divided into small pieces. The analysis of the kinetics of phase transitions for the different crystal forms was performed as follows. The crystals were placed into a sealed DSC pan and measurements carried out under isothermal condition as was used elsewhere [31]. The Avrami–Erofeev equation [32] was used for the interpretation of the time-dependency of the heat effect:

$$-\ln(1-\alpha^{*})=kt^{n} \qquad (2)$$

where α^{*} is the fraction of γ-phase transformed until time, t:

$$\alpha^{*}=\Delta_{tr}H(t)/\Delta_{tr}H_{sum} \qquad (3)$$

$\Delta_{tr}H(t)$ is the enthalpy of phase transition until time, t; $\Delta_{tr}H_{sum}$ is the total enthalpy of the phase transition. The index n in Eq. (2) was determined from the slope of the plot of $\ln[-\ln(1-\alpha^{*})]$ *vs.* $\ln(t)$ according to the theory on nucleation-growth during crystallisation [32].

It is interesting to note that for rhombus-like crystals the value n is Eq. (2), hence it is observed a two-dimensional nucleus growth with a constant number of nuclei (the nucleation rate is equal zero). For the triangle-like crystals, the value n increases to 3. This corresponds to three-dimensional nucleus growth with a constant number of nuclei (the nucleation rate is equal zero). Short periods of two-dimensional growth and subsequent conversion into long period three-dimensional growth is observed with pyramid-like small crystals. Similar behaviour is also observed for big pyramid-like crystals: however, in some cases stages with n=3 substitute for n=4 (a constant rate of homogenous nucleation and three-dimension growth). It is proposed, that after a number of nuclei of the growing phase are finished, the mechanism of the reaction of the phase transition is changed.

In the following part of this study, estimation of the activation energy of the phase transition γ- $\rightarrow$ α-glycine is described. For this, isothermal measurements were carried out at the different constant temperatures and dependencies of $\alpha^{*}=f(T,t)$ were collected. The activation energy at strictly fixed α^{*} values, $E_a(\alpha^{*})$, was calculated from the slope of the plot of $\ln(t_{\alpha^{*}})$ *vs.* $1/T$ according to [32] (where $t_{\alpha^{*}}$ is a time of phase transition for fraction reacted is equal α^*). Dependencies between the $\ln(t_{\alpha^*})$ *vs.* $1/T$ for the crystals rhombus and triangle-like are listed in Figs 5 and 6, respectively.

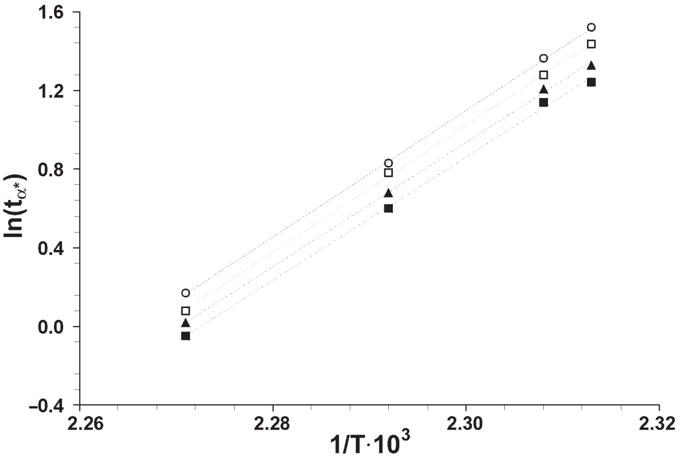


Fig 5 Dependencies between the $\ln(t_{\alpha^*})$ *vs.* $1/T$ for the crystals rhombus-like form: ■ – α^*=70%; ▲ – 75% ; □ – 80%; o – 85%

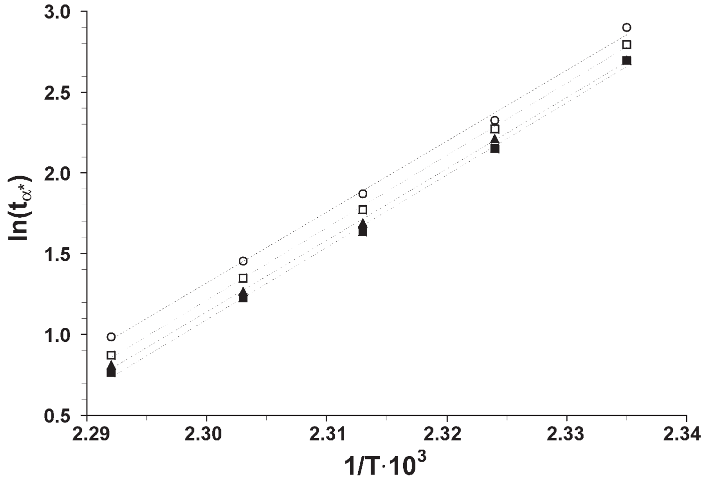


Fig 6 Dependencies between the $\ln(t_{\alpha^*})$ *vs.* $1/T$ for the crystals triangle-like form: ■– α^*=70%; ▲ – 75% ; □ – 80%; o – 85%

The results of the calculations of the activation energies of γ- → α-glycine phase transition for the respective geometry of the crystals are shown in Table 4.

Table 4 The activation energies, E_a, of the γ- →α-glycine phase transition for different geometry of the crystals

α^*/%	E_a/kJ mol^{-1}	
	rhombus≡E_a('2')	triangle≡E_a('3')
65	263±7	368±9
70	261±7	372±9
75	263±5	367±5
80	269±3	372±5
85	268±2	366±10
$\overline{E}_a$	265±5	369±8

As can be seen from the table, the activation energy for three-dimension growth in triangle-like crystals of α-phase, E_a('3'), is 1.4 times bigger than for the two-dimensional nuclei growth in rhombus-like crystals, E_a('2'). If one takes into account Šesták's [32] approach, it may be proposed that the total activation energy of a phase transition process is a sum of two terms: nucleation energy, E_N, and growth energy, E_G:

$$E_a = E_N + nE_G \tag{4}$$

where n is the order of the dimension of the growth process.

If a constant number of nuclei is assumed ($E_N \rightarrow 0$): E_a('3')=3E_G and E_a('2')=2E_G:

$$E_G = (E_a(\text{'2'}) + E_a(\text{'3'}))/5 \approx 218 \text{ kJ mol}^{-1} \tag{5}$$

Presumably the phase transition first takes place on defects crystal structure (Iitaka [10] mentioned this fact). Therefore, the limiting stages of this process are the increase of the defects and their diffusion to the reaction centres. Unfortunately, there are no publications estimating the energies of increasing and diffusion of different defects in organic crystals, in particularly for glycine. However, it may be sufficient to roughly estimate the kind of structure defects, which are responsible for γ- → α-phase transition: if the energetic characteristics of nucleation and movement of the various defects in copper [33] were used, the bivacancy mechanism would be more suitable.

The β-modification glycine

All the efforts in order to observe heat effects of the phase transition of the β-Gly in a temperature interval of 25 up to 220°C (for different heating rate and isothermal treatments) was not successful and no heat effects were observed. Moreover, a special experiment was carried out as follows. The single crystal of β-modification was heated from 25 up to 180°C (v=10 K min^{-1}) and then isothermally treated for 30 min at this temperature. After this procedure, the crystal was identified by X-ray diffraction. The initial and tempered crystal had the same parameters of unit cell. According to Burger's and Ramberger's rules [27], the β-modification of glycine is monotropic with respect to other phases.

It should be noted that in contrast to α- and γ-phases, the active sublimation process was taking place in the temperature range from 210 to 240°C (v=10 K min^{-1}) with melting and decomposition at higher temperatures. Melting (and decomposition) temperature of α-glycine (v=10 K min^{-1}) is 250°C. On the basis of these observations it may be assumed that the crystal lattice energy of β-glycine is less than that of the α-modification. The confirmation of the fact will be shown in the next section of the present study.

Solution calorimeter measurements

It should be mentioned that the investigation of isoenergetic polymorphs is a delicate experimental problem. This is connected, first of all, with the fact that the difference between the crystal lattice energies in many cases is of the same range as the experimental errors. In this respect water was chosen as the solvent since the studied polymorphs dissolve in it better than in any other solvent. The mass of substance was adjusted such that the experimental signal was similar to the optimum signal for the equipment used. The mass of each sample was close to 63 mg (m≈(8.4±0.1)·10^{-3}) and gave heat effects of about 12 J. The dilution enthalpy for concentrations between m_s=8.08·10^{-3} to m_f=4.06·10^{-3} mol kg^{-1} is equal 0.8±0.4 J mol^{-1} [34]. The differences of concentrations for the present experiments were less than 3% (m≈(8.4±0.1)·10^{-3}). Therefore, the dilution enthalpy correction to the solution enthalpy could be neglected in the present study. In order to avoid mistakes due to artefacts under preparation of the crystals (size, defects, etc.), all the crystals were grown under the same conditions and small single crystals of approximately identical sizes were chosen. DSC and X-ray identified the investigated phases before the solution calorimeter measurements.

The solution enthalpies of the examined phases are presented in Table 5.

Table 5 The solution enthalpies, $\Delta_{sol}H_m$, of the different polymorphic phases of glycine

N	α-phase		β-phase		γ-phase	
	M/mg	$\Delta_{sol}H_m$/ J mol^{-1}	M/mg	$\Delta_{sol}H_m$/ J mol^{-1}	M/mg	$\Delta_{sol}H_m$/ J mol^{-1}
1	63.468	14488	63.598	14170	61.856	14775
2	63.613	14481	63.794	14243	62.528	14925
3	63.347	14503	63.577	14180	62.998	14851
4	62.632	14502	63.390	14205	63.200	14795
5	61.527	14581	63.323	14190	63.049	14738
6	61.462	14561			63.857	14769
7	63.106	14523			63.121	14776
8	63.055	14636			64.074	14701
9	63.070	14433				
	$\Delta_{sol}\overline{H}_m$	14523±76	$\Delta_{sol}\overline{H}_m$	14198±73	$\Delta_{sol}\overline{H}_m$	14791±84

It is well known that:

$$\Delta_{\mathrm{sol}}H_{\mathrm{m}} = \Delta_{\mathrm{sub}}H + \Delta_{\mathrm{solv}}H_{\mathrm{m}} \tag{6}$$

where $\Delta_{\mathrm{sol}}H_{\mathrm{m}}$ is a solution enthalpy for concentration solute of m; $\Delta_{\mathrm{sub}}H$ is a sublimation enthalpy; E_{cr} is the crystal lattice energy (negative); $\Delta_{\mathrm{sub}}H \approx -E_{\mathrm{cr}}$; $\Delta_{\mathrm{solv}}H_{\mathrm{m}}$ is a solvation enthalpy for concentration solute of m.

$$\begin{gathered}\Delta_{\mathrm{tr}}H(A\to B)=\Delta\Delta_{\mathrm{sol}}H_{\mathrm{m}}(A\to B)=\Delta_{\mathrm{sol}}H_{\mathrm{m}}(B)-\Delta_{\mathrm{sol}}H_{\mathrm{m}}(A)=\\ \Delta_{\mathrm{sub}}H(B)-\Delta_{\mathrm{sub}}H(A)=-\Delta E_{\mathrm{cr}}(A\to B)\end{gathered} \tag{7}$$

It should be emphasised that the differences between the crystal lattice energies of the studied polymorphs may be small, but exceed the experimental error. In this respect it should be mentioned that growth of the β-phase is in some cases observed while preparing the α-phase. On the other hand, sometimes α-modification grows when preparing γ-phase. However, the growth of a definite crystal lattice from a saturated solution is presumably determined by the degree of association (the size and structure of a cluster created in the solution). For example, the molecules of glycine in an aqueous saturated solution exist mostly as dimers [35]. It may be assumed that the structure of the crystal lattices of the various polymorphs reflects partly the structure of clusters in the saturated solutions. Based on analysis of the $\Delta_{\mathrm{sol}}H_{\mathrm{m}}$, the phases can be arranged in a descending order of their absolute values of the lattice energies: γ->α->β-modification.

As was elucidated above, the network of hydrogen bonds plays an essential role in organisation of the crystal structure of glycine. Therefore, it is interesting to examine IR spectra of the polymorphic phases [7]. The absorption occurring at 3154 cm^{-1} in α-glycine corresponds to the highest N–H stretching frequency. This absorption shifts to a lower value, 3093 in γ-glycine, and shifts to a higher value, 3180 cm^{-1}, in β-glycine. The shift in γ-Gly may be interpreted as an indication for the weakest hydrogen bond in the α-form being weaker than the weakest hydrogen bond in the γ-form. The analogous situation reveals between β- and α-forms: the weakest hydrogen bond in the β-phase is weaker than the corresponding hydrogen bond in the

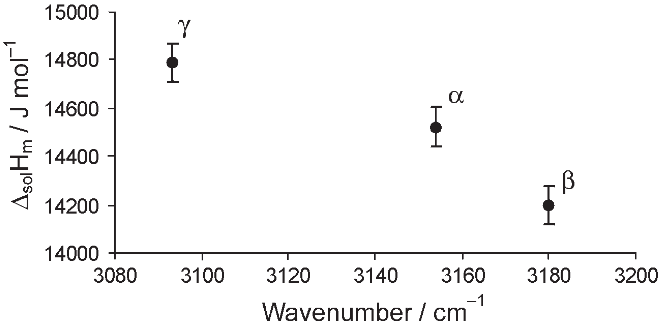


Fig 7 Dependence between the N–H stretching frequency and $\Delta_{\mathrm{sol}}H_{\mathrm{m}}$ for the various crystal modifications of glycine

α-phase. In β-glycine, each single layer is held to one another by weaker hydrogen bonds than those contributing to the formation of double layers in the α-form. The correlation between the N–H stretching frequency and $\Delta_{sol}H_m$ examined on the three phases of glycine is presented in Fig. 7. This result confirms once more the importance of the network of the hydrogen bonds for the crystal structure.

Conclusions

The temperature of the phase transition γ- → α-glycine turned out to be affected by a) conditions under which the crystals of the γ-modification are grown, b) tempering of the crystals prior to transition experiments, c) form (geometry) of crystals.

The kinetics of the phase transition γ- → α-glycine of rhomboedric single crystals of γ-phase glycine is described best by the equation for two-dimension nuclei growth, whereas for the crystals of triangle geometry it is the equation for three-dimension growth.

Based on the energies measured for the growth of the new phase in the γ- → α-phase transition, it may be supposed that a bivacancy mechanism of the movement of crystalline defects would be plausible.

The network of hydrogen bonds plays an essential role in the organisation of the crystal structure of glycine. Considering $\Delta_{sol}H_m$, the investigated polymorphs can be arranged in descending order of absolute values of their lattice energies as follows: γ->α->β-modification.

The β-modification of glycine is a monotropic phase with respect to the other forms, whereas γ- and α-polymorphs are enantiotropically related.

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