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ORIGINAL PAPER

Crystal Structure and Phase Transition of Diglycine Perchlorate

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Abstract Diglycine perchlorate (DGPCl), a new 2:1 adduct formed between glycine and perchloric acid has been obtained and studied using differential scanning calorimetry and single crystal X-ray diffraction. DGPCl undergoes a reversible first-order phase transition at 261.5 K. The crystal structures at 150 and 293 K have been determined to be triclinic, space group P-1, $Z = 2$, suggesting the first-order phase transition to be an isostructural phase transition. The DGPCl crystal consists of five glycinium-monoprotonated glycinium dimers and five perchlorate anions in an asymmetric unit. The glycine moieties in the glycinium-monoprotonated glycinium dimers are non-planar. Two types of hydrogen bonds are present in the crystal, strong O–H···O hydrogen bonds and a weak N–H···O hydrogen bonds. The short, strong O–H···O hydrogen bond connects the glycinium ion and mono protonated glycinium ion. In four of the dimers, the O–H and H···O bond lengths are different, indicating the hydrogen atom to be located more close to the monoprotonated glycinium ion. However, in one of the glycinium-monoprotonated glycinium dimer the O··H and H··O bond lengths are nearly equal, suggesting the hydrogen atom (O···H···O) to be attached to the oxygen atoms of both glycine moieties. On thermal transition some of these hydrogen bonds are weakened and in all dimers the hydrogen atom seems to be located more close to the mono protonated glycinium ion.

Keywords Diglycine perchlorate · Single crystal X-ray diffraction · DSC

Introduction

Glycine, an optically inactive (no stereoisomers) amino acid, in its pure form exists as a zwitterion ($NH_3^+CH_2COO^-$) and has amphoteric character, being able to accept an H atom at the carboxylate group from even moderately weak acids and donate the amino H atom in basic environments. Consequently, glycine, in the presence of different inorganic acids or salts, forms compounds which exhibit various types of structural phase transitions, some of these compounds, triglycine sulfate (TGS), triglycine selenate (TGSe), triglycine sulfophosphate (TGSP), glycinium phosphite (GPI), diglycine nitrate crystal (DGN) being ferroelectric. These compounds are molecular type crystals with glycine–oxygen–anion complexes (SO_4^{2-} in TGS, SeO_4^{2-} in TGSe, ($SO_4^{2-} + HPO_4^{2-}$) in TGSP, $H_2PO_3^-$ in GPI, NO_3^- in DGN) and undergo phase transition of the order–disorder type [8].

Triglycine sulfate, a well studied ferroelectric material, undergoes ferroelectric to paraelectric transition at 322 K [6]. During this transition the space group changes from $P2_1$ in the ferroelectric phase to $P2_1/m$ in the paraelectric phase. The structural analysis of TGS in ferroelectric phase by [6] indicated the presence of three crystallographically independent glycine molecules (two zwitterionic and one cationic (monoprotonated glycinium ions)), designated as GI, GII, and GIII and a sulphate ion in an asymmetric unit cell of

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TGS. According to the authors the NH_3 group of GI and/or the hydrogen bond between GII and GIII is responsible for the ferroelectric to paraelectric transition. DGN, another ferroelectric compound obtained from glycine and nitric acid is ferroelectric below 206 K (space group Pa), and above the transition temperature it is paraelectric with the centerosymmetry space group $P2_1/a$ [12, 13]. The asymmetric unit cell of DGN was shown to contain two glycine molecules (a zwitterionic and a monoprotonated glycinium ion) and a nitrate ion. The structural arrangement of two glycine molecules as well as a hydrogen bond between them and a mechanism of the phase transition were found to be similar to those of TGS [12, 13]. However, in contrast to the TGS crystal where the spontaneous polarization vector P_s is parallel to the twofold axis of symmetry [010] direction, in DGN crystal this vector lies in the symmetry plane [101]. In glycinium phosphite (GPI) the crystal structures are shown to be built of amino acid layers which are held together by strong hydrogen bonds to infinite chains of hydrogen-bonded phosphite anions. These hydrogen bonded infinite chains of phosphite anions are directed along the crystallographic c axis [2]. GPI undergoes ferroelectric to paraelectric transition at 224 K [1]. The mechanism of the ferroelectric to paraelectric transition is connected to a dynamical disorder of the protons in the interphosphite hydrogen bonds which is coupled to the motions of the ammonium groups of glycinium cations [10, 15].

We report in this communication the procedure to obtain crystals of a new 2:1 adduct formed between glycine and perchloric acid [glycine perchlorate $((\text{glycine})_{10}(HClO_4)_5)$ (DGPCl)] and the differential scanning calorimetry (DSC) measurements on this compound. The results of the structure analysis of DGPCl crystal both for the low-temperature phase (LTP) and high-temperature phase (HTP) using single crystal X-ray diffraction is also reported.

Experimental

Crystal Growth

Glycine perchlorate single crystals were grown by the slow evaporation method from aqueous solution containing αglycine and perchloric acid in 2:1 M ratio. The clear aqueous solution was left undisturbed at 20 °C to get single crystals. Good quality plate shaped single crystals were obtained which were used to perform DSC and single crystal X-ray diffraction experiments.

Differential Scanning Calorimetry (DSC)

Mettler Toledo DSC 822 was used for thermal measurements of the samples, with an empty aluminum pan as a reference. Temperature and enthalpy calibration of the instrument were done, using cyclohexane and indium. The transition temperature, T_c, reported is the peak temperature. The transition enthalpy of the endothermic curve is calculated by using the software supplied by Mettler Toledo. The expected experimental errors in temperature and enthalpy values were ± 0.1 °C and ± 5%, respectively. For measuring (i) low-temperature transition 25 – 30 mg crystal and (ii) crystal to isotropic melting 1–2 mg crystal was used. The DSC experiments were repeated many times with the (a) same sample to check the reversibility of the transitions and (b) fresh samples from different synthesis to check the reproducibility of the DSC data.

Single-Crystal X-ray Diffraction

X-ray diffraction data on DGPCl crystal of $0.24 \times 0.28 \times 0.34$ mm^3 were collected on an Oxford XCalibur-S CCD-based diffractometer with graphite-monochromated Mo Kα radiation ($\gamma = 0.71073$ Å) equipped with an Oxford Instruments low-temprature attachment. The crystal to detector distance was fixed at 50 mm. The strategy for the data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan' techniques, and were scaled and reduced using CrysAlisPro RED software.

Structure Refinements

The structures were solved by direct methods using SHELXS-97^{15b} and refined by full matrix least squares with SHELXL-97^{15b}, refining on F^2. The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally $1.2 \times U_{eq}$ of their parent atoms. All computation was carried out on a PC using the SHELXTL-PC program package. Molecular graphics were done using Mercury for Windows (downloaded from http://www.ccdc.cam.ac.uk/mercury).

The crystallographic data and details of the data collection and refinement for 150 and 293 K are given in Table 1.

Computer programs used: CrysAlis CCD and CrysAlis RED [11], SHELXS97 [14], SHELXL97 [14], ORTEPIII [4], WinGX publication routines [5].

Results and Discussions

Differential Scanning Calorimetry

The DSC experiments of DGPCl crystals were carried out to check for existence of any polymorphic phase other than

Table 1 :X-ray diffraction data at 150 and 295 K for DGPCl((glycine)$_{10}$ (HClO$_4$)$_5$)

Identification code	150 K	293 K
Empirical formula	$C_{20}H_{55}Cl_5N_{10}O_{40}$	$C_{20}H_{55}Cl_5N_{10}O_{40}$
Formula weight	1252.99	1252.99
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Triclinic, P-1	Triclinic, P-1
Unit cell dimensions		
a (Å)	8.6581 (3)	8.7127 (5)
b (Å)	14.7732 (9)	14.870 (4)
c (Å)	19.1263 (10)	19.4336 (19)
Alpha (°)	98.942 (5)	98.756 (13)
Beta (°)	93.099 (4)	93.032 (6)
Gama (°)	105.479 (4)	106.059 (13)
Volume (Å^3)	2317.3 (2)	2379.3 (6)
Z, Calculated density (gm cm^{-3})	2, 1.796	2, 1.749
Absorption coefficient (mm^{-1})	0.445	0.433
F(000)	1300	1300
Crystal size (mm)	0.34 × 0.28 × 0.24	0.34 × 0.28 × 0.24
Theta min–max (°)	3.11–25.00	3.08–25.00
Index ranges	$-10 \leq h \leq 10$, $-17 \leq k \leq 17$, $-22 \leq l \leq 22$	$-10 \leq h \leq 10$, $-17 \leq k \leq 17$, $-23 \leq l \leq 22$
Reflections collected/unique	20149/8161 [*R* (int) = 0.0247]	23731/8366 [*R* (int) = 0.0226]
Data collection instrument	Oxford XCalibur-S	Oxford XCalibur-S
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9008 and 0.8636	0.9032 and 0.8668
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F$^{\wedge 2}$
Data/restraints/parameters	8161/0/816	8366/0/816
Goodness-of-fit on F^2	0.929	0.980
Final *R* indices [I > 2sigma(I)]	$R_1 = 0.0306$, $wR_2 = 0.0746$	$R_1 = 0.0327$, $wR_2 = 0.0825$
R indices (all data)	$R_1 = 0.0488$, $wR_2 = 0.0807$	$R_1 = 0.0531$, $wR_2 = 0.0917$
Largest diff. peak and hole (e/Å^3)	0.233 and −0.473	0.281 and −0.398

the melting transition. The DSC heating thermograms of DGPCl and glycine obtained in the temperature range 160 – 580 K are shown in Fig. 1a, b. The crystal to isotropic melting transition of pure glycine is seen at 519.5 K and the enthalpy associated with this transition is 1026 Jgm^{-1}. The melting (decomposition) thermogram of DGPCl is different from that of pure glycine, indicating formation of a new compound. The transition temperatures and the enthalpy associated with melting transitions in DGPCl are 376.5, 396 and 489 K and 285 Jgm^{-1} (total enthalpy), respectively. On further heating the compound decomposes as indicated by exothermic transition at 535.6 K.

However, when the samples are heated in temperature range 160 to 300 K the DGPCl crystal shows an endothermic transition at temperature, T_c, 261.5 K and the enthalpy, ΔH associated with this transition is 1.9 Jg^{-1}. This transition is obtained in repeated cooling and heating cycles, indicative of a reversible transition. However, in 160 to 300 K temperature range glycine does not show any transition (Fig. 1a).

To see if this transition is associated with structural change the crystal structure of the DGPCl is obtained at 150 and 293 K, respectively.

Single-Crystal X-ray Diffraction: DGPCl Crystal Structure and Packing at 150 K (in Low-Temperature Phase) and 293 K (in High-Temperature Phase)

Both, low-temperature phase (LTP) and high-temperature phase (HTP) belongs to the triclinic centrosymmetric space group P-1, with ten glycine molecules (five zwitterionic ($NH_3^+CH_2COO^-$) and five cationic ($NH_3^+CH_2COOH$)) and five perchlorate ions (ClO_4^-) in an asymmetric unit (Fig. 2). The LTP to HTP change does not induce any change in the crystal symmetry. The average crystal structure of both LTP and HTP phases are similar. From

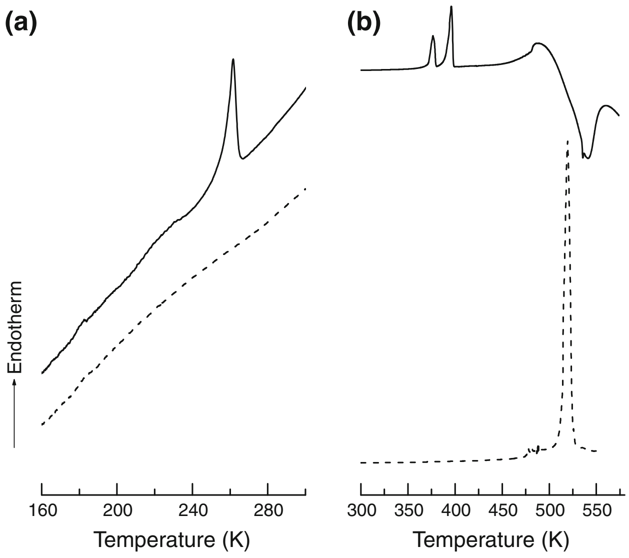

Fig. 1 DSC heating thermograms at 5°K/min of DGPCl (*solid curve*) and glycine (*dash curve*) in **a** 160 to 300 K and **b** 300 to 580 K temperature range

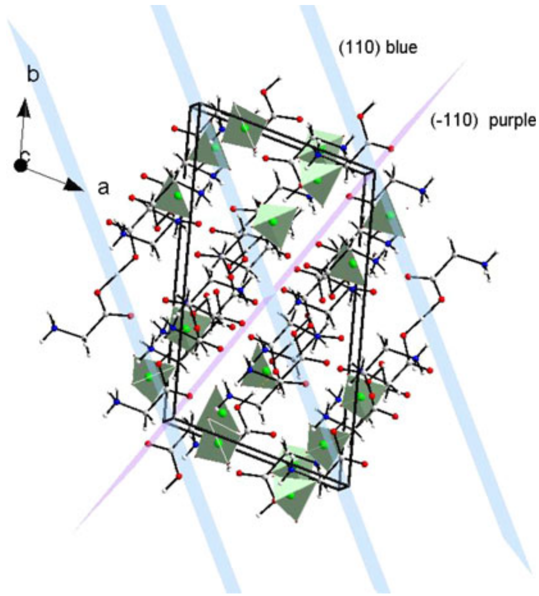

Fig. 3 Projection of the layer parallel to the (−110) plane

projection along a axis it is seen that the crystal structure is formed with layers parallel to (−110) plane (Fig. 3). This layer contains crystallographically independent glycine molecules and perchlorate ions. The crystal arrangement is stabilized by a three-dimensional network of hydrogen bonds between the glycine molecules and perchlorate ions.

The chlorine atom in perchlorate ion is tetrahedrally bonded to four oxygen atoms. All four Cl–O bonds in perchlorate ion are almost identical as a result of the delocalization of the negative charge between them. The mean value of the O–Cl–O angles is 109.47(9)°. These bond lengths and angles are in good agreement with those observed in similar compounds [3, 16]. Therefore, the perchlorate ion has a four-bar symmetry within experimental error. On comparing the Cl–O bond lengths (1.438(2) Å in LTP and 1.430(2) Å in HTP) and O–Cl–O angles of the perchlorate anions in LTP and HTP no significant differences were observed.

In DGPCl the glycine molecules are present in zwitterionic [glycinium (G_{zw})] and cationic [monoprotonated glycinium (G_{mp})] forms. These glycine moieties exist as dimers (H [NH$_3$CH2COO]$_2^+$) due to strong hydrogen bonding interaction between the C=O and C–OH groups of the zwitterionic and cationic glycine moieties, respectively. There are five crystallographically non-equivalent glycine dimers in an asymmetric unit of DGPCl which possess almost identical geometry (Fig. 2a, b). The two glycine moieties in the dimers (i) $G_{zw}2$ and $G_{mp}3$ (N2/N5 glycine), (ii) $G_{mp}4$ and $G_{zw}5$ (N6/N10 glycine), (iii) $G_{mp}5$ and $G_{zw}1$ (N8/N1glycine), (iv) $G_{mp}2$ and $G_{zw}3$ (N4/N7 glycine), and

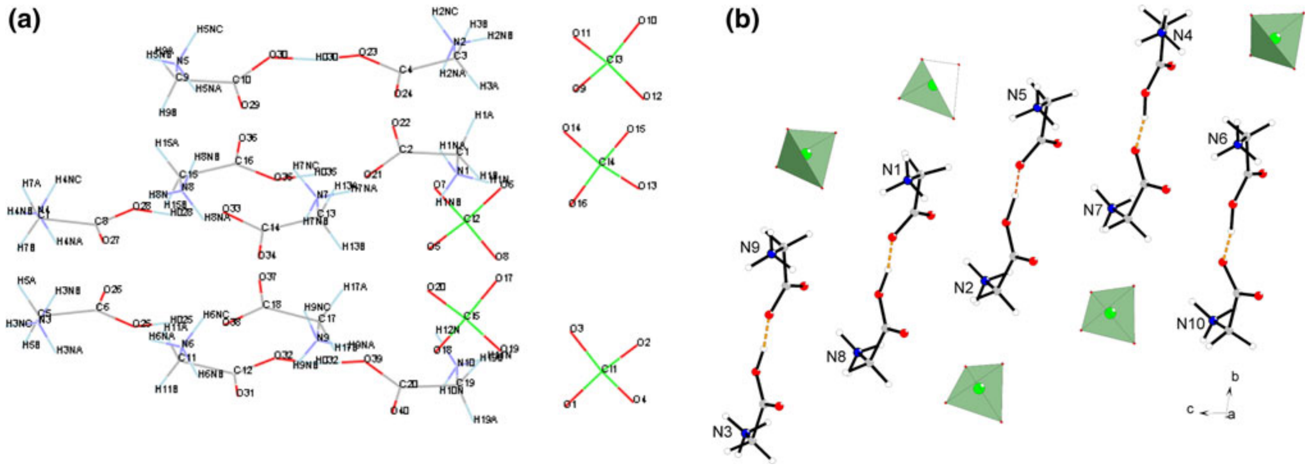

Fig. 2 **a** Asymmetric unit of DGPCl at 150 K with atom labelling scheme and **b** unit cell showing glycine dimers

(v) G_{mp}1and G_{zw}4 (N3/N9 glycine) are linked by short, strong and symmetric O···H···O and O···H···O hydrogen bonds with O···O distances in the range 2.452 – 2.468 Å at 150 K and 2.46 to 2.474 Å at 293 K (Tables 2, 3).

On comparing the O–H···O bond lengths at 150 K in each of the glycinium-monoprotonated glycinium dimer it is found that for N2/N5 glycine dimer, O–H (O30···HO30:1.272 Å), and H···O (HO30···O23:1.202 Å) bond lengths are nearly equal. Thus in this glycine dimer the hydrogen atom (O···H···O) appears to be attached to oxygen atom of both the glycine molecules. Similar hydrogen bond glycine dimers were found in TGS, TGSe, and DGN [6, 12, 13]. The bridging O···H···O hydrogen bonds in DGPCl are as strong as those found in TGS and DGN crystals. In the remaining four glycinium-monoprotonated glycinium dimers, the O–H···O bond lengths are different, indicating the hydrogen atom to be located more close to the monoprotonated glycinium ion (Table 2). However, in HTP the N2/N5 glycine dimer's bond lengths O–H (O30···HO30: 1.35 Å) and H···O (HO30···O23: 1.13 Å) were different suggesting the hydrogen atom to be located more close to the monoprotonated glycinium ion (Table 3). Thus in HTP all dimers have similar type of O–H···O bond lengths.

In both types of glycine (H_3N^+–CH_2–COO^-/COOH) molecules, the C–N, C–H, C–C bond lengths are similar. The glycine carboxyl skeleton, which includes two oxygen and two carbon atoms is planar. In the carboxyl groups the corresponding bond angles for all ten glycine molecules (for zwitterionic and cationic forms) are nearly equal. The angles N–C–C are in the range, 111–112°, and hence do not deviate significantly from the formal tetrahedral angle. The orientation of NH_3^+ and CH_2 groups along the C–N axis for all glycine molecules is close to staggered configuration. In both LTP and HTP the displacements of the non-hydrogen atoms from the respective plane in all glycine molecules are similar as indicated by the torsion angles given in Table 4. In other words, the nitrogen atom is not in the plane of the glycine molecule but displaced from the plane containing the remaining four atoms. The distance of the nitrogen atom from the best plane for these glycine moieties were in the range 0.361 to 0.452 Å for LTP and 0.310 to 0.430 Å for HTP. This behavior is different from that observed in TGS and DGN wherein the glycinium-monoprotonated glycinium dimer are essentially planar [6, 12, 13]. However, in the crystals of α glycine, β glycine, and γ glycine the nitrogen atom of the zwitterionic type glycine was displaced from the plane containing the remaining four atoms and the distance of the nitrogen atom from the best plane were 0.436, 0.583, and 0.309 Å, respectively [7, 9]. These observations suggest that the conformation of the glycine moieties in DGPCl is similar to the glycine moieties in α glycine, β glycine and γ glycine

Table 2 Hydrogen-bonding geometry((A,°) at 150 K

	D–H	H···*A*	*D*···A	*D*–H···*A*
N3–H3NB···O27	0.93 (2)	1.90 (2)	2.811 (2)	168.7 (19)
N5–H5NA···O36	0.98 (2)	1.81 (2)	2.777 (3)	171.4 (19)
N7–H7NB···O37^{i}	0.91 (2)	1.93 (2)	2.828 (2)	168 (2)
N2–H2NA···O22^{ii}	0.99 (3)	1.85 (3)	2.806 (2)	162 (2)
N9–H9NC···O34	1.00 (2)	1.85 (3)	2.824 (3)	161 (2)
N8–H8NB···O29^{iii}	0.93 (3)	1.91 (3)	2.814 (2)	162 (2)
N1–H1NA···O24^{iv}	0.95 (2)	1.85 (3)	2.784 (3)	167 (2)
N1–H1NB···O20^{v}	0.95 (3)	2.10 (3)	2.964 (3)	150 (2)
N1–H1NB···Cl5^{v}	0.95 (3)	2.98 (3)	3.632 (2)	126.8 (18)
N8–H8NA···O37	0.93 (3)	2.01 (3)	2.933 (3)	172 (2)
N5–H5NC···O14^{vi}	0.94 (3)	2.08 (3)	2.967 (3)	157 (2)
N5–H5NC···Cl4^{vi}	0.94 (3)	2.94 (3)	3.650 (2)	134 (2)
N9–H9NB···O40	0.92 (2)	1.97 (2)	2.895 (2)	174.7 (19)
N4–H4NC···O12^{iii}	0.90 (2)	2.08 (3)	2.922 (3)	155 (2)
N7–H7NA···O7^{vii}	0.88 (2)	2.22 (2)	2.957 (3)	140.4 (16)
N7–H7NA···O5^{vii}	0.88 (2)	2.58 (2)	3.255 (3)	134.3 (18)
N7–H7NA···Cl2^{vii}	0.88 (2)	2.93 (2)	3.718 (2)	149.8 (17)
N3–H3NA···O1^{v}	0.90 (3)	2.10 (3)	2.964 (3)	159 (2)
N3–H3NA···Cl1^{v}	0.90 (3)	2.99 (3)	3.674 (2)	134.1 (18)
N10–H10 N···O31^{iii}	0.97 (2)	1.83 (2)	2.788 (2)	166.8 (19)
N9–H9NA···O18^{viii}	0.84 (2)	2.29 (2)	2.975 (3)	139.0 (18)
N9–H9NA···O20^{viii}	0.84 (2)	2.58 (2)	3.214 (3)	133.9 (19)
N9–H9NA···Cl5^{viii}	0.84 (2)	2.97 (2)	3.709 (2)	148.0 (19)
N5–H5NB···O10^{iii}	0.85 (3)	2.25 (3)	3.000 (3)	147 (2)
N5–H5NB···O12^{iii}	0.85 (3)	2.42 (3)	3.141 (3)	143 (3)
N5–H5NB···Cl3^{iii}	0.85 (3)	2.87 (3)	3.673 (2)	159 (2)
N7–H7NC···O29	0.94 (3)	1.97 (3)	2.907 (3)	174 (2)
N10–H11 N···O3^{ix}	0.82 (3)	2.15 (3)	2.931 (3)	159 (2)
N10–H11 N···O1^{ix}	0.82 (3)	2.60 (3)	3.238 (3)	135 (2)
N10–H11 N···Cl1^{ix}	0.82 (3)	2.90 (3)	3.677 (2)	158 (2)
N4–H4NA···O26^{iii}	1.01 (3)	1.81 (3)	2.800 (3)	167 (2)
N1–H1 N···O16^{i}	0.88 (3)	2.08 (3)	2.899 (3)	155 (2)
N1–H1 N···O14^{i}	0.88 (3)	2.58 (3)	3.257 (3)	135 (2)
N1–H1 N···Cl4^{i}	0.88 (3)	2.84 (3)	3.649 (2)	155 (2)
N2–H2 NB···O11^{ii}	0.91 (2)	2.29 (2)	3.010 (3)	136.7 (16)
N10–H12 N···O5^{ix}	0.98 (3)	2.06 (3)	2.967 (3)	152 (3)
N10–H12N···Cl2^{ix}	0.98 (3)	2.94 (3)	3.641 (2)	130 (2)
N4–H4NB···O6^{iii}	0.81 (3)	2.16 (3)	2.883 (3)	149 (2)
O28–H028···O33	1.03 (2)	1.43 (2)	2.454 (2)	169 (2)
O35–H035···O21^{x}	1.07 (2)	1.39 (2)	2.452 (2)	170 (2)
O35–H035···O22^{x}	1.07 (2)	2.52 (2)	3.251 (2)	124.6 (14)
O32–H032···O39^{viii}	1.12 (2)	1.35 (2)	2.462 (2)	170 (2)
O32–H032···O40^{viii}	1.12 (2)	2.50 (2)	3.261 (2)	124.1 (12)
O23–H030···O30^{xi}	1.20 (3)	1.27 (3)	2.468 (2)	172 (2)
O23–H030···O29^{xi}	1.20 (3)	2.47 (2)	3.237 (2)	119.3 (14)
O25–H025···O38^{i}	0.99 (3)	1.47 (3)	2.455 (2)	171 (3)
O25–H025···O37^{i}	0.99 (3)	2.65 (3)	3.365 (2)	129.2 (17)
N8–H8 N···O27^{iii}	0.91 (3)	2.33 (3)	3.116 (2)	144 (2)

Table 2 continued

	D–H	H···*A*	*D*···A	*D*–H···*A*
N8–H8 N···O13^{iii}	0.91 (3)	2.37 (3)	3.021 (3)	128.3 (18)
N6–H6NB···O40	0.95 (3)	1.87 (3)	2.810 (3)	169 (2)
N6–H6NA···O26^{iii}	0.89 (3)	2.37 (3)	3.129 (2)	142.6 (19)
N6–H6NA···O2^{iii}	0.89 (3)	2.42 (2)	3.078 (3)	130.4 (18)
N3–H3NC···O19^{ix}	0.86 (3)	2.10 (3)	2.904 (3)	155 (2)
N3–H3NC···Cl5^{ix}	0.86 (3)	2.95 (3)	3.796 (2)	167 (2)
N2–H2NC···O22	0.92 (3)	2.01 (3)	2.924 (3)	174 (2)
N6–H6NC···O34	0.91 (3)	2.01 (3)	2.911 (3)	173 (2)

Symmetry codes: (i) 1 + x, y, z; (ii) 2−x, −1−y, 1−z; (iii) −1 + x, y, z; (iv) 3−x, −1−y, 1−z; (v) 2−x, −y, 2−z; (vi) 1−x, −y, 1−z; (vii) x, 1 + y, z; (viii) 1−x, 1−y, 2−z; (ix) 1−x, −y, 2−z; (x) −1 + x, 1 + y, z; (xi) 2−x, −y, 1−z

Table 3 Hydrogen-bonding geometry(A,°) at 293 K

	D–H	H···*A*	*D*···A	*D*–H···*A*
N3–H3NB···O27	0.930 (19)	1.908 (19)	2.825 (2)	168.4 (17)
N5–H5NA···O36	0.97 (2)	1.84 (2)	2.803 (2)	173 (2)
N7–H7NB···O37^{i}	0.832 (17)	2.044 (18)	2.855 (2)	164.7 (16)
N2–H2NA···O22^{ii}	0.94 (2)	1.91 (2)	2.832 (2)	169.4 (19)
N9–H9NC···O34	0.972 (19)	1.91 (2)	2.851 (2)	162.6 (16)
N8–H8NB···O29^{iii}	0.90 (2)	1.95 (2)	2.828 (2)	165.2 (19)
N1–H1NA···O24^{iv}	0.90 (2)	1.92 (2)	2.804 (2)	165.8 (18)
N1–H1NB···O20^{v}	0.93 (2)	2.15 (2)	3.006 (2)	153 (2)
N1–H1NB···Cl5^{v}	0.93 (2)	3.02 (2)	3.698 (2)	131.1 (18)
N8–H8NA···O37	0.94 (2)	2.03 (2)	2.956 (2)	170.1 (18)
N5–H5NC···O14^{vi}	0.89 (2)	2.17 (2)	2.998 (2)	156.1 (19)
N5–H5NC···Cl4^{vi}	0.89 (2)	3.03 (2)	3.711 (2)	135.0 (17)
N9–H9NB···O40	0.93 (2)	1.99 (2)	2.913 (2)	176.9 (16)
N4–H4NC···O12^{iii}	0.92 (2)	2.09 (2)	2.942 (2)	153.7 (16)
N7–H7NA···O7^{vii}	0.91 (2)	2.250 (19)	2.986 (2)	138.0 (14)
N7–H7NA···O5	0.91 (2)	2.58 (2)	3.231 (2)	128.8 (15)
N7–H7NA···Cl2	0.91 (2)	2.95 (2)	3.7299 (19)	144.4 (15)
N3–H3NA···O1^{v}	0.85 (2)	2.19 (2)	2.992 (2)	158.4 (17)
N3–H3NA···Cl1^{v}	0.85 (2)	3.10 (2)	3.738 (2)	133.9 (15)
N10–H10 N···O31^{iii}	0.93 (2)	1.89 (2)	2.813 (2)	167.8 (17)
N9–H9NA···O18^{viii}	0.83 (2)	2.32 (2)	3.002 (2)	140.1 (16)
N9–H9NA···O20^{viii}	0.83 (2)	2.58 (2)	3.200 (2)	132.1 (17)
N9–H9NA···Cl5^{viii}	0.83 (2)	3.00 (2)	3.7221 (19)	147.2 (17)
N5–H5NB···O10^{iii}	0.85 (3)	2.26 (3)	3.018 (2)	148.3 (19)
N5–H5NB···O12^{iii}	0.85 (3)	2.40 (2)	3.140 (2)	146 (2)
N5–H5NB···Cl3^{iii}	0.85 (3)	2.86 (3)	3.6862 (19)	164.0 (19)
N7–H7NC···O29	0.93 (2)	2.00 (2)	2.927 (2)	170.4 (17)
N10–H11 N···O3^{ix}	0.81 (2)	2.19 (2)	2.949 (2)	155.7 (18)
N10–H11 N···O1^{ix}	0.81 (2)	2.58 (2)	3.228 (2)	137.5 (19)
N10–H11 N···Cl1^{ix}	0.81 (2)	2.91 (2)	3.6851 (19)	158.9 (19)
N4–H4NA···O26^{iii}	0.96 (2)	1.88 (2)	2.821 (2)	165.4 (17)
N1–H1 N···O16^{i}	0.86 (2)	2.11 (2)	2.925 (2)	156.4 (17)
N1–H1 N···O14^{i}	0.86 (2)	2.57 (2)	3.238 (2)	135.1 (17)
N1–H1 N···Cl4^{i}	0.86 (2)	2.86 (2)	3.6623 (19)	156.4 (17)
N2–H2 NB···O11^{ii}	0.87 (2)	2.38 (2)	3.055 (2)	135.3 (15)
N10–H12 N···O5^{viii}	0.91 (3)	2.18 (3)	3.017 (3)	152 (2)
N10–H12N···Cl2^{viii}	0.91 (3)	3.05 (3)	3.707 (2)	130.7 (19)
N4–H4NB···O6^{iii}	0.80 (2)	2.18 (2)	2.913 (2)	152.6 (18)
O28–H028···O33	1.07 (2)	1.40 (2)	2.4678 (17)	175.8 (18)
O35–H035···O21^{x}	1.076 (19)	1.40 (2)	2.4606 (17)	168.8 (18)
O35–H035···O22^{x}	1.076 (19)	2.534 (18)	3.2722 (18)	125.1 (12)
O32–H032···O39^{viii}	1.09 (2)	1.38 (2)	2.4693 (17)	175.0 (19)
O32–H032···O40^{viii}	1.09 (2)	2.58 (2)	3.2835 (19)	121.4 (12)
O23–H030···O30^{xi}	1.13 (2)	1.35 (2)	2.4737 (17)	173 (2)
O23–H030···O29^{xi}	1.13 (2)	2.52 (2)	3.2560 (18)	121.4 (13)
O25–H025···O38^{i}	1.01 (2)	1.47 (2)	2.4669 (17)	173 (2)
O25–H025···O37^{i}	1.01 (2)	2.68 (2)	3.3808 (18)	127.0 (14)
N8–H8 N···O27^{iii}	0.93 (2)	2.33 (2)	3.1370 (19)	144.4 (16)
N8–H8 N···O13^{iii}	0.93 (2)	2.41 (2)	3.071 (2)	127.5 (15)
N6–H6NB···O40	0.93 (2)	1.92 (2)	2.830 (2)	164.5 (19)
N6–H6NA···O26^{iii}	0.90 (2)	2.42 (2)	3.165 (2)	139.7 (15)
N6–H6NA···O2^{iii}	0.90 (2)	2.45 (2)	3.129 (2)	132.3 (15)
N3–H3NC···O19^{ix}	0.82 (2)	2.18 (2)	2.929 (2)	152.5 (19)
N3–H3NC···Cl5^{ix}	0.82 (2)	2.98 (2)	3.7870 (19)	169.2 (19)
N2–H2NC···O22	0.95 (2)	2.00 (2)	2.946 (2)	176.0 (19)
N6–H6NC···O34	0.92 (2)	2.02 (2)	2.935 (2)	170 (2)

Symmetry codes: (i) 1 + x, y, z; (ii) 2−x, −1−y, 1−z; (iii) −1 + x, y, z; (iv) 3−x, −1−y, 1−z; (v) 2−x, −y, 2−z; (vi) 1−x, −y, 1−z; (vii) x, 1 + y, z; (viii) 1−x, 1−y, 2−z; (ix) 1−x, −y, 2−z; (x) −1 + x, 1 + y, z; (xi) 2−x, −y, 1−z

but different from the glycine moieties in TGS and DGN. In DGPCl the hydrogen atoms of NH_3^+ group are hydrogen bonded to the Cl–O of the perchlorate ions and C=O of the glycine molecules. Thus, the deviation of nitrogen atom from the plane seems to depend on the type of hydrogen bond formed and the packing of the molecules in the crystal structure.

The perchlorate anions are located in the glycine dimer plane with Cl–O groups directed toward hydrogen atoms of the NH_3^+ groups of the glycine. The NH_3^+ groups act as proton donors forming week N–H···O hydrogen bonds with N···O distance in the range 2.884 to 3.257 Å at 150 K and 2.912 to 3.237 Å at 293 K. From the unit cell of DGPCl it is seen that some of the Cl–O groups of the perchlorate anions interact with NH_3^+ groups of different glycine dimers. The H atom of the NH_3^+ group of the glycine dimers also form weak hydrogen bonds with the C=O group of the glycine moieties with N···O distance in the range 2.777 to 3.129 Å at 150 K and 2.803 to 3.164 Å at 293 K (Tables 2, 3).

Table 4 Selected torsion angles (°) at 150 and 293 K (in parentheses)

For Zwitterionic glycine	
N1–C1–C2–O22 = −165.26 (18) (−165.91 (19))	N1−C1−C2−O21 = 15.95 (27) (14.90 (27))
N2–C3–C4–O24 = −162.22 (20) (−162.54 (20))	N2–C3–C4–O23 = 19.43 (27) (19.36 (27))
N7–C13–C14–O34 = 164.19 (19) (164.11 (20))	N7–C13–C14–O33 = −16.93 (28) (−17.14 (28))
N9–C17–C18–O37 = −163.88 (18) (−164.07 (19))	N9–C17–C18–O38 = 17.25 (27) (17.45 (28))
N10–C19–C20–O40 = −164.39 (19) (−165.08 (19))	N10–C19–C20–O39 = 15.99 (28) (15.74 (28))
For Cationic glycine	
N3–C5–C6–O26 = −162.44 (19)(−162.70 (19))	N3–C5–C6–O25 = 19.29 (27) (19.30 (27))
N4–C7–C8–O27 = 161.56 (19) (162.30 (19))	N4–C7–C8–O28 = −20.01 (26) (−19.19 (26))
N5–C9–C10–O29 = 161.60 (19)(162.73 (19))	N5–C9–C10–O30 = −19.73 (27) (−17.89 (28))
N6–C11–C12–O31 = 164.72 (19) (164.68 (19))	N6–C11–C12–O32 = −16.67 (26) (−16.75 (27))
N8–C15–C16–O36 = −164.40 (19) (−164.58 (20))	N8–C15–C16–O35 = 16.99 (27) (16.44 (27))

These N–H···O bonds link glycine dimers into infinite chains parallel to the b axis.

The single crystal X-ray diffraction data obtained at 150 and 293 K suggests that the LTP to HTP transition to be an isostructural phase transition and both glycine ions and the perchlorate anion act as rigid groups. The isostructural phase transition from LTP to HTP involves reorganization of the molecular packing. As seen from Tables 2 and 3, with increasing temperature, most of the hydrogen bonds of perchlorate ions are broken or weakened. Some of the hydrogen bond between N–H and C=O/Cl–O groups are weakened in HTP as indicated by increased N–O distance. The short strong O–H···O hydrogen bond between glycinium-monoprotonated glycinium dimer seems to play an important role in LTP to HTP transition. As discussed above in one of the glycine dimer (N2/N5) the O–H (1.272 Å) and H···O (1.202 Å) bond lengths are nearly equal at 150 K suggesting the hydrogen atom (O···H···O) to be attached to oxygen atom of both the glycine molecules. However, at 293 K the bond lengths O–H (1.332 Å) and H···O (1.146 Å) were different in this glycine dimer suggesting the hydrogen atom to be located more close to the monoprotonated glycinium. Thus the hydrogen atom moves from the position close to the oxygen atom of the glycine N2 to the site close to that of the glycine N5. That is, the glycine N2 becomes monoprotonated glycinium while N5 becomes glycinium ion and is accompanied by slight rotation of the perchlorate ion. Similar type of structural transition was seen in DGN [13]. Thus the phase transition is most probably associated with weakening of the H-bond interaction between (i) the perchlorate ions and glycine molecules and (ii) one of the glycine-dimer.

Conclusions

Diglycine perchlorate, a new 2:1 adduct formed between glycine and perchloric acid undergoes a reversible phase transition at 261.5 K, as evidenced by DSC measurement. The transition seems to be associated with slight rotation of both cations and anions brought about by reduced strength of the hydrogen bonds at elevated temperature. The single crystal X-ray diffraction data obtained at 150 and 293 K suggests the transition to be an isostructural phase transition. The DGPCl crystal being centrosymmetric (triclinic space group P−1) in both LTP and HTP rules out the possibility that this transition is ferroelectric to paraelectric transition as seen with TGS and DGN.

Supplementary Material

Crystallographic data can be obtained from the Cambridge Crystallographic Data Center, by quoting the reference number CCDC 738370 & 738371 for DGPCl at 150 and 295 K, respectively. Copies of these information can be obtained free of charge from the Director, CCDC, 12, Union Road, Cambridge, CB21Ez, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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