# Crystal Structure and Solid–Solid Phase Transition of 1-Dodecylamine Hydrobromide

By Yupu Liu, Youying Di\*, Wenyan Dan and Donghua He

College of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, Shandong Province, P.R. China

(Received March 15, 2010; accepted May 27, 2010)

### 1-Dodecylamine Hydrobromide / X-ray Crystallography / Adiabatic Calorimetry / Low-temperature Heat Capacity / Solid–solid Phase Transition

1-dodecylamine hydrobromide was synthesized. The crystal structure of the compound was determined by X-ray crystallography. Low-temperature heat capacities of the title compound were measured by an adiabatic calorimeter over the temperature range from 78 to 390 K. Three solid–solid phase transitions were observed at the peak temperatures of ( $329.278\pm0.234$ ), ( $337.805\pm0.326$ ), and ( $347.371\pm0.154$ ) K. The molar enthalpies and entropies of the three phase transitions of the substance were calculated based on the analysis of heat capacity curves. Experimental values of heat capacities for the title compound were fitted to two polynomial equations. Three solid–solid phase transitions and a melting process of 1-dodecylamine hydrobromide were verified by DSC technique. In addition, the reversibility and repeatability of the three phase transitions were discussed.

# 1. Introduction

With the increasing seriousness of the energy crisis, the study about the phase change materials (PCMs) [1,2] has become the focus in recent years. The solid–solid phase change materials (SSPCMs) [3,4] have the advantages of high energy density, no liquid or gas generated during the phase transitions, simple device, small size, environmental friendliness, and flexible design over other kinds of phase change materials, and they also are user-friendly and easy to handle. Therefore, the investigation on the solid–solid phase change materials in all kinds of energy storage materials are most frequently conducted owing to the wide application foreground of these materials.

<sup>\*</sup> Corresponding author. E-mail: diyouying@126.com

The bis(n-alkylammonium) halometallates (II) (abbreviated as  $C_{12}M$ ) [1,5] are important organometallic compounds of the generalized formula  $(C_{12}H_{25}NH_3)_2MX_n$  (n = 4 or 6), where M is a divalent or trivalent metal ion  $(M = Zn^{2+}, Cu^{2+}, Mn^{2+}, Cd^{2+}, Co^{2+}, etc.)$  and X is a negative haloid ion. They are characterized by high enthalpy change and excellent reversibility of a solid-solid phase transition between two polymorphic forms in the temperature range of 273–393 K. As the necessary intermediate or raw material, 1-dodecylamine hydrobromide  $(C_{12}H_{25}NH_3Br)$  plays an important role in the formation of  $C_{12}M$  in which the  $C_{12}H_{25}NH_3^+$  cation bonds with the  $MX_n^{2^-}$  anion through ionic bonds.

In recent years, it is found that n-alkylammonium halide can exhibit the phenomena of the distinct solid–solid phase transitions. A great attention has been paid to the application of 1-dodecylamine hydrobromide and dodecyl ammonium salts in many fields such as energy storage and textile industry. In 1953, Gordon *et al.* investigated the crystal structure and some properties of n-dodecylammonium bromide by X-ray diffractometer, automatic variable-temperature moving-film powder camera, and single-crystal techniques [6]. In 1974, Lunden gave a three-dimensional single-crystal study of n-dodecylammonium bromide [7]. However, some important thermodynamic properties of the title compound have not been found in the literature, which restricts the progress of relevant theoretical studies and application development of the compound. Heat capacity is one of the most fundamental thermodynamic properties of materials and necessary for many theoretical studies in physics, chemistry, and engineering technology which are related to materials.

Adiabatic calorimetry is the most reliable method to obtain heat capacities and various thermodynamic data of substances. It is an important and effective experimental method used for the study of the solid–solid phase transitions by measuring low-temperature heat capacities and calculating relevant thermodynamic data. Much work has been done to measure heat capacities with adiabatic calorimetric instruments all over the world [8,9].

In the present work, the crystal structure of the title compound was determined by X-ray crystallography. Low-temperature heat capacities and thermodynamic properties of the title compound were determined by a precision automated adiabatic calorimeter over the temperature range from 78 to 390 K. The phase transition of the title compound was investigated by means of the analysis of the heat capacity curve. Furthermore, three solid–solid phase transitions and the melting process were further studied by DSC technique.

#### 2. Experimental

# 2.1 Synthesis and characterization of 1-dodecylamine hydrobromide $(1\text{-}C_{12}H_{25}NH_3Br)(s)$

1-dodecylamine and hydrobromic acid ( $\geq 40$  mass %) chosen as the reactants and anhydrous ethyl alcohol (A. R.) used as the solvent were of analytical grade.

1-dodecylamine was dissolved into the right amount of the absolute alcohol in a three-neck flask, and excess of hydrobromic acid was gradually added to the above solution under sufficient stirring. The solution was boiled and refluxed for 2 h, whereafter the mixture was condensed by boiling off some of the liquid until crystal membrane emerged on the surface of the solution. The final solution was naturally cooled to room temperature, filtered, and colorless crystal was obtained. The product was re-crystallized three times with anhydrous ethyl alcohol and colorless transparent crystal was gained. Finally, the sample was placed in a vacuum desiccator to dry in vacuum at the temperature of 303 K for 6 h.

The final product was put into a weighing bottle and preserved in a desiccator. The mass fraction purity of the compound was determined to be > 0.995 by HPLC. The contents of the bromide in the compound were determined by chemical analysis. Elemental analysis (C, H, and N) was carried out on a Vario EL III CHNOS instrument made in Germany. These results showed that the mass fraction purity of the compound was > 0.995.

A single crystal suitable for X-ray crystallography was glued to a fine glass fiber. All diffraction data for the compound were collected on a Bruker Smart-1000 CCD diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at T =(298±2) K using the program SMART and processed by SAINT-plus [10]. Absorption corrections were applied by SADABS. The structure was solved by direct methods and expanded using Fourier techniques with SHELXTL-97 program [11], and refined with full-matrix least-squares technique on  $F^2$ . All nonhydrogen atoms were refined anisotropically. All H-atoms were located theoretically and refined. The structural plots were drawn using the SHELXTL program.

#### 2.2 Adiabatic calorimetry

A precision automatic adiabatic calorimeter was used to measure heat capacities of the compound over the temperature range  $78 \le (T/K) \le 400$ . The calorimeter was established in the Thermochemistry Laboratory in the College of Chemistry and Chemical Engineering, Liaocheng University, China. The principle and structure of the adiabatic calorimeter were described in detail elsewhere [12,13].

The calorimetric system was composed of a calorimetric cryostat, a data collection system, an adiabatic controlling system and a high vacuum pump system. The calorimetric cryostat mainly comprised a sample cell, a platinum resistance thermometer, an electric heater, inner, middle and outer adiabatic shields, three sets of six-junction chromel-copel thermocouple piles installed between the calorimetric cell and the inner shield, between the inner and middle shields, and between the middle and outer shields, respectively. The miniature platinum resistance thermometer (IPRT No.2, produced by the Shanghai Institute of Industrial Automatic Meters, 16 mm in length, 1.6 mm in diameter and a nominal resistance of 100  $\Omega$ ) was applied to measure the temperature of the sample. The thermometer was calibrated on the basis of ITS-90 by the Station of Low-Temperature Metrology and Measurements, Academia Sinica.

The data collection system consisted of a multi-channel data acquisition/ switch unit (Agilent, 34970A) for electric energy collection, a 7 1/2 digit nanovolt/microohm Meter (Agilent, 34420A) for acquisition of the temperature of the sample cell, and a P4 computer equipped with a matched module and interface card GPIB (IEEE 488). The adiabatic controlling system consisted of a high precision temperature controller (Model: 340 Lake Shore), inner, middle and outer adiabatic shields, and three sets of six-junction chromel-copel thermocouple piles. The high vacuum pump system consisted of a combined rotational mechanical pump and oil diffusion pump (Edwards, Model NXK 333000).

The sample cell used for the heat capacity measurement was made of 0.3 mm thick gold-plated copper, 20 mm in length, and 20 mm in diameter with an inner volume of about 6 cm<sup>3</sup>. Three sheaths were fixed at the bottom of the cell for inserting the platinum resistance thermometer and thermocouples. Electric heating wire (insulated Karma wire of 0.12 mm in diameter,  $R = 120 \Omega$ ) used as the heater of the cell was bifilarly wound on the outer surface of the cell. The heater was covered with about 50  $\mu$ m thick aluminum foil to decrease the heat leakage by radiation and the temperature nonuniformity on the surface of the cell. The heater and aluminum foil were insulated and fixed by W30–11 varnish. A small amount of thermally conductive silicone sealant (Type HT916, produced by Shanghai Huitian New Chemical Material Company, Limited Shanghai, China) was used to seal the lid to the main body of the cell. On the lid, there was a section of copper capillary used for pumping out the air in the cell and introducing the helium gas to promote thermal equilibrium. The capillary was pinched off and the resultant fracture was soldered to ensure the sealing of the cell.

To verify the accuracy of the calorimeter, heat capacities of synthetic sapphire ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, Standard Reference Material 720) were measured over the temperature range 78  $\leq$  (T/K)  $\leq$  400. The sample mass used was 1.7143 g, which was equivalent to 0.0168 mol based on its molar mass,  $M(Al_2O_3) = 101.9613 \text{ g} \cdot \text{mol}^{-1}$ . In order to compare the values with those recommended by NIST [14], the molar heat capacities of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in the temperature range of 80 to 400 K were calculated with an interval of 5 K using the non-linear inserting method based on the measured molar heat capacity data. Temperature variability of balance period is an important indicator used to weigh the stability and reliability of the adiabatic system in the experimental process. The variability of the temperature of all the measuring points in the temperature range of 78 to 400 K. Most of the deviations of our values from the NIST recommended values were within ±0.30 %, which proved that the performance of the newly constructed calorimetric apparatus had been improved compared with previous calorimeters.

Heat capacity measurements were continuously and automatically carried out by means of the standard method of intermittently heating the sample and alternately measuring the temperature. The heating rate and temperature increments were generally controlled at 0.1 K  $\cdot$  min<sup>-1</sup> to 0.4 K  $\cdot$  min<sup>-1</sup> and 1 K to 3 K. The heating duration was 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were always kept within  $10^{-3} \text{ K} \cdot \min^{-1}$  to  $10^{-4} \text{ K} \cdot \min^{-1}$  during the acquisition of all heat-capacity data. The data of heat capacities and corresponding equilibrium temperature had been corrected for heat exchange of the sample cell with its surroundings [13]. The sample mass used for calorimetric measurements was 1.62363 g, which was equivalent to 0.006098 mol in terms of its molar mass,  $M = 266.26 \text{ g} \cdot \text{mol}^{-1}$ .

### 2.3 Differential scanning calorimetry (DSC)

DSC analysis was carried out in a Perkin-Elmer diamond DSC made by Perkin-Elmer Corporation, USA. The phase transition temperature and the latent heat were calibrated using high-pure indium (purity: 99.999 %) as a standard. The heating rate was 5 K  $\cdot$  min<sup>-1</sup>. The material was protected by high purity nitrogen with a discharge rate of 40 cm<sup>3</sup>  $\cdot$  min<sup>-1</sup>. Because the measurement on energy storage characteristics of the 1-dodecylamine hydrobromide was carried out at the same condition, the results of the temperatures and the enthalpies of the phase transitions were reliable.

# 3. Results and Discussion

## 3.1 Description of crystal structure

The molecular structure of 1-dodecylamine hydrobromide  $(1-C_{12}H_{25}NH_3Br)$  is plotted in Fig. 1. The crystal parameters, data collection, and refinement results for the compound are listed in Table 1. The crystal system of the compound is monoclinic, space group is  $P2_1/m$ , unit cell dimensions are a = 6.0450(7) Å, b =6.9681(8) Å, c = 17.850(2) Å;  $\alpha = 90^\circ$ ,  $\beta = 91.8920(10)^\circ$ ,  $\gamma = 90^\circ$ , and Z = 2. The calculated density of the compound is 1.177 Mg · m<sup>-3</sup> and the volume of formula unit is 751.47(15) Å<sup>3</sup>. Non-hydrogen atomic coordinates (× 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> × 10<sup>3</sup>) are shown in Table 2. The geometries of the hydrogen bonding are listed in Table 3. Each Br<sup>-</sup> ion forms three N-H<sup>...</sup>Br hydrogen bonds with three neighboring 1-dodecylammonium cations with N<sup>...</sup>Br distances of: 3.284 Å, 3.499 Å and 3.499 Å, as seen in Table 3.

As shown in Fig. 2, hydrogen bonds of N(1)-H(1A)...Br(1), N(1)-H(1B)... Br(1) and N(1)-H(1C)...Br(1) together with the van der Waals forces exist in the crystal to stabilize the structure. All hydrogen atoms are placed in geometrically idealized positions and constrained to ride on their parent atom (N). Chemical bonds N(1)-H(1A), N(1)-H(1B), and N(1)-H(1C) have almost same bond length, 0.8900 Å.





Fig. 1. Molecular structure of the title compound 1-dodecylamine hydrobromide.



Fig. 2. Packing diagram of the compound 1-dodecylamine hydrobromide.

In comparison with the literature [6,7], it can be seen that the crystal data and the structure of 1-dodecylamine hydrobromide determined in this paper basically agrees with that in references.

#### **3.2 Heat capacities of the sample**

All experimental results for the first experiment are listed in Table 4. The 59 experimental points in the temperature region from 78 to 300 K before the first phase transition, and 17 experimental points between 357 and 390 K after the third phase transition are fitted by means of least squares method, respectively, and two polynomial equations of the experimental molar heat capacities  $(C_{p,m}/J \cdot K^{-1} \cdot mol^{-1})$  vs. the reduced temperature (X), X = f(T), have been obtained:

(1) Before the first phase transition in the temperature range from 78 to 300 K,  $% \left( {{\rm{T}}_{\rm{T}}} \right) = {{\rm{T}}_{\rm{T}}} \left$ 

$$C_{p,m}/(J \times K^{-1} \times mol^{-1}) = 267.242 + 114.143X + 16.625X^{2} + 6.283X^{3} - 0.877X^{4}$$
 (1)

where X is the reduced temperature, X = (T/K - 189)/111, in which 189 is half of the upper limit (300 K) plus the lower limit (78 K) in the temperature region of 78–300 K, and 111 is half of the upper limit (300 K) minus the lower limit (78 K) in the same region. The reduced temperature (X) obtained by the

Final R indices [I > 2 sigma(I)]

Largest diff. peak and hole

R indices (all data)

Empirical formula	C <sub>12</sub> H <sub>28</sub> BrN		
Formula weight	266.26		
Temperature	298(2) K		
Wavelength	0.71073 Å		
Crystal system, space group	Monoclinic, $P2(1)/m$		
	$a = 6.0450(7)$ Å $\alpha = 90^{\circ}$		
Unit cell dimensions	$b = 6.9681(8)$ Å $\beta = 91.8920(10)^{\circ}$		
	$c = 17.850(2)$ Å $\gamma = 90^{\circ}$		
Volume	751.47(15) Å <sup>3</sup>		
Z, Calculated density	2, 1.177 Mg/m <sup>3</sup>		
Absorption coefficient	$2.708 \text{ mm}^{-1}$		
F(000)	284		
Crystal size	$0.30 \times 0.28 \times 0.27 \text{ mm}$		
Theta range for data collection	2.28 to 25.01 °		
Limiting indices	$-6 \le h \le 7, -8 \le k \le 5, -21 \le l \le 21$		
Reflections collected / unique	3903 / 1429 [R(int) = 0.0895]		
Completeness to theta = $25.01$	99.4 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.5284 and 0.4972		
Refinement method	Full-matrix least-squares on $F^2$		
Data / restraints / parameters	1429 / 0 / 94		
Goodness-of-fit on $F^2$	1.012		

Table 1. Crystal data and structure refinement for 1-C<sub>12</sub>H<sub>25</sub>NH<sub>3</sub>Br(s).

method is placed between +1 and -1, and deviations of the smoothed heat capacities from the experimental values would become smaller and smaller with the increase of the power of the fitted polynomial equation according to the statistical principle. The correlation coefficient for the fitting  $R^2 = 0.99995$ .

 $R_1 = 0.1076, wR_2 = 0.2733$  $R_1 = 0.1249, wR_2 = 0.2839$ 

1.892 and  $-1.198 \text{ e} \cdot \text{\AA}^{-3}$ 

(2) After the third phase transition in the temperature range from 357 to 390 K,

$$C_{p,m}/(J \times K^{-1} \times mol^{-1}) = 495.955 + 2.121X + 0.22169X^{2} + 0.09734X^{3} - 0.23587X^{4}$$
(2)

where X = (T/K - 373.5)/16.5, in which 373.5 is half of the upper limit (390 K) plus the lower limit (357 K) in the temperature region of 357–390 K, and 16.5 is half of the upper limit (390 K) minus the lower limit (357 K) in the same region. The correlation coefficient for the fitting  $R^2 = 0.99971$ .

Three series of the experiments in the region of three phase transition of the title compound are carried out so that the reversibility and repeatability of the

Atom	x	У	Z	U(eq)
N(1)	7650(20)	2500	5448(7)	67(4)
C(1)	8050(30)	2500	6265(9)	71(5)
C(2)	6220(40)	2500	6720(11)	98(7)
C(3)	6430(30)	2500	7544(9)	73(5)
C(4)	4620(30)	2500	8017(11)	96(7)
C(5)	4650(30)	2500	8818(10)	78(5)
C(6)	2890(40)	1890(40)	9307(12)	79(10)
C(7)	2990(30)	2500	10113(10)	74(5)
C(8)	1150(40)	1880(40)	10577(12)	78(10)
C(9)	1210(30)	2500	11390(10)	77(5)
C(10)	-600(30)	3070(40)	11875(12)	78(11)
C(11)	-620(30)	2500	12665(10)	83(6)
C(12)	-2460(30)	2500	13150(12)	105(9)
Br(1)	2566(2)	2500	4718(1)	60(1)

**Table 2.** Non-hydrogen atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\mathring{A}^2 \times 10^3$ ) for 1-C<sub>12</sub>H<sub>25</sub>NH<sub>3</sub>Br(s).

Table 3. Geometry of the hydrogen bond (distance and angle).

D-H <sup></sup> A	d(D-H)/Å	$d(H^{\cdots}A) \mathop{\big/} \mathring{A}$	<dha th="" °<=""><th><math>d(D^{\dots}A)/\mathring{A}</math></th><th>Symmetry code</th></dha>	$d(D^{\dots}A)/\mathring{A}$	Symmetry code
N(1)-H(1A) <sup></sup> Br(1)	0.890	2.396	174.92	3.284	[ x+1, y, z ]
N(1)-H(1B)Br(1)	0.890	2.788	137.86	3.499	[ -x+1, -y+1, -z+1]
N(1)-H(1C)···Br(1)	0.890	2.769	140.14	3.499	[-x+1, -y, -z+1]

phase transitions of the sample are verified. The results of the three series of heat capacity measurements are plotted in Fig. 3. The results in Fig. 3 are obtained from the repeated measurements of the same sample undismantled from the adiabatic system.

Fig. 3 shows that the structure of the compound is stable over the temperature range between 78 and 300 K. However, there are three endothermic peaks appearing in the curve of experimental molar heat capacities when the sample is heated for the first time, but only one obvious peak appears when the sample is heated in the second and third repeated experiments over the temperature range from 300 to 357 K. Two small peaks before the obvious peak can not almost be observed, the enthalpy changes of the two phase transitions can be estimated to be much less than 0.1 kJ  $\cdot$  mol<sup>-1</sup> according to the method of diagrammatic area integration, and may be omitted in comparison with the big peak.

The melting point of the title compound is measured to be about 462.0–463.5 K according to the results obtained from the microscopic melting point device, therefore, the three peaks appearing in the curve of experimental molar heat capacities are ascribed to the solid–solid phase transitions. A reasonable explanation may be that [15] the first and second phase transitions ( $T_{trs,1}$ ,  $T_{trs,2}$ )

$T(\mathbf{K})$	$C_{p, m}/$	<i>T</i> (K)	$C_{p, m}/$	<i>T</i> (K)	$C_{p, m}/$	<i>T</i> (K)	$C_{p, m}/$
	$(J \cdot K^{-1} \cdot mol)$	<sup>-1</sup> ) (	$J \cdot K^{-1} \cdot mol$	-1)	$(J \cdot K^{-1} \cdot mol)$	<sup>-1</sup> ) (J	$\cdot \mathrm{K}^{-1} \cdot \mathrm{mol}^{-1}$
78.229	162.34	177.68	255.22	284.10	381.03	340.767	547.32
80.215	164.71	181.44	259.51	288.11	386.41	342.825	518.12
83.904	168.12	185.34	263.80	291.94	391.41	344.771	629.67
87.380	170.75	189.18	268.00	296.01	397.53	346.370	1476.7
90.856	174.51	193.22	272.21	299.84	403.97	347.425	3327.4
94.260	177.66	197.05	276.23	303.17	411.19	350.982	1226.8
97.666	180.81	200.88	279.73	305.16	418.94	353.820	549.33
100.86	183.70	205.56	284.90	306.65	426.25	355.806	501.39
105.18	187.73	210.31	289.71	307.99	433.21	357.792	493.86
109.72	192.28	214.14	293.65	309.91	441.65	359.850	494.18
113.13	195.43	218.19	298.03	311.85	456.08	361.836	494.51
116.68	198.58	221.95	302.84	313.69	473.34	363.822	494.71
120.36	201.30	225.85	307.22	315.38	491.68	365.808	494.98
123.91	204.54	229.75	311.86	317.12	509.83	367.794	495.27
127.60	1 207.86	233.72	317.03	318.94	532.83	369.852	495.47
130.94	210.58	237.70	321.58	320.83	556.46	371.838	495.78
134.62	213.55	241.81	326.83	322.75	585.06	373.824	495.98
138.31	217.32	246.28	331.12	324.64	618.62	375.810	496.27
142.00	221.52	250.82	336.64	326.51	686.24	377.797	496.49
145.76	225.72	254.65	341.71	327.79	800.26	379.783	496.81
149.45	228.79	258.55	346.35	328.78	1129.19	381.769	497.04
154.13	233.25	262.38	351.17	329.54	1423.65	383.755	497.37
158.81	237.89	264.94	355.28	330.16	1734.86	385.671	497.61
162.64	241.04	268.60	359.90	332.68	1004.53	387.657	497.88
166.33	244.02	272.43	364.66	334.81	1099.9	389.643	498.11
170.16	247.08	276.27	368.73	336.87	1632.7		
173.85	250.58	280.27	375.27	338.33	2506.6		

**Table 4.** Experimental molar heat capacities of  $1-C_{12}H_{25}NH_3Br$  (s) (M = 266.26 g·mol<sup>-1</sup>).

from the low temperature phase  $(P2_1/m)$  to the intermediate temperature phase is possibly due to the breaking of hydrogen bonds and leads to a dynamic order– disorder transition of rigid alkyl chains, whereas the third phase transition  $(T_{trs,3})$ from the intermediate to the high temperature phase is related to cooperative conformational changes of the alkyl chains and the complete disorder of the conformation is assumed to be similar to a "molten" state. In the intermediate phase the rigid alkyl chains are flipping around their long axes between two equivalent orientations separated by 90°. The two transitions are somewhat analogous to the ones found in the lipid bilayer membranes and can be described by order parameters used for smectic liquid crystals. In the second and third experiments, the first two peaks almost disappear. The breaking of hydrogen bonds



**Fig. 3.** Plot of experimental molar heat capacities  $(C_{p,m})$  against the absolute temperature (T/K) of the compound  $C_{12}H_{25}NH_3Br$  (s), in which "o", " $\Delta$ ", and " $\pi$ " represent the first, the second, and the third series of heat capacity measurements for the same sample, respectively.

and an irreversible dynamic order–disorder transition of rigid alkyl chains take place when the sample is heated in the first experiment. In crystal structure of the compound, the formed hydrogen bonds are the type of N-H<sup>...</sup>Br, which has a weak strength and low bond energy different from hydrogen bond of the type N-H<sup>...</sup>Cl with a strong bond energy in the compound  $C_{12}H_{25}NH_3Cl(s)$  [16]. After the first heat capacity measurements are fulfilled and the temperature is reduced to < 300 K by cooling the adiabatic system using natural temperature falling, the hydrogen bonds in the sample are not completely formed, the dynamic order– disorder transition of rigid alkyl chains do not almost take place during the second and third repeated measurements. The third peak appears in all three experiments, and only some slight differences in heights and widths, which exhibit good reversibility and repeatability. This also verifies that the third phase transition ( $T_{trs,3}$ ) is related to cooperative conformational changes of the alkyl chains and the complete disorder of the conformation similar to a "molten" state.

#### 3.3 Molar enthalpies and entropies of phase transitions

Fig. 4 shows the plots of experimental molar heat capacities  $(C_{p, m})$  against the absolute temperature (T/K) of the compound  $C_{12}H_{25}NH_3Br(s)$  for three experiments, and new sample is used for each heat capacity measurements. It can be seen from Fig. 4 that all three endothermic peaks appearing in the first experiment of Fig. 3 appear if each series of heat capacity measurements are carried out by using new sample. Although there are some slight differences in heights and widths of peaks corresponding to each series of heat-capacity measurements during the phase changes, the three phase transitions basically exhibit good re-



**Fig. 4.** Plot of experimental molar heat capacities  $(C_{p, m})$  against the absolute temperature (T) of the compound  $C_{12}H_{25}NH_3Br(s)$ , in which "o", " $\Delta$ ", and " $\Leftrightarrow$ " represent the first, the second, and the third series of heat capacity measurements for the different samples in the same batch, respectively.

versibility and repeatability. A nearly agreement in  $C_{p, m}$  values of each series of repeated experiment is obtained.

The molar enthalpy changes of the first and second phase transitions in  $C_{p, \text{m}} \sim T$  curve are calculated with the method of diagrammatic area integration [17] because the two peaks are partly folded together. The molar enthalpy of the third phase transition  $\Delta_{\text{trs}}H_{\text{m}}$  (kJ·mol<sup>-1</sup>) is evaluated in terms of the equation (3) [17], and molar entropies  $\Delta_{\text{trs}}S_{\text{m}}(J \cdot K^{-1} \cdot \text{mol}^{-1})$  of the three phase transitions are calculated with the following thermodynamic Equation (4):

$$\Delta_{\rm trs} H_{\rm m} = \left[ Q - n \cdot \int_{T_{\rm i}}^{T_{\rm is}} C_{p,{\rm m}({\rm i})} {\rm d} \ T - n \cdot \int_{T_{\rm trs}}^{T_{\rm fr}} C_{p,{\rm m}({\rm f})} {\rm d} T - \int_{T_{\rm i}}^{T_{\rm fr}} H_0 {\rm d} T \right] / n \quad ({\rm kJ} \times {\rm mol}^{-1})$$
(3)

$$\Delta_{\rm trs} S_{\rm m} = \Delta_{\rm trs} H_{\rm m} / T_{\rm trs} \quad (J \times K^{-1} \times {\rm mol}^{-1}) \tag{4}$$

where  $T_i$  in Equation (3) is a temperature slightly lower than the starting phase transition temperature,  $T_f$  is a temperature slightly higher than the finishing transition temperature,  $C_{p, m (i)}$  is the heat capacity at the temperature  $T_i$ ,  $C_{p, m (f)}$  is the heat capacity at the temperature  $T_f$ , Q is the total heat quantity introduced to the calorimeter from temperature  $T_i$  to  $T_f$ ,  $T_{trs}$  is the transition temperature of the sample measured, n is the mole number of the sample, and  $H_o$  is the heat capacity of the empty sample cell. Values of Q and  $H_o$  are calculated with the program stored in the computer linked with the adiabatic calorimetric system, and printed along with experimental results of heat capacities. The results of phase transition temperatures, phase transition enthalpies, and phase transition entropies of three series of repeated measurements are presented Table 5.

Thermodynamic	Series 1	Series 2	Series 3	Mean value
properties	$\mathbf{X}_i$	X <sub>i</sub>	$\mathbf{x}_i$	$(\bar{x} \pm \sigma_a^*)$
$T_{\rm trs,1}~({\rm K})$	329.686	329.271	328.876	(329.278±0.234)
$T_{\rm trs,2}~({\rm K})$	338.330	337.877	337.208	(337.805±0.326)
$T_{\rm trs,3}~({\rm K})$	347.425	347.081	347.608	(347.371±0.154)
$\frac{\Delta_{\rm trs} H_{\rm m,1}}{(\rm kJ\cdot mol^{-1})}$	8.770	8.448	8.527	(8.582±0.097)
$\Delta_{\rm trs} H_{\rm m,2}$ (kJ·mol <sup>-1</sup> )	7.585	7.421	7.798	(7.601±0.109)
$\Delta_{\rm trs} H_{\rm m,3}$ (kJ · mol <sup>-1</sup> )	9.438	9.477	10.042	(9.652±0.195)
$\Delta_{\text{trs}}S_{\text{m},1}$ $(\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\text{mol}^{-1})$	26.601	25.657	25.928	(26.062±0.281)
$ \begin{array}{c} \Delta_{\mathrm{trs}} S_{\mathrm{m},2} \\ (\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathrm{mol}^{-1}) \end{array} $	22.419	21.964	23.125	(22.503±0.338)
$\Delta_{\text{trs}}S_{\text{m},3}$ $(\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\text{mol}^{-1})$	27.166	27.305	28.889	(27.787±0.553)

**Table 5.** Thermodynamic properties of three phase transitions obtained from three series of repeated heat capacity measurements of 1-dodecylamine hydrobromide<sup>a</sup>.

<sup>a</sup>  $T_{trs,1}$  (K),  $T_{trs,2}$  (K),  $T_{trs,3}$  (K),  $\Delta_{trs}H_{m,1}$  (kJ · mol<sup>-1</sup>),  $\Delta_{trs}H_{m,2}$  (kJ · mol<sup>-1</sup>),  $\Delta_{trs}H_{m,3}$  (kJ · mol<sup>-1</sup>),  $\Delta_{trs}S_{m,1}$  (J · K<sup>-1</sup> · mol<sup>-1</sup>),  $\Delta_{trs}S_{m,2}$  (J · K<sup>-1</sup> · mol<sup>-1</sup>), and  $\Delta_{trs}S_{m,3}$  (J · K<sup>-1</sup> · mol<sup>-1</sup>) represent the peak temperatures, molar enthalpies and molar entropies of the first, the second, and the third phase transitions, respectively.

 ${}^{*}\sigma_{a} = \sqrt{\frac{\sum_{i=1}^{n} (x_{i} - \bar{x})^{2}}{n(n-1)}}, \text{ in which } n \text{ is experimental number } (n = 3); x_{i}, \text{ experimental value of each series of repeated measurement; } \bar{x}, \text{ mean value.}}$ 

# 3.4 Smoothed heat capacities and thermodynamic functions of the compound

The smoothed molar heat capacities and thermodynamic functions are calculated based on the fitted polynomial equation of the heat capacities as a function of the reduced temperature (X) according to the following thermodynamic Equations,

$$(H_T - H_{298.15}) = \int_{298.15}^T C_{p, \text{m}} \cdot dT$$
(5)

$$(S_T - S_{298.15}) = \int_{298.15}^T C_{p,m} \cdot T^{-1} dT$$
(6)

$$(G_T - G_{298.15}) = \int_{298.15}^T C_{p, \,\mathrm{m}} \cdot dT - T \int_{298.15}^T C_{p, \,\mathrm{m}} \cdot T^{-1} dT \tag{7}$$

The polynomial fitted values of the molar heat capacities and fundamental thermodynamic functions of the sample relative to the standard reference temperature 298.15 K are tabulated in Table 6 at intervals of 5 K.

#### 3.5 Results of DSC analysis of the compound

The DSC results of 1-dodecylamine hydrobromide in the cycle of the first heating and succedent cooling are given in Fig. 5. It can be seen from Fig. 5 that there are four endothermic processes in the temperature range from 300 to 470 K when the sample is heated. Because the first and second peaks appearing in the DSC curve are joined together, their thermodynamic properties may be calculated by coming down to one big peak. The peak temperatures and molar enthalpies of the endothermic peaks are determined to be 338.76 K, 16.025 kJ  $\cdot$  mol<sup>-1</sup> for the first and second peaks, 345.85 K, 9.157 kJ  $\cdot$  mol<sup>-1</sup> for the third peak, and 465.45 K, 8.121 kJ  $\cdot$  mol<sup>-1</sup> for the fourth peak, respectively, as shown in Fig. 5. The first, second, and third endothermic peaks in the DSC curve are in accordance with the three phase transition peaks appearing in  $C_{p, m} \sim T$  curve. The melting point of the compound is measured to be about 462.0–463.5 K using the microscopic melting point device, so the fourth endothermic peak should be the melting process of the substance.

It can be seen from the DSC curve in Fig. 5 that there are two exothermic peaks appearing in the temperature range from 470 to 300 K when the sample is cooled down, and the number of the peaks are not the same as that of endothermic peaks when the sample is heated. The peak temperatures and molar enthalpies of the exothermic peaks are determined to be 463.35 K,  $-7.792 \text{ kJ} \cdot \text{mol}^{-1}$  for the first exothermic peak, and 342.70 K,  $-8.580 \text{ kJ} \cdot \text{mol}^{-1}$  for the second exothermic peak, respectively, as shown in Fig. 5. So, it can be found that the first exothermic peak corresponds to the fourth endothermic peak during the heating, and the second exothermic peak corresponds to the third endothermic peak during the heating, while no more exothermic peak appears and corresponds to the first and second endothermic peaks and second peaks appearing in the DSC curve. In comparison with the  $C_{p,m} \sim T$  curve in Fig. 3 and Fig. 4, it can be seen that the thermodynamic properties of 1-dodecylamine hydrobromide determined by DSC technique almost agree with those from adiabatic calorimetric method.

# 4. Conclusions

1-dodecylamine hydrobromide was synthesized. The crystal structure of the title compound was determined by X-ray crystallography.

Low-temperature heat capacities of the title compound were measured by the adiabatic calorimeter over the temperature range from 78 to 390 K. Three solid-solid phase transitions were found in the  $C_{p,m} \sim T$  curve, and the possible mechanism of the phase transition was discussed. Three solid–solid phase transitions were observed at the peak temperatures of (329.278±0.234), (337.805±0.326), and (347.371±0.154) K. The molar enthalpies of the three phase transitions of the substance were determined to be (8.582±0.097), (7.601±0.109), and

<i>T</i> (K)	$\frac{C_{p, \mathbf{m}}}{(\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathbf{mol}^{-1})}$	$H_{\rm T} - H_{298.15}$ (kJ·mol <sup>-1</sup> )	$S_T - S_{298.15}$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )	$G_T - G_{298.15}$ (k.I · mol <sup>-1</sup> )
80	164.42	-59.448	- 326.72	-33.310
85	169.05	-58.614	-316.64	-31.700
90	173.65	-57.758	-306.84	-30.142
95	178.24	-56.878	-297.32	-28.633
100	182.81	-55.975	-288.04	-27.172
105	187.37	-55.050	-278.99	-25.756
110	191.94	-54.016	-270.14	-24.386
115	196.50	-53.131	-261.50	-23.058
120	201.07	-52.137	-253.03	-21.773
125	205.66	-51.120	-244.73	-20.529
130	210.26	-50.080	-236.57	-19.325
135	214.88	-49.017	-228.56	-18.162
140	219.52	-47.931	-220.67	-17.037
145	224.20	-46.822	-212.90	-15.951
150	228.90	-45.689	-205.24	-14.904
155	233.65	-44.533	- 197.67	-13.894
160	238.44	-43.353	- 190.19	-12.923
165	243.27	-42.148	- 182.79	-11.988
170	248.16	-40.920	-175.46	-11.091
175	253.10	-39.667	- 168.21	-10.231
180	258.09	-38,389	-161.01	-9.4069
185	263.15	-37.086	-153.87	-8.6196
190	268.27	-35.757	-146.78	-7.8684
195	273.46	-34.403	- 139.74	-7.4530
200	278.72	-33.022	-132.75	-6.4733
205	284.06	-31.615	-125.79	-5.8289
210	289.47	-30.182	-118.87	-5.2196
215	294.97	-28.721	-111.98	-4.6450
220	300.55	-27.232	-105.12	-4.1049
225	306.21	-25.715	-98.293	-3.5989
230	311.97	-24.170	-91.490	-3.1268
235	317.82	-22.595	-84.710	-2.6882
240	323.77	-20.991	-77.951	-2.2830
245	329.81	-19.357	-71.210	-1.9108
250	335.95	-17.693	-64.485	-1.5716
255	342.20	- 15.998	- 57.775	-1.2650
260	348.55	-14.271	-51.075	-0.99120
265	355.01	-12 512	-44 384	-0.75006

Table 6. Smoothed heat capacities and thermodynamic functions of  $1-C_{12}H_{25}NH_3Br(s)$ .

<i>T</i> (K)	$C_{p, \mathbf{m}}$ $(\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathbf{mol}^{-1})$	$H_{\rm T}-H_{298.15}$ (kJ·mol <sup>-1</sup> )	$S_T - S_{298.15}$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$G_T - G_{298.15}$ (kJ·mol <sup>-1</sup> )
270	361.58	-10.720	-37.699	-0.54172
275	368.26	-8.8959	-31.016	-0.36641
280	375.06	-7.0376	-24.332	-0.22450
285	381.97	-5.1451	-17.644	-0.11650
290	389.00	-3.2177	-10.947	-0.043092
295	396.15	-1.2549	-4.2363	-0.005176
298.15	400.71	0	0	0
300	403.42	0.74396	2.4927	-0.0038590
305	Phase transition			
310	Phase transition			
315	Phase transition			
320	Phase transition			
325	Phase transition			
330	Phase transition			
335	Phase transition			
340	Phase transition			
345	Phase transition			
350	Phase transition			
355	Phase transition			
360	494.21	27.605	79.113	27.526
365	494.89	30.078	79.092	29.999
367	495.14	31.068	79.084	30.989
370	495.51	32.554	79.071	32.475
375	496.15	35.033	79.051	34.954
380	496.82	37.516	79.031	37.437
385	497.52	40.002	79.012	39.923
390	498.16	42.491	78.993	42.412

Table 6	6 <b>a.</b> (co	ontinued)
---------	-----------------	-----------

 $(9.652\pm0.195)$  kJ·mol<sup>-1</sup>, and their corresponding molar entropies were calculated as  $(26.062\pm0.281)$ ,  $(22.503\pm0.338)$ , and  $(27.787\pm0.553)$  J·mol<sup>-1</sup>·K<sup>-1</sup>, respectively, based on the analysis of heat capacity curves. The relevant thermodynamic functions were determined based on the fitted polynomial equations. Further researches of the thermochemical properties for this compound were carried out by means of DSC technique and the reversibility and repeatability of the three phase transitions were discussed.



**Fig. 5.** DSC curve in the heating <u>and</u> cooling of 1-dodecylamine hydrobromide with a scanning rate of 5 K/min.

#### Acknowledgement

This work was financially supported by the National Natural Science Foundations of China under the contract NSFC No. 20673050 and 20973089.

#### References

- 1. K. W. Lee, C. E. Lee, J. Kim, and J. K. Kang, Solid State Commun. **124** (2002) 185.
- 2. D. W. Hawes, D. Banu, and D. Feldman, Solar Energy Mater. 21 (1990) 61.
- R. Jakubas, G. Bator, M. Gosniowska, Z. Ciunik, J. Baran, and J. Lefebvre, J. Phys. Chem. Solids. 58 (1997) 989.
- 4. W. P. Li, D. S. Zhang, T. P. Zhang, T. Z. Wang, D. S. Ruan, D. Q. Xing, and H. B. Li, Thermochim. Acta. **326** (1999) 183.
- 5. D. S. Ruan, W. P. Li, and Q. Z. Hu, J. Thermal Analysis. 45 (1995) 235.
- 6. M. Gordon, Acta Cryst. 6 (1953) 739.
- 7. B. M. Lunden, Acta Cryst. B30 (1974) 1756.
- 8. Z. C. Tan, and Y. Y. Di, Prog. Chem. 18 (2006) 1234.
- 9. A. Inaba, J. Chem. Thermodyn. 15 (1983) 1137.
- X. K. Gao, J. M. Dou, D. C. Li, F. Y. Dong, and D. Q. Wang, Journal of Molecular Structure. 733 (2005) 181.
- 11. H. D. Yin, S. W. Chen, L.W. Li, and D. Q. Wang, Inorg. Chim. Acta. **360** (2007) 2215.
- 12. Z. C. Tan, Q. Shi, B. P. Liu, and H. T. Zhang, J Therm Anal. Calorim. **92** (2008) 367.
- Y. Y. Di, Z. C. Tan, L. W. Li, S. L. Gao, and L. X. Sun, J. Therm. Anal. Calorim. 89 (2007) 545.

- 14. D. G. Archer, J. Phys. Chem. Ref. Data. 22 (1993) 1441.
- R. Kind, S. Plesko, H. Arend, R. Blinc, B. Zeks, J. Seliger, B. Lozar, J. Slak, A. Levstik, C. Filipic, V. Zagar, G. Lahajnar, F. Milia, and G. Chapuis, J. Chem. Phys. **71** (1979) 2118.
- 16. Y. X. Kong, Y. Y. Di, Y. Q. Zhang, W. W. Yang, and Z. C. Tan, Int. J. Thermophys. 30 (2009) 1960.
- 17. Y. Y. Di, Z. C. Tan, X. M. Wu, S. H. Meng, and S. S. Qu, Thermochimica Acta. 356 (2000) 143.

- 10.1524/zpch.2010.5546 Downloaded from De Gruyter Online at 09/20/2016 06:23:53AM via Cornell University Library