

Scientific paper

# Low-temperature Heat Capacities and Thermodynamic Properties of Crystalline 2-Aminopyridinium Benzoate ( $C_{12}H_{12}N_2O_2$ ) (s)

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## Abstract

2-Aminopyridinium benzoate was synthesized. Chemical analysis, elemental analysis, and X-ray crystallography were applied to characterize the composition and crystal structure of the compound. The lattice potential energy of the title compound was calculated to be  $U_{\text{pot}} = 284.297 \text{ kJ mol}^{-1}$ . Low-temperature heat capacities of the compound were measured by a precision automatic adiabatic calorimeter over the temperature range from 78 K to 365 K. A polynomial equation of heat capacities against the temperature in the region of 78 K to 365 K was fitted by a least square method. Based on the fitted polynomial equation, the smoothed heat capacities and thermodynamic functions of the compound relative to the standard reference temperature 298.15 K were calculated at intervals of 5 K. According to the synthesis reaction, the standard molar enthalpies of dissolution for the reactants and product in the selected solvent were measured by an isoperibol solution-reaction calorimeter, respectively. Accordingly, the enthalpy change of the synthesis reaction was calculated to be  $\Delta_r H_m^\circ = -(20.016 \pm 0.182) \text{ kJ mol}^{-1}$ . Finally, the standard molar enthalpy of formation of 2-aminopyridinium benzoate was determined to be  $\Delta_f H_m^\circ = -(365.416 \pm 0.961) \text{ kJ mol}^{-1}$  in accordance with Hess law.

**Keywords:** 2-Aminopyridinium benzoate; X-ray crystallography; Lattice potential energy; Adiabatic calorimetry; Low-temperature heat capacity; Isoperibol solution-reaction calorimeter; Standard molar enthalpy of formation

## 1. Introduction

Inorganic nonlinear optical (NLO) materials have been studied at an earlier time.<sup>1</sup> In recent years, it is found that the research of new organic nonlinear optical (NLO) materials was more attractive for their advantages over the inorganic nonlinear optical materials. The organic nonlinear optical molecules generally have the larger second-order nonlinear optical coefficient, and hence they are widely used in many applications like optical communication, informational storage, optical switching, etc.<sup>2</sup> Several similar nonlinear optical complexes formed from aminopyridine and carboxylates have been crystallized, and their structural, optical, and thermal properties have been investigated because of their significant impact on laser technology, optical communication and optical data storage technology.<sup>2,3</sup> In

this paper, a nonlinear optical material, 2-aminopyridinium benzoate, was synthesized, which exhibits the nonlinear optical properties because it is characterized by the chiral carbons, a proton-donating carboxyl ( $-\text{COOH}$ ) group and a proton-accepting imino ( $-\text{NH}$ ) group, where the carboxyl group is dissociated and imino group is protonated.<sup>3</sup> Mustafa Odabasoglu et al. had synthesized crystalline 2-aminopyridinium benzoate and characterized its crystal structure (CCDC: 204055).<sup>4</sup> However, up to now, the thermodynamic properties of the 2-aminopyridinium benzoate have not been found in the literature, which is needed in order to develop its new application fields and carry out relevant theoretical research. For these purposes, in this work, some thermochemical properties of the compound were investigated. A precise automated adiabatic calorimeter was used to measure low-temperature heat capacities of the 2-aminopyridi-

nium benzoate over the temperature range from 78 K to 365 K and the standard molar enthalpy of formation of the title compound was determined by an isoperibol solution-reaction calorimetry.

## 2. Experimental

### 2. 1. Synthesis of the Complex

#### 2-aminopyridinium Benzoate

2-Aminopyridine and benzoic acid as reactants and anhydrous ethyl alcohol as the solvent were all of analytical grade, the reactants were accurately weighed at the molar ratio of  $n(2\text{-aminopyridine}) : n(\text{benzoic acid}) = 1 : 1$  and slowly dissolved into anhydrous ethyl alcohol. The mixtures were heated by the electric jacket and stirred under boiling and refluxing for 4 h. The final solution was laid quietly, and several days later, a colourless transparent crystal was obtained. The crystal was recrystallized for three times with anhydrous ethyl alcohol and washed by ether for three times. Finally, the sample was placed in a vacuum desiccator at  $T = 320$  K to dry in vacuum for 6 h, the final product was put into a weighing bottle and preserved in a desiccator. The actual purity of the compound

was determined to be  $> 0.995$  in mass fraction by HPLC. The contents of the C, H, N, and O in the compound were determined by chemical and elemental analyses (model: PE-2400, Perkin Elmer, USA). These results showed the purity of the sample prepared was  $> 0.995$  in mass fraction.

### 2. 2. X-ray Crystallography

A crystal with dimensions of  $0.49 \text{ mm} \times 0.45 \text{ mm} \times 0.43 \text{ mm}$  was glued to fine glass fiber and was then mounted on the Bruker Smart-1000 CCD diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.071073 \text{ nm}$ ). The intensity data were collected at 298(2) K in the  $\varphi$ - $\omega$  scan mode. The structure was solved by direct methods and expanded using Fourier techniques with SHELXL-97 program.<sup>5</sup> The non-hydrogen atoms were refined anisotropically by full-matrix least-square calculations on  $F^2$  using the SHELXL-97 program.<sup>5</sup> The hydrogen atoms were added theoretically, riding on the concerned atoms and not refined. Crystal data and details of data collection and refinements for complex were summarized in Table 1. The hydrogen bond lengths and angles of the title compound (CCDC number: 772717) were presented in Table 2.

**Table 1.** Crystal data and structure refinement for 2-aminopyridinium

Crystallographic data	Structure refinement
Empirical formula	C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>
Formula weight	216.24
Temperature	298(2) K
Wavelength	0.071073 nm
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
Unit cell dimensions	$a = 1.21428(11) \text{ nm}$ ; $\alpha = 90^\circ$ ; $b = 1.15070(9) \text{ nm}$ ; $\beta = 90^\circ$ ; $c = 1.57142(15) \text{ nm}$ ; $\gamma = 90^\circ$
Volume	$2.1957(3) \text{ nm}^3$
Z	8
Calculated density	$1.308 \text{ g}\cdot\text{cm}^3$
Absorption coefficient	$0.091 \text{ mm}^{-1}$
$F(000)$	912
Crystal size	$0.49 \times 0.45 \times 0.43 \text{ mm}$
$\theta$ range for data collection	$2.59$ to $25.01^\circ$
Limiting indices	$-12 \leq h \leq 14$ , $-13 \leq k \leq 13$ , $-18 \leq l \leq 16$
Reflections collected / unique	9161 / 1938 [ $R(\text{int}) = 0.0520$ ]
Completeness to $\theta 25.01$	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9619 and 0.9568
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	1938 / 0 / 146
Goodness-of-fit on $F^2$	1.091
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0426$ , $wR2 = 0.0945$
$R$ indices (all data)	$R1 = 0.0928$ , $wR2 = 0.1305$
Extinction coefficient	0.0104(13)
Largest diff. peak and hole	224 and $-163 \text{ e nm}^{-3}$

**Table 2.** Hydrogen bond lengths (nm) and bond angles ( $^{\circ}$ ) for 2-aminopyridinium benzoate(s).<sup>a</sup>

D–H $\cdots$ A	d(D–H)	d(H $\cdots$ A)	d(D $\cdots$ A)	$\angle$ DHA
N(1)–H(1) $\cdots$ O(1)	0.0860	0.1804	0.2656	170.39
N(2)–H(2A) $\cdots$ O(2)	0.0860	0.1934	0.2784	169.55
N(2)–H(2B) $\cdots$ O(1)#1	0.0860	0.2008	0.2859	170.22

<sup>a</sup> Symmetry code: #1  $[-x+1/2, y-1/2, z]$ .

### 2. 3. Adiabatic Calorimetry

A precision automatic adiabatic calorimeter was used to measure heat capacities of the compound over the temperature range  $78 \leq (T/K) \leq 365$ . The calorimeter was established in the Thermochemistry Laboratory of the College of Chemistry and Chemical Engineering, Liaocheng University, China. The principle and performance of the adiabatic calorimeter and the procedures of heat capacity measurements have been described in detail elsewhere.<sup>6,7</sup> 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 liquid nitrogen was used as the coolant. The heating rate and temperature increments were generally controlled at  $0.1 \text{ K min}^{-1}$  to  $0.4 \text{ K min}^{-1}$  and  $1 \text{ K}$  to  $3 \text{ K}$ . The heating duration was 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were always kept within  $10^{-3} \text{ K min}^{-1}$  to  $10^{-4} \text{ K min}^{-1}$  during the acquisition of all heat-capacity data. The data of heat capacities and corresponding equilibrium temperature have been corrected for heat exchange of the sample cell with its surroundings.<sup>7</sup> The reliability of the performance of the calorimeter had been confirmed by the measurement of the heat capacities of the reference standard material ( $\alpha\text{-Al}_2\text{O}_3$ ) over the temperature range  $77 \leq (T/K) \leq 402$ . Deviations of the experimental results from those of the smoothed curve lie within  $\pm 0.20\%$ , while the uncertainty is  $\pm 0.30\%$ , as compared with the values given by the former National Bureau of Standards<sup>8</sup> over the whole temperature range.

The sample mass used for calorimetric measurements was 1.77959 g, which was equivalent to 0.00823 mol in terms of its molar mass,  $M = 216.24 \text{ g mol}^{-1}$ .

### 2. 4. Isoperibol Solution-reaction Calorimetry

The isoperibol solution-reaction calorimeter consisted primarily of a precise temperature controlling system, an electric energy calibration system, a calorimetric body, an electric stirring system, a thermostatic bath made from transparent silicate glass, a precise temperature measuring system and a data acquisition system. The principle and structure of the calorimeter were described in detail elsewhere.<sup>9</sup>

The reliability of the calorimeter was verified previously by measuring dissolution enthalpy of KCl (calori-

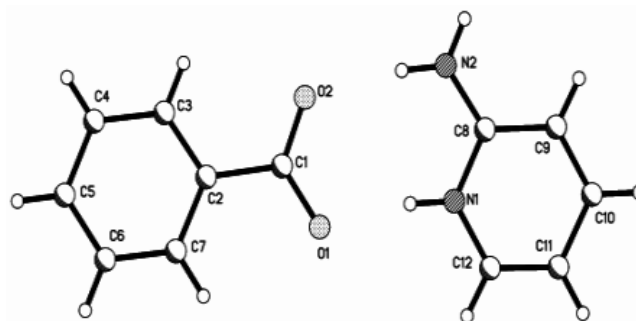
metric primary standard) in double distilled water at  $T = 298.15 \text{ K}$ . According to the molar ratio of KCl to water,  $n_{\text{KCl}} : n_{\text{H}_2\text{O}} \approx 1 : 1110$ , the KCl was dissolved in  $100 \text{ cm}^3$  of double-distilled water at  $T = (298.15 \pm 0.001) \text{ K}$ . The mean dissolution enthalpy was  $(17547 \pm 13) \text{ J mol}^{-1}$  for KCl, which compared with published data<sup>10</sup>  $(17536 \pm 3.4) \text{ J mol}^{-1}$  under the same experimental condition. It showed that relative deviation between the literature value and the measuring value was within  $\pm 0.3\%$ .

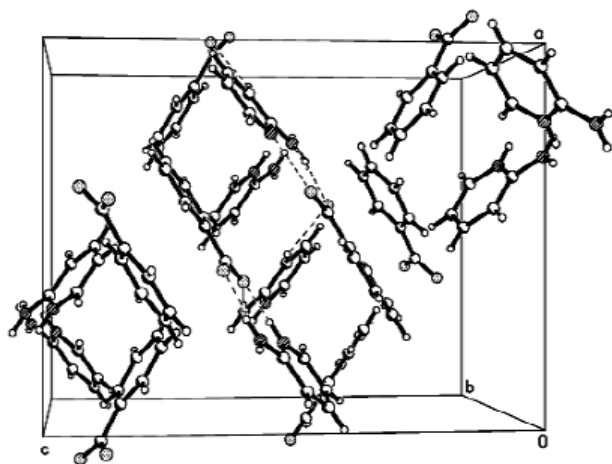
In all dissolution experiments of the sample,  $100 \text{ cm}^3$  of  $1 \text{ mol dm}^{-3} \text{ NaOH}$  was chosen as the calorimetric solvent.

## 3. Results and Discussion

### 3. 1. Crystal Structure of 2-aminopyridinium Benzoate

The molecular structure of 2-aminopyridinium benzoate is plotted in Figure 1, and the packing of the cell structure is shown in Figure 2. It is found from Table 1 that the crystal structure of the compound is monoclinic, the space group is  $Pbca$ , unit cell dimensions are  $a = 1.21428(11) \text{ nm}$ ,  $b = 1.15070(9) \text{ nm}$ ,  $c = 1.57142(15) \text{ nm}$ ,  $\alpha = \beta = \gamma = 90^{\circ}$ , respectively. 2-Aminopyridine contains a strong electron-donating group (imino group) and benzoic acid has a strong electron-attracting group (carboxyl). A hydrogen atom is removed from carboxyl, and the nitrogen of pyridine ring is protonated. This preparative method makes electrons flow in the whole  $\pi$  system, optimizes molecular structure, and achieves nonlinear materials with high magnetic susceptibility.<sup>11</sup>

**Figure 1.** Molecular structure of the compound 2-aminopyridinium benzoate.



**Figure 2.** Packing of structure of the compound 2-aminopyridinium benzoate in unit cell.

All hydrogen atoms were placed in geometrically idealized positions and constrained to reside on their parent atom. Chemical bonds N(1)-H(1), N(2)-H(2B) and N(2)-H(2A) have the same bond length, 0.0860 nm. There are three kinds of hydrogen bonds (see Table 2), and these hydrogen bondings play a key role in molecular recognition. In comparison with the literature,<sup>4</sup> it can be seen that the crystal data and the structure of 2-aminopyridinium benzoate measured in the paper almost agreed with those in the literature.<sup>4</sup>

### 3. 2. Lattice Potential Energy

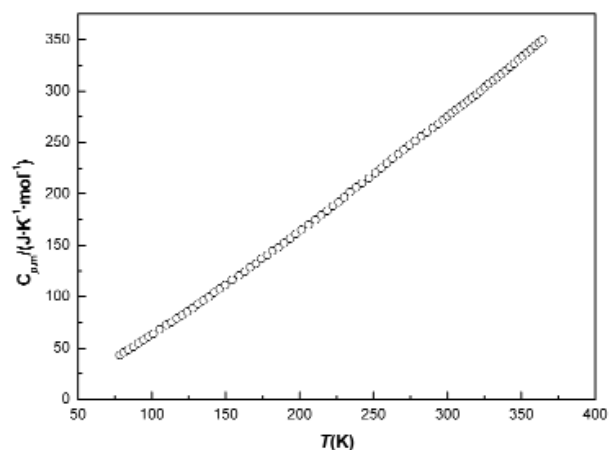
The compound 2-aminopyridinium benzoate can be regarded as a salt of the type MX (charger ratio 1: 1), and the lattice potential energy ( $U_{\text{POT}}$ ) of the compound can be obtained from the the following formula,<sup>12</sup>

$$U_{\text{POT}} (\text{kJ mol}^{-1}) = 2I[\alpha_1(V_m)^{-1/3} + \beta_1] \quad (1)$$

In which  $I$  is the ionic strength  $\{I = 1/2 \sum n_i z_i^2\}$ , where  $n_i$  is the number of ions of type  $i$  with charge  $z_i$  in the formula unit;  $V_m$  is the molecule volume  $\{V_m = 2.1957(3) \text{ nm}^3$  for 2-aminopyridinium benzoate (see Table 1)};  $\alpha_1 = 117.3 \text{ kJ mol}^{-1} \text{ nm}$  and  $\beta_1 = 51.9 \text{ kJ mol}^{-1}$  for MX (charge ratio 1: 1) salts.<sup>12</sup> So the lattice potential energy of the compound 2-aminopyridinium benzoate is calculated to be  $U_{\text{POT}} = 284.297 \text{ kJ mol}^{-1}$ .

### 3. 3. Low-temperature Heat Capacities

All heat-capacity experimental results are plotted in Figure 3, which shows that the structure of the compound is stable over the temperature range between  $T = 78 \text{ K}$  and  $T = 365 \text{ K}$ . None of phase change, association and thermal decomposition of the title compound occurred in the temperature region. The experimental heat capacities were fit-



**Figure 3.** Curve of experimental molar heat capacities of the compound 2-aminopyridinium benzoate with the temperature.

ted by means of the least square method, and a polynomial equation of the experimental molar heat capacities ( $C_{p,m}$ ) vs. reduced temperature ( $X$ ),  $X = f(T)$ , has been obtained,<sup>13</sup>

$$C_{p,m} (\text{J K}^{-1} \text{ mol}^{-1}) = 187.386 + 157.572 X + 7.055 X^2 - 4.149 X^3 + 2.243 X^4 \quad (2)$$

In which  $X = (T - 221.5)/143.5$ . The correlation coefficient for the fitting  $R^2$  equals 0.99997. In which 221.5 is half of the upper limit 365 K plus the lower limit 78 K, while 143.5 is half of the upper limit 365 K minus the lower limit 78 K. The reduced temperatures ( $X$ ) obtained using the method are placed between +1 and -1, and deviations of the smoothed heat capacities from the experimental values will become smaller and smaller with the increase of the power of the fitted polynomial equation according to the statistical principle. The above equation is valid in the temperature range from 78 to 365 K, with an uncertainty of  $\pm 0.2\%$  except for several points around the limits of the lower and upper temperatures.

### 3. 4. Smoothed Heat Capacities and Thermodynamic Functions of the Compound

The smoothed molar heat capacities and thermodynamic functions were 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,<sup>14</sup>

$$(H_T - H_{298.15}) = \int_{298.15}^T C_{p,m} dT \quad (3)$$

$$(S_T - S_{298.15}) = \int_{298.15}^T C_{p,m} \cdot T^{-1} dT \quad (4)$$

$$(G_T - G_{298.15}) = \int_{298.15}^T C_{p,m} dT - T \cdot \int_{298.15}^T C_{p,m} \cdot T^{-1} dT \quad (5)$$

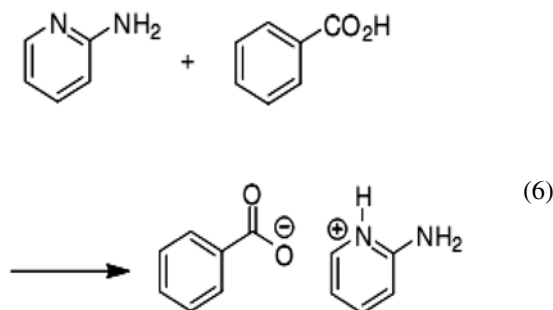
**Table 3.** Smoothed molar heat capacities and thermodynamic functions of the complex 2-aminopyridinium benzoate(s) [ $M(C_{12}H_{12}N_2O_2) = 216.24 \text{ g mol}^{-1}$ ].

$T$ (K)	$C_{p,m}$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$H_T - H_{298.15}$ ( $\text{kJ mol}^{-1}$ )	$S_T - S_{298.15}$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$G_T - G_{298.15}$ ( $\text{kJ mol}^{-1}$ )
80	44.969	-33.68	-161.70	-20.74
85	49.292	-33.44	-158.93	-19.93
90	53.690	-33.18	-156.09	-19.14
95	58.161	-32.90	-153.18	-18.35
100	62.700	-32.60	-150.21	-17.58
105	67.306	-32.28	-147.18	-16.82
110	71.976	-31.93	-144.10	-16.08
115	76.705	-31.56	-140.95	-15.35
120	81.492	-31.16	-137.76	-14.63
125	86.334	-30.74	-134.51	-13.93
130	91.228	-30.30	-131.21	-13.24
135	96.172	-29.83	-127.87	-12.57
140	101.16	-29.34	-124.48	-11.91
145	106.20	-28.82	-121.05	-11.27
150	111.28	-28.28	-117.58	-10.64
155	116.40	-27.71	-114.06	-10.03
160	121.55	-27.11	-110.51	-9.430
165	126.75	-26.49	-106.92	-8.849
170	131.97	-25.84	-103.29	-8.284
175	137.23	-25.17	-99.625	-7.736
180	142.52	-24.47	-95.926	-7.204
185	147.84	-23.75	-92.194	-6.689
190	153.19	-22.99	-88.428	-6.191
195	158.56	-22.21	-84.630	-5.711
200	163.95	-21.41	-80.801	-5.247
205	169.37	-20.57	-76.941	-4.801
210	174.81	-19.71	-73.050	-4.373
215	180.26	-18.83	-69.130	-3.963
220	185.74	-17.91	-65.181	-3.571
225	191.23	-16.97	-61.203	-3.198
230	196.74	-16.00	-57.197	-2.843
235	202.27	-15.00	-53.164	-2.507
240	207.81	-13.98	-49.103	-2.191
245	213.36	-12.92	-45.015	-1.894
250	218.93	-11.84	-40.900	-1.617
255	224.51	-10.73	-36.760	-1.360
260	230.1	-9.597	-32.594	-1.1230
265	235.7	-8.432	-28.402	-0.9058
270	241.32	-7.240	-24.186	-0.7098
275	246.94	-6.019	-19.944	-0.5345
280	252.58	-4.770	-15.679	-0.3803
285	258.22	-3.493	-11.390	-0.2473
290	263.88	-2.188	-7.078	-0.1357
295	269.54	-0.8546	-2.743	-0.04559
298.15	273.12	0	0	0
300	275.22	0.5072	1.6147	0.02284
305	280.90	1.898	5.9936	0.06950
310	286.60	3.316	10.393	0.09433
315	292.31	4.764	14.814	0.09727
320	298.03	6.239	19.253	0.07831
325	303.76	7.744	23.712	0.03748
330	309.50	9.277	28.188	-0.02516
335	315.25	10.84	32.682	-0.1095
340	321.02	12.43	37.191	-0.2154
345	326.81	14.05	41.715	-0.3426
350	332.61	15.70	46.253	-0.4909
355	338.42	17.38	50.803	-0.6599
360	344.26	19.08	55.364	-0.8493
365	350.11	20.82	59.935	-1.0590

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 were tabulated in Table 3 at the intervals of 5 K.

### 3. 5. The Enthalpy Change of the Synthesis Reaction and the Standard Molar Enthalpy of Formation of 2-Aminopyridinium Benzoate

The synthesis reaction is shown as follows:

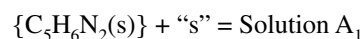


The standard molar enthalpies of dissolution for the reactants and product of the above reaction in the selected solvent (100 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> NaOH) were measured by an isoperibol solution-reaction calorimeter, respectively.

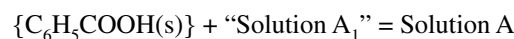
The enthalpy change of the reaction was calculated from the data of the above standard molar enthalpies of dissolution. Finally, the standard molar enthalpy of formation of 2-aminopyridinium benzoate was determined in accordance with Hess law.

Before measuring the standard molar enthalpies of dissolution, the solid reactants (2-aminopyridine and benzoic acid) and product (2-aminopyridinium benzoate) were ground within an agate mortar into the fine powder, respectively, and placed in a vacuum desiccator at 310 K to dry in vacuum for 4 h respectively.

Firstly, about 0.094 g of 2-aminopyridine was accurately weighed and dissolved in 100 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> NaOH solution at  $T = 298.15$  K. The experimental results of the process ( $\Delta_s H_{m,1}^o$ ) were listed in Table 4. The final solution obtained was named as solution A<sub>1</sub>. If “s” represented 100 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> NaOH, the dissolution process was expressed as follows:



Secondly, about 0.122 g of benzoic acid was accurately weighed and dissolved in solution A<sub>1</sub> at  $T = 298.15$  K. The experimental results of the process ( $\Delta_s H_{m,2}^o$ ) were shown in Table 5. The dissolution process may be expressed as follows:



**Table 4.** Dissolution enthalpy of the 1mmol 2-aminopyridine in 100 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> NaOH at  $T = 298.15$  K [ $M(C_5H_6N_2) = 94.1146$  g mol<sup>-1</sup>].<sup>b</sup>

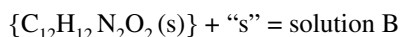
No.	W(g)	$\Delta E_s/\Delta E_e$	$t_e/s$	$Q_s(J)$	$\Delta_s H_{m,1}^o$ (kJ mol <sup>-1</sup> )
1	0.09462	-2.872	9.453	13.234	13.164
2	0.09431	-3.162	8.735	13.464	13.436
3	0.09418	-2.719	10.343	13.708	13.699
4	0.09484	-2.383	11.359	13.197	13.096
5	0.09488	-2.534	10.687	13.203	13.096
$(\bar{x} \pm \sigma_a)$					$\Delta_s H_{m,1}^o = (13.298 \pm 0.118)$ kJ mol <sup>-1</sup>

<sup>b</sup> In which  $W$  is mass of sample;  $\Delta E_s$  is the voltage change during the sample dissolution;  $\Delta E_e$  is the voltage change during the electrical calibration;  $t_e$  is the heating duration of electrical calibration;  $Q_s$  is heat effect of sample dissolution  $\{Q_s = -(\Delta E_s/\Delta E_e) I^2 R t_e\}$ ;  $\Delta_s H_m^o$  is dissolution enthalpy;  $\Delta_s H_m^o = Q_s/n = -(\Delta E_s/\Delta E_e) I^2 R t_e (M/W)$ , where  $R$  is the electrical resistance of the heater ( $R = 1216.9 \Omega$  at  $T = 298.15$  K);  $I$  is the current through the heater ( $I = 20.015$  mA);  $M$  is the molar mass of the sample;  $\bar{x}$  is the mean value of a set of measurement results;  $\sigma_a = \sqrt{\sum_{i=1}^n (x_i - \bar{x})^2 / n(n-1)}$ ,  $n$  is the experimental number;  $x_i$  is a single value in a set of measurements.

**Table 5.** Dissolution enthalpy of the 0.001 mol of benzoic acid in solution A<sub>1</sub> at  $T = 298.15$  K at  $T = 298.15$  K [ $M(C_6H_5COOH) = 122.12$  g mol<sup>-1</sup>].

No.	W(g)	$\Delta E_s/\Delta E_e$	$t_e/s$	$Q_s(J)$	$\Delta_s H_{m,2}^o$ (kJ mol <sup>-1</sup> )
1	0.12289	2.306	23.859	-26.824	-26.656
2	0.12241	2.175	25.016	-26.519	-26.457
3	0.12214	2.087	26.406	-26.868	-26.864
4	0.12246	2.107	25.859	-26.561	-26.487
5	0.12222	2.012	27.203	-26.680	-26.658
$(\bar{x} \pm \sigma_a)$					$\Delta_s H_{m,2}^o = -(26.624 \pm 0.073)$ kJ mol <sup>-1</sup>

In accordance with stoichiometric coefficient of the reactions and product in the reaction (6). About 0.216 g of 2-aminopyridinium benzoate was accurately weighed and dissolved in 100 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> NaOH. The dissolution process was expressed as follows and the detailed results ( $\Delta_s H_{m,3}^{\circ}$ ) obtained from five tests were presented in Table 6.



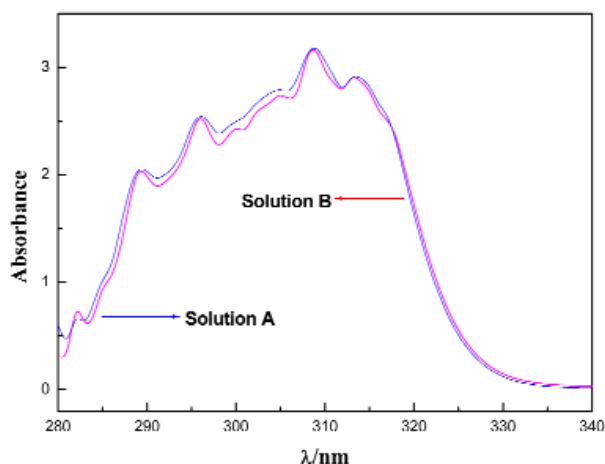
**Table 6.** Dissolution enthalpy of the 1 mmol of 2-aminopyridinium benzoate in 100 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> NaOH at  $T = 298.15$  K [ $M(C_{12}H_{12}N_2O_2) = 216.24$  g mol<sup>-1</sup>].

No.	W(g)	$\Delta E_s/\Delta E_c$	$t_c/s$	$Q_s(J)$	$\Delta_s H_{m,3}^{\circ} (kJ mol^{-1})$
1	0.21660	-1.0355	13.657	6.894	6.883
2	0.21667	-1.4006	9.969	6.807	6.793
3	0.21606	-1.4477	9.609	6.781	6.787
4	0.21678	-1.5496	8.828	6.669	6.652
5	0.21642	-1.3801	9.421	6.338	6.333
$(\bar{x} \pm \sigma_a)$		$\Delta_s H_{m,3}^{\circ} = -(6.690 \pm 0.096)$ kJ mol <sup>-1</sup>			

Then the enthalpy change of the synthesis reaction was calculated from the data of the above standard molar enthalpies of dissolution. The calculation process was expressed as follows:

$$\begin{aligned} \Delta_r H_m^{\circ} &= \sum \Delta_s H_m^{\circ} (\text{reactants}) - \sum \Delta_s H_m^{\circ} (\text{product}) \\ &= (\Delta_s H_{m,1}^{\circ}) + (\Delta_s H_{m,2}^{\circ}) - (\Delta_s H_{m,3}^{\circ}) \\ &= 13.298 + (-26.624) - 6.690 \\ &= -(20.016 \pm 0.182) \text{ kJ mol}^{-1}. \end{aligned}$$

Finally, with the auxiliary thermodynamic data,<sup>15</sup>  $\Delta_f H_m^{\circ}(C_5H_6N_2, s) = (39.4 \pm 0.8)$  kJ mol<sup>-1</sup>,<sup>16</sup>  $\Delta_f H_m^{\circ}(C_6H_5COOH, s) = -(384.8 \pm 0.50)$  kJ mol<sup>-1</sup>, the standard molar enthalpy of formation of 2-aminopyridinium benzoate was determined as,  $\Delta_f H_m^{\circ}(C_{12}H_{12}N_2O_2, s) = \Delta_f H_m^{\circ} + \Delta_f H_m^{\circ}(C_5H_6N_2, s) + \Delta_f H_m^{\circ}(C_6H_5COOH, s) = -20.016 + 39.4 + (-384.8) = -(365.416 \pm 0.961)$  kJ mol<sup>-1</sup>.



**Figure 4.** UV-Vis spectra of solution A and solution B.

The results of UV/Vis spectroscopy and refractive indexes are a basic method for determining the chemical composition and physicochemical properties of two types of solution whether same or not. The results of UV / Vis spectra of two solutions was plotted in Figure 4, which of solution A and solution B was almost identical and they have the same thermodynamic state. Therefore, the designed Hess thermochemical cycle is reasonable and can be used to calculate the standard molar

enthalpy of formation of complex 2-aminopyridinium benzoate.

## 4. Conclusions

This paper mainly reported the lattice potential energy, low temperature heat capacities in the range region from 78 to 365 K, and thermodynamic properties of the solid state compound 2-aminopyridinium benzoate. The enthalpy change of the synthesis reaction (6) was calculated to be  $\Delta_r H_m^{\circ} = -(20.016 \pm 0.182)$  kJ mol<sup>-1</sup>, which is an exothermic reaction. Finally, the standard molar enthalpy of formation of compound 2-aminopyridinium benzoate was calculated.

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## Povzetek

Pripravili smo 2-aminopiridinijev benzoat. Za določitev sestave in kristalne strukture spojine smo uporabili kemijsko in elementno ter rentgensko difrakcijsko analizo. Izračunali smo potencialno mrežno energijo za kristale te spojine:  $U_{\text{POT}} = 284.297 \text{ kJ mol}^{-1}$ . Toplotno kapaciteto spojine pri nizki temperaturi smo izmerili z natančnim, avtomatskim adiabatnim kalorimetrom v temperaturnem območju med 78 K in 365 K. Odvisnost toplotne kapacitete od temperature v območju med 78 K in 365 K smo razvili v polinom, ki smo ga izpilili z metodo najmanjših kvadratov. Skladno z izpiljenim polinomom smo izračunali toplotne kapacitete in vrednosti ostalih termodinamskih funkcij za to spojino pri različnih temperaturah (v korakih po 5 K) glede na standardno referenčno temperaturo 298.15 K. Glede na sintezno reakcijo smo s kalorimetrično metodo v raztopini izoperibola izmerili standardne molske entalpije raztapljanja reaktantov in produkta v izbranem topilu. Tako smo ugotovili razliko v entalpiji pri tej sintezni reakciji:  $\Delta_f H_m^0 = -(20.016 \pm 0.182) \text{ kJ mol}^{-1}$ . Standardno molsko entalpijo tvorbe 2-aminopiridinijevega benzoata smo določili skladno s Hessovim zakonom:  $\Delta_f H_m^0 = -(365.416 \pm 0.961) \text{ kJ mol}^{-1}$ .