

Low Temperature Calorimetry of 3-Fluoro-5-(3-pyridinyloxy) Benzenamine and N-[3-Fluoro-5-(3-Pyridinyloxy)Phenyl]-N'-3-Pyridinyl Urea

Rongchun Li,^a Keyan Sun,^b Yushan Hua,^a Zhicheng Tan,^b Quan Shi^{b,*}

^aKey Laboratory of Coordination Chemistry and Functional Materials, College of Chemistry and Chemical Engineering, Dezhou University, Dezhou, Shandong 253023, China

^bThermochemistry Laboratory, Liaoning Province Key Laboratory of Thermochemistry for Energy and Materials, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

*E-mail: shiquan@dicp.ac.cn

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Abstract

The investigation on thermodynamic properties of drug intermediates plays a crucial role in the design and synthesis of new drugs as well as understanding their biological activities in vivo. In this work, the thermodynamic properties of two drug intermediates of 3-fluoro-5-(3-pyridinyloxy) benzenamine and N-[3-fluoro-5-(3-pyridinyloxy)phenyl]-N'-3-pyridinyl urea were studied by means of low temperature calorimetry performed in a Physical Property Measurement System calorimeter. The heat capacities of these two compounds were measured over the temperature region from (1.9 to 300) K, and the corresponding thermodynamic functions were consequently calculated on the basis of the heat capacity curve fitting. Additionally, a group additivity method were employed for estimating the heat capacity values of these two compounds at 298.15 K, which are in good agreement with the values measured in this work.

Keywords: 3-fluoro-5-(3-pyridinyloxy) benzenamine; N-[3-fluoro-5-(3-pyridinyloxy)phenyl]-N'-3-pyridinyl urea; low temperature calorimetry; heat capacity; thermodynamic properties.

1. Introduction

3-fluoro-5-(3-pyridinyloxy) benzenamine (FPB) and N-[3-fluoro-5-(3-pyridinyloxy)phenyl]-N'-3-pyridinyl urea (FPU) are two important drug intermediates which are generally used in the field of health professionals and pharmaceutical industry [1-5]. The molecular structures of these two compounds are shown in Scheme 1. Most importantly, FPB and FPU are generally employed as structural scaffolds for design and synthesis of anticancer drugs, antibacterial agents and other new medicines for diabetes and heart disease [6-7]. For example, the first, selective, small molecule activator of cardiac myosin has been successfully synthesized based on FPB and FPU for the treatment of systolic heart failure [7]. On the other hand, the design and synthesis of new drugs as well as study and understanding their biological activities behaving in vivo are in urgent need of their thermodynamic properties [8-9], and therefore the thermodynamic investigation on these two compounds are necessary in the related research field.

Low temperature calorimetry has been usually used to obtain the heat capacity of condensed matters, with which the corresponding entropy, enthalpy and Gibbs energy can be consequently calculated [10-13]. However, as far as we known, the low temperature calorimetric study on FPB and FPU has never been reported in literature. In the present work, we have measured the heat capacities of FPB and FPU using a Physical Property Measurement System

(PPMS) calorimeter in the temperature range from (1.9 to 300) K, and the heat capacity data has been fitted to a series of theoretical models and polynomial functions. The thermodynamic functions over the temperature region from (0 to 300) K have been calculated using the heat capacity fitting parameters. Additionally, the experimental heat capacity data of FPB and FPU at 298.15 K have also been compared with those estimated using the Chickos' group additivity model.

2. Experimental

The FPB and FPU samples used in this study were synthesized according to the route reported previously in literature [7]. The detailed synthesis procedure has been presented in the supplementary information (SI). Consequently, the as-prepared samples were further characterized using the HPLC/MS and ¹NMR techniques; FPB: ¹H NMR (300 MHz, DMSO-*d*₆) ppm 8.38-8.50 (m, 2H), 7.42-7.51 (m, 2H), 6.10-6.14 (d, *J* = 12 Hz, 1H), 6.00 (s, 2H), 5.63 (s, 2H); FPB: LCMS (ES, *m/z*) 205.0 [M + H]⁺; FPU: ¹H NMR (400 MHz, DMSO-*d*₆) ppm 9.17 (s, 1H), 8.91 (s, 1H), 8.57 (d, *J* = 2.5 Hz, 1H), 8.43-8.49 (m, 2H), 8.21 (dd, *J* = 4.7, 1.4 Hz, 1 H), 7.91 (ddd, *J* = 8.3, 2.6, 1.5 Hz, 1H), 7.58 (ddd, *J* = 8.4, 2.8 1.4 Hz, 1H), 7.49 (dd, *J* = 8.4, 4.6 Hz, 1H), 7.32 (dd, *J* = 8.3, 4.7 Hz, 1H), 7.20 (dt, *J* = 11.3, 2.1 Hz, 1H), 6.93 (s, 1H), 6.59 (dt, *J* = 9.9, 2.3 Hz, 1H); FPU: LCMS (ES, *m/z*) 325.1 [M+H]⁺. These results indicate that the molecular structures of as-prepared samples

Table 1. Description of FPB and FPU samples

Sample	Molecular formula	CAS No.	Source	^a Mass fraction purity
FPB	C ₁₁ H ₉ FN ₂ O	791644-59-2	Synthesized in-house	0.986
FPU	C ₁₇ H ₁₃ FN ₄ O ₂	1241384-88-2	Synthesized in-house	0.996

^a The mass fraction purity was measured using a HPLC/MS.

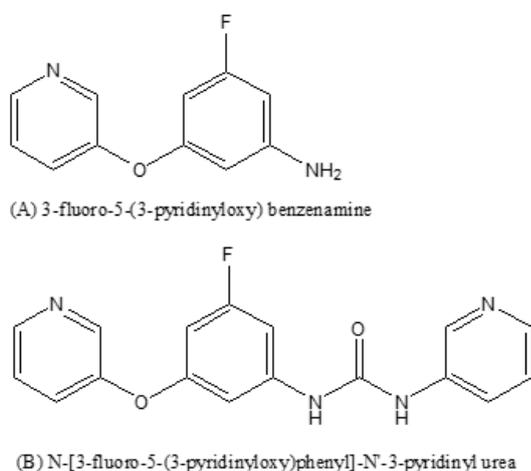


Figure 1. Molecular structures of FPB (A) and FPU (B) studied in this work.

are those shown in Figure 1. The more descriptions including the purity of the two samples determined by LCMS are listed in Table 1.

The low temperature calorimetric measurement was performed using a Quantum Design PPMS equipped with a thermal relaxation heat capacity option. The heat capacity measurement accuracy was determined to be $\pm 3\%$ in the temperature region from 1.9 to 20 K and $\pm 3\%$ from 20 to 400 K by measuring the heat capacities of standard materials of copper pellet, α -Al₂O₃ (SRM720) and benzoic acid (SRM39j) [14]. The heat capacities of FPB and FPU were measured using a logarithmic temperature interval in the region from 1.9 to 100 K and 10 K interval from 100 to 300 K. The detailed sample preparation and measurement procedure can be found in the previous publications [15-16]. The sample masses used in the heat capacity measurement are 13.32 mg and 7.88 mg for FPB and FPU, respectively.

3. Results and Discussion

The collected heat capacity data of FPB and FPU from the PPMS calorimeter are listed in Table 2 and plotted in Figure 2. It can be seen from the figure that the heat capacity of these two compounds gradually increase with the temperature increasing, and on any thermal anomalies could be detected in the entire temperature region. Also, the FPB sample behaves a smaller heat capacity tendency due to its smaller molecular weight than that of FPU.

To calculate the thermodynamic functions of FPB and FPU, we have fitted the heat capacity data to different models in the following three temperature region. In the temperature region below 10 K, the heat capacity was fitted using a theoretical model [17-18]:

$$C_{p,m}^o = B_3T^3 + B_5T^5 + B_7T^7 + B_9T^9 \quad (1)$$

where these odd-power terms in temperature represent the lattice vibration heat capacity contribution at low temperatures. In the middle temperature region from (10 to

60) K, the heat capacity was fitted to the following orthogonal polynomial function [19]:

$$C_{p,m}^o = A_0 + A_1T + A_2T^2 + A_3T^3 + A_4T^4 + A_5T^5 + A_6T^6 \quad (2)$$

In the high temperature region above 60 K, the heat capacity was fitted to a combination of Debye and Einstein function [20]:

$$C_{p,m}^o = n_D D(\theta_D) + n_E E(\theta_E) + aT + bT^2 \quad (3)$$

where n_D and n_E are Debye and Einstein parameters, $D(\theta_D)$ and $E(\theta_E)$ are Debye and Einstein functions, θ_D and θ_E are Debye and Einstein temperatures, and the term of $(aT + bT^2)$ represents a correction for the difference of $(C_p - C_v)$.

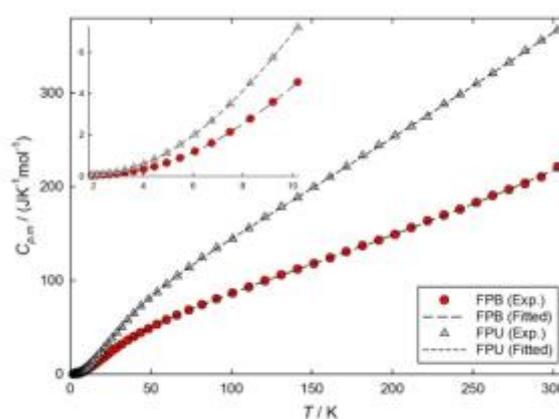


Figure 2. The collected heat capacity data of FPB and FPU from the PPMS calorimeter.

Table 2. Experimental molar heat capacities at constant pressure for FPB and FPU from 1.9 to 300 K ^a

FPB		FPU	
T/K	C _{p,m} ^o / (J·K ⁻¹ ·mol ⁻¹)	T/K	C _{p,m} ^o / (J·K ⁻¹ ·mol ⁻¹)
1.93	0.034239	1.93	0.062297
2.14	0.047027	2.14	0.084902
2.38	0.065455	2.38	0.11905
2.64	0.090328	2.64	0.16547
2.93	0.12556	2.93	0.23159
3.25	0.17557	3.25	0.32207
3.61	0.24496	3.61	0.44644
4.01	0.34029	4.01	0.61414
4.45	0.47207	4.45	0.84110
4.93	0.65213	4.93	1.1422
5.48	0.89095	5.47	1.5390
6.07	1.2062	6.07	2.0495
6.74	1.6110	6.74	2.6867
7.48	2.1346	7.48	3.5088
8.30	2.7875	8.30	4.5281
9.21	3.5903	9.20	5.7549
10.21	4.5531	10.21	7.2157

11.30	5.7284	11.30	8.9930
12.55	7.1280	12.54	11.127
13.92	8.7810	13.92	13.637
15.44	10.707	15.44	16.522
17.15	12.905	17.15	19.942
19.03	15.401	19.02	23.825
21.12	18.194	21.11	28.250
23.44	21.223	23.45	32.988
26.01	24.562	26.01	38.356
28.88	28.127	28.89	44.242
32.06	31.802	32.06	50.516
35.55	35.922	35.55	57.664
39.46	40.051	39.46	64.913
43.80	44.263	43.79	72.439
48.61	48.443	48.60	80.017
53.94	53.009	53.97	87.547
59.86	57.774	59.88	95.782
66.43	62.892	66.45	104.70
73.75	68.228	73.75	113.95
81.85	74.217	81.86	124.44
90.84	80.210	90.85	134.59
100.78	86.337	100.81	144.26
110.94	92.870	110.96	155.47
120.99	99.588	120.99	167.44
131.09	105.90	131.05	178.34
141.17	111.92	141.20	188.34
151.31	117.95	151.28	199.31
161.41	124.14	161.41	210.08
171.49	130.40	171.48	221.46
181.60	136.82	181.54	233.14
191.69	142.90	191.61	244.16
201.78	148.94	201.75	254.42
211.90	156.23	211.85	264.37
221.99	163.32	221.99	274.61
232.12	169.80	232.06	288.30
242.15	175.83	242.11	298.58
252.30	183.23	252.21	309.78
262.37	190.49	262.34	320.95
272.43	197.08	272.43	332.74
282.52	203.27	282.43	345.20
292.65	210.44	292.56	355.95
302.66	221.14	302.61	367.07

^a The expanded uncertainties in the value of the heat capacities are $\pm 0.03C_{p,m}^o$ from $T = 1.9$ to 20 K and $\pm 0.01C_{p,m}^o$ from $T = 20$ to 400 K.

All the fitting parameters as well as %RMS (percent root mean square) deviations from the fitting models are listed in Table 3. The fitted heat capacity data are also plotted as a form of dashed line in Figure 2. The thermodynamic functions of FPB and FPU have been calculated using these fitting parameters and the corresponding thermodynamic relationship in the temperature region from (0 to 300) K. The calculated results are listed in Table 4 with 1 K interval below 10 K, 5 K interval from (10 to 50) K, and 10 K interval from (50 to 300) K, including the values at 273.15 K and 298.15 K. The standard molar heat capacities, entropies and enthalpies at

298.15 K and 0.1M Pa are consequently obtained to be $(216.03 \pm 2.16) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $(234.13 \pm 2.34) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $(34.107 \pm 0.341) \text{ kJ}\cdot\text{mol}^{-1}$, respectively for FPB, and $(362.32 \pm 3.62) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $(391.15 \pm 3.91) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $(57.508 \pm 0.575) \text{ kJ}\cdot\text{mol}^{-1}$, respectively for FPU.

Table 3. Summary of the fitting parameters of heat capacities of FPB and FPU covering the entire temperature range from 1.9 to 300 K.

Fitting Parameter	Coefficients	
	FPB	FPU
	below 5.40 K	below 5.22 K
B_3	4.58523E-03	8.51145E-03
B_5	5.85969E-05	8.38175E-05
B_7	-1.18862E-06	-2.11694E-06
B_9	5.76668E-09	1.11295E-08
	%RMS = 0.82	%RMS = 1.66
	from 5.40 to 55.50 K	from 5.22 to 60.9 K
A_0	1.09647E+00	1.07480E+00
A_1	-6.69193E-01	-7.66995E-01
A_2	1.38109E-01	1.85073E-01
A_3	-4.55090E-03	-5.91500E-03
A_4	7.51603E-05	1.00649E-04
A_5	-6.33689E-07	-9.23387E-07
A_6	2.17461E-09	3.55922E-09
	%RMS = 0.15	%RMS = 0.25
	above 55.50 K	above 60.90 K
n	2.04	2.54
θ_D	148.38	162.34
m	0.81	0.44
θ_E	403.93	605.58
a	2.66533E-01	8.22201E-01
b	7.75224E-04	5.27555E-04
	%RMS = 0.30	%RMS = 0.33

Moreover, it should be pointed out that Chiockos *et al.* reported a group additivity method for the estimation of heat capacities of organic liquids and solids at 298.15 K [21-22], which could be used to estimate the heat capacity of FPB and FPU for the comparison with our values measured using the PPMS. The group values used for estimating the heat capacities of these two compounds are listed in Table 5, and then the heat capacity can be calculated by a sum of the values of all the corresponding groups included in the formula of FPB and FPU. As a result, the heat capacity of FPB at 298.15 K can be estimated to be $226.51 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ by assuming that it corresponds to the sum of the group values of $(7*(=\text{C}_a\text{H}-) + 4*(=\text{C}_a\text{R}-) + (-\text{O}_c-) + (=N_c-) + (-\text{F}) + (-\text{NH}_2))$, and the heat capacity of FPU to be $360.91 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ assuming the sum of values of $(11*(=\text{C}_a\text{H}-) + 5*(=\text{C}_a\text{R}-) + (-\text{O}_c-) + 2*(=N_c-) + (-\text{F}) + (-\text{NHCONH-}))$. These estimated heat capacities are comparable with our measured values of $(216.03 \pm 2.16) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for FPB and $(362.32 \pm 3.62) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for FPU. The deviations of the above estimated value from the measured are within $\pm 4.5\%$ for FPB and $\pm 0.4\%$ for FPU, suggesting that Chiockos' method could provide an estimation of heat capacities at 298.15 K with a high accuracy for condensed organic compounds [21].

Table 4. Standard thermodynamic functions of FPB and FPU from (0 to 300) K. $M = 204.20 \text{ g}\cdot\text{mol}^{-1}$ for FPB and $324.31 \text{ g}\cdot\text{mol}^{-1}$ for FPU

T/K	FPB			FPU		
	$C_{p,m}^0/$ ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)	$\Delta^T_0S^0_m/$ ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)	$\Delta^T_0H^0_m/$ ($\text{kJ}\cdot\text{mol}^{-1}$)	$C_{p,m}^0/$ ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)	$\Delta^T_0S^0_m/$ ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)	$\Delta^T_0H^0_m/$ ($\text{kJ}\cdot\text{mol}^{-1}$)
1	4.6426E-03	1.5400E-03	1.1559E-06	8.5932E-03	2.8536E-03	2.1416E-06
2	0.038408	0.012581	1.8929E-05	0.070509	0.023196	3.4873E-05
3	0.13555	0.043756	9.9030E-05	0.24577	0.080040	1.8087E-04
4	0.33550	0.10720	3.2432E-04	0.59880	0.19411	5.8578E-04
5	0.67467	0.21566	8.1663E-04	1.1822	0.38582	1.4557E-03
6	1.1628	0.37977	1.7241E-03	1.9813	0.66919	3.0220E-03
7	1.7886	0.60430	3.1887E-03	2.9721	1.0466	5.4833E-03
8	2.5395	0.89085	5.3430E-03	4.1380	1.5178	9.0246E-03
9	3.3998	1.2386	8.3042E-03	5.4585	2.0800	0.013811
10	4.3550	1.6455	0.012174	6.9149	2.7294	0.019987
15	10.122	4.4567	0.047813	15.683	7.1212	0.075622
20	16.686	8.2597	0.11470	25.821	13.003	0.17906
25	23.279	12.695	0.21470	36.317	19.892	0.33440
30	29.511	17.498	0.34687	46.609	27.429	0.54188
35	35.241	22.484	0.50897	56.421	35.358	0.79968
40	40.474	27.536	0.69845	65.639	43.500	1.1051
45	45.282	32.585	0.91300	74.219	51.733	1.4550
50	49.750	37.590	1.1507	82.147	59.969	1.8462
60	57.996	47.399	1.6900	96.130	76.218	2.7395
70	65.571	56.916	2.3083	109.38	92.060	3.7689
80	72.681	66.140	2.9999	121.46	107.46	4.9237
90	79.486	75.096	3.7609	132.97	122.44	6.1962
100	86.072	83.813	4.5889	144.15	137.03	7.5820
110	92.494	92.319	5.4818	155.12	151.28	9.0785
120	98.791	100.64	6.4383	165.97	165.24	10.684
130	105.00	108.79	7.4574	176.76	178.96	12.398
140	111.16	116.80	8.5382	187.51	192.45	14.219
150	117.29	124.68	9.6805	198.24	205.75	16.148
160	123.43	132.44	10.884	208.99	218.89	18.184
170	129.58	140.11	12.149	219.75	231.88	20.328
180	135.78	147.69	13.476	230.53	244.75	22.579
190	142.04	155.20	14.865	241.36	257.50	24.938
200	148.36	162.65	16.317	252.22	270.16	27.406
210	154.77	170.04	17.833	263.14	282.73	29.983
220	161.28	177.39	19.413	274.12	295.22	32.669
230	167.88	184.70	21.058	285.15	307.65	35.466
240	174.59	191.99	22.771	296.26	320.02	38.373
250	181.42	199.26	24.551	307.43	332.34	41.391
260	188.37	206.51	26.399	318.68	344.62	44.521
270	195.44	213.75	28.318	330.00	356.86	47.765
273.15	197.69	216.03	28.938	333.59	360.70	48.810
280	202.63	220.98	30.309	341.41	369.06	51.122
290	209.96	228.22	32.371	352.90	381.24	54.593
298.15	216.03	234.13	34.107	362.32	391.15	57.508
300	217.42	235.47	34.508	364.47	393.40	58.180

Table 5. Group values for estimating the heat capacity of FPB and FPU at 298.15 K using Chicos' method [22].

Description of group	Formula	Values / (J·K ⁻¹ ·mol ⁻¹)
tertiary aromatic sp ² C	=C _a H-	17.5
quaternary aromatic sp ² C	=C _a R-	8.5
cyclic ether	-O _c -	9.71
cyclic tertiary sp ² N	=N _c -	13.9
Fluorine	-F	24.8
second sp ³ Nitrogen	-NH ₂	21.6
cyclic urea	-NHCONH-	63.6

4. Conclusions

The thermodynamic properties of FPB and FPU have been investigated by means of low temperature calorimetry. The heat capacities have been measured in the temperature range from 1.9 K to 300 K using the PPMS calorimeter, and the corresponding thermodynamic functions have been calculated based on the curve fitting of the heat capacity data. The standard molar heat capacities, entropies and enthalpies at 298.15 K and 0.1M Pa have been determined to be (216.03±2.16) J·K⁻¹·mol⁻¹, (234.13±2.34) J·K⁻¹·mol⁻¹ and (34.10±0.341) kJ·mol⁻¹, respectively for FPB, and (362.32 ± 3.62) J·K⁻¹·mol⁻¹, (391.15±3.91) J·K⁻¹·mol⁻¹ and (57.50±0.575) kJ·mol⁻¹, respectively for FPU. As a comparison, the heat capacities of FPB and FPU at 298.15 K have been estimated to be 226.51 J·K⁻¹·mol⁻¹ and 360.91 J·K⁻¹·mol⁻¹, respectively, using the group additivity method developed by Chiockos *et al.* [21]. The deviations between the estimated and measured heat capacities are within ±4.5% for FPB and ±0.4% for FPU, suggesting that Chiockos' method is reliable for estimating heat capacities of condensed organic compounds at 298.15 K.

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