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Thermodynamic Study of Benzamide, *N*-Methylbenzamide, and *N*,*N*-Dimethylbenzamide: Vapor Pressures, Phase Diagrams, and Hydrogen Bond Enthalpy

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A static method was used to measure the vapor pressures of crystalline and liquid phases of benzamide, *N*-methylbenzamide, and *N*,*N*-dimethylbenzamide, in the temperature ranges (344.8 to 438.2) K, (322.9 to 388.4) K, and (297.0 to 361.7) K, respectively. The vapor pressures of the crystalline phase of benzamide were also measured using the Knudsen effusion method in the temperature range (324.1 to 344.2) K. From the experimental results, the standard molar Gibbs energies and enthalpies of sublimation and of vaporization, at $T = 298.15$ K, and the triple points coordinates (p,T) for the three compounds were derived. The temperatures and molar enthalpies of fusion were also determined using differential scanning calorimetry and were compared with the values derived from the vapor pressure measurements. The results enabled the determination of the hydrogen bond enthalpies in the studied compounds.

Introduction

The study of the NH···O bond has particular importance for the interpretation of the structure and behavior of proteins. Values for the enthalpy of this intermolecular bond in the crystalline phase have been reported in literature for several compounds, but large discrepancies exist between reported values. After studies on the vapor pressures of several crystalline amides, Aihara estimated that the enthalpy of this hydrogen bond per molecule ranges from (14.6 to 29.3) $\mathrm{kJ \cdot mol^{-1}}$.[1] For benzamide, where two different NH···O bonds exist per molecule, Aihara reported the value of 18.2 $\mathrm{kJ \cdot mol^{-1}}$ for the mean enthalpy of the hydrogen bonds (two hydrogen bonds per molecule), while for *N*-methylbenzamide (just one hydrogen bond per molecule) the value of 16.7 $\mathrm{kJ \cdot mol^{-1}}$ was estimated by this author.[1] To verify these results we decided to measure the vapor pressures of benzamide, *N*-methylbenzamide, and *N*,*N*-dimethylbenzamide, in both liquid and crystal phases, with the main purpose of determining the NH···O bond enthalpy taking into account the existant crystal packing information on these compounds. With this approach we aimed to minimize the need of group contribution values for determining the enthalpies of these important intermolecular bonds.

Experimental Section

Materials. The three compounds studied in this work are commercial products from Aldrich Chemical Co. with the following molar purity certificates: benzamide (CAS Registry No. 55-21-0), 99.99 %; *N*-methylbenzamide (CAS Registry No. 613-93-4), 99.6 %; and *N*,*N*-dimethylbenzamide (CAS Registry No. 611-74-5), 99.8 %. Considering the assessed purities, the compounds were studied without further purification.

Differential Scanning Calorimetry (DSC). The temperature and enthalpy of fusion of the samples (sealed in aluminum crucibles) were measured using a Setaram DSC 141 apparatus, under a heating rate of $3.3 \cdot 10^{-2}\ \mathrm{K \cdot s^{-1}}$. The calibration of the power scale of the calorimeter was performed using high-purity indium (mass fraction > 0.99999). The temperature scale of the calorimeter was calibrated by measuring the melting temperature of the following high purity reference materials: naphthalene, benzoic acid, and indium.[2] For each compound at least four independent runs were performed. Mean results and experimental uncertainties (calculated as twice the standard deviations) of the temperatures of fusion (observed at the onset of the calorimetric peaks), T_{fus}, and of the molar enthalpies of fusion, $\Delta_{\mathrm{cr}}^{\mathrm{l}} H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{fus}})$, are presented in Table 7. No crystalline transitions were detected between the temperature 298 K and the temperature of fusion of the studied compounds.

Vapor Pressure Measurements. The vapor pressures of the three compounds were measured at different temperatures in both crystalline and liquid phases using a static apparatus based on capacitance diaphragm gauges that was previously described in detail,[3] so only a short description is presented here. The apparatus includes capacitance diaphragm absolute gauges, commercially available from MKS Instruments, Inc., operating at self-controlled constant temperatures: gauge I, Baratron 631A01TBEH ($T_{\mathrm{gauge}} = 423$ K) for measuring pressures in the range (0.4 to 133) Pa and in the temperature range (253 to 413) K; and gauge II, Baratron 631A11TBFP ($T_{\mathrm{gauge}} = 473$ K), capable of measuring pressures in the range (3 to 1330) Pa and in the temperature range (253 to 463) K.

The temperatures of the condensed samples were measured using a platinum resistance thermometer Pt100 class 1/10 (in a four-wire connection). This thermometer was calibrated by comparison with a standard platinum resistance thermometer (SPRT, 25 Ω; Tinsley, 5187A). To avoid condensation of the vapor, the tubing between the cell containing the condensed sample and the pressure gauge is kept at a temperature higher than the temperature of the sample and lower than the temperature of the gauge. The uncertainty of the temperature measurements is estimated to be better than ± 0.01 K, and the uncertainty in the pressure measurements is adequately described by the expression $\sigma(p/\mathrm{Pa}) = 0.01 + 0.0025(p/\mathrm{Pa})$.

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Table 1. Effusion Vapor Pressure Results for Crystalline Benzamide[a]

T/K	324.11	326.19	328.19	330.10	332.16	334.18	336.10	338.17	340.19	342.11	344.18	346.18
p/Pa	0.108	0.136	0.169	0.215	0.267	0.332	0.415	0.513	0.634	0.794	0.981	1.205

[a] For each temperature, the presented vapor pressures are the mean of the results obtained with three different effusion orifices.

Table 2. Experimental Effusion Results for Benzamide Where a and b Are from the Clausius−Clapeyron Equation $\ln(p/\mathrm{Pa}) = a - b(\mathrm{K}/T)$, and $b = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\langle T\rangle)/R$

a	b	$\langle T\rangle$ K	$p(\langle T\rangle)$ Pa	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\langle T\rangle)$ kJ·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}\,a}$(298.15 K) kJ·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}\,a}$(298.15 K) kJ·mol^{-1}	R^2
35.71 ± 0.13	12298 ± 44	335.14	0.373	102.2 ± 0.4	103.1 ± 0.4	42.32 ± 0.04	0.9999

[a] $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$ (298.15 K) and $\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}$ (298.15 K) were derived from Clarke Glew eq 2 considering the reference pressure $p^{\mathrm{o}} = 0.1$ MPa.

Table 3. Static Vapor-Pressure Results for Benzamide

T/K	p/Pa	100 $\Delta p/p$	T/K	p/Pa	100 $\Delta p/p$	T/K	p/Pa	100 $\Delta p/p^a$
				Crystalline Phase				
344.80	1.10	−1.3	362.68	6.31	−0.8	380.48	30.68	0.9
346.78	1.35	−1.0	364.64	7.69	1.0	382.47	35.96	0.2
348.77	1.66	−0.4	366.62	9.06	−0.6	384.44	42.27	0.2
350.76	2.04	0.4	368.60	10.95	0.6	386.42	49.49	−0.2
352.74	2.47	0.0	370.59	12.99	0.0	388.40	58.00	−0.3
354.72	3.01	0.5	372.59	15.56	0.4	390.38	67.96	−0.2
356.71	3.66	0.9	374.55	18.29	−0.4	392.32	78.56	−1.0
358.69	4.38	0.0	376.53	21.77	0.0	394.32	92.24	−0.5
360.68	5.34	1.1	378.52	25.86	0.3			
				Liquid Phase				
380.43	42.63	0.4	402.25	159.7	−0.5	424.23	520.8	1.0
382.43	48.10	−0.5	404.42	180.5	−0.5	426.18	567.6	−0.1
384.38	54.55	−0.4	406.32	199.2	−1.2	428.17	626.2	0.1
386.56	62.85	0.0	408.40	225.7	−0.1	430.15	683.6	−0.7
388.30	70.20	0.2	410.17	247.9	−0.4	432.17	759.6	0.2
390.51	80.51	0.3	412.21	279.0	0.5	434.17	826.4	−0.8
392.28	89.70	0.3	414.31	308.8	−0.5	436.20	922.0	0.7
394.51	102.0	−0.2	416.23	346.2	0.8	438.20	1002	−0.2
396.37	114.4	0.2	418.37	381.9	−0.4			
398.34	129.0	0.7	420.28	424.6	0.4			
400.40	145.3	0.7	422.20	466.7	0.1			

[a] $\Delta p = p - p_{\mathrm{calc}}$.

The vapor pressure of the crystalline phase of benzamide was also measured in the range (0.11 and 1.2) Pa using a Knudsen effusion apparatus which was also described in detail before.[4] This apparatus enables the simultaneous operation of nine effusion cells contained in cylindrical holes inside three temperature-controlled aluminum blocks. During an effusion experiment, each aluminum block is kept at a constant temperature, different from the other two blocks, and contains three effusion cells with effusion orifices of different areas: one "small" ($A_{\mathrm{o}} \approx 0.5$ mm^2: series A), one "medium" ($A_{\mathrm{o}} \approx 0.8$ mm^2: series B), and one "large" ($A_{\mathrm{o}} \approx 1.1$ mm^2: series C). The exact areas and Clausing factors of each used effusion orifice in platinum foil of 0.0125 mm thickness are presented in the Supporting Information (SI), Table S1. The temperature of each block is measured using a platinum resistance thermometer Pt100 class 1/10 (in a four-wire connection) previously calibrated by comparison with an SPRT (25 Ω; Tinsley, 5187 A). For each effusion experiment, the loss of mass of the samples during a convenient effusion time period t is determined by weighing the effusion cells to ± 0.01 mg before and after the effusion period. For the temperature T, measured with an uncertainty better than ± 0.01 K, the vapor pressure p of the crystalline sample contained in each effusion cell is calculated by eq 1 where m is the sublimed mass during the effusion time period t, M is the molar mass of the effusing vapor, R is the gas constant, A_{o} is the area of the effusion orifice, and w_{o} is the respective Clausing factor. The uncertainty of the measured pressures is estimated to be better than ± 0.02 (p/Pa).

$$p = (m/A_{\mathrm{o}}w_{\mathrm{o}}t)(2\pi RT/M)^{1/2} \tag{1}$$

Results and Discussion

Effusion Vapor Pressures of Benzamide. Table 1 presents the experimental results for benzamide obtained using the Knudsen effusion method. For each temperature, the mean of the vapor pressures related to the small, medium, and large effusion orifices (presented in SI, Table S2) is presented. Table 2 presents thermodynamic parameters derived from the effusion mean vapor pressures of benzamide: the detailed parameters of the Clausius−Clapeyron equation, $\ln(p/\mathrm{Pa}) = a - b(\mathrm{K}/T)$, where a is a constant and $b = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\langle T\rangle)/R$; the standard molar enthalpy of sublimation at the mean temperature of the experiments $T = \langle T\rangle$; and the standard molar enthalpy and Gibbs energy of sublimation at the reference temperature $\theta = 298.15$ K. The values at $\theta = 298.15$ K were derived fitting the experimental results of the vapor pressures by the Clarke and Glew eq 2,[5]

$$R\ln\left(\frac{p}{p^{\mathrm{o}}}\right) = -\frac{\Delta_{\mathrm{cd}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}(\theta)}{\theta} + \Delta_{\mathrm{cd}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\theta)\left(\frac{1}{\theta} - \frac{1}{T}\right) + \Delta_{\mathrm{cd}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}}(\theta)\left[\left(\frac{\theta}{T}\right) - 1 + \ln\left(\frac{T}{\theta}\right)\right] \tag{2}$$

where p is the vapor pressure at the temperature T, p^{o} is a selected reference pressure ($p^{\mathrm{o}} = 10^5$ Pa in this work), θ is a

Table 4. Static Vapor-Pressure Results for *N*-Methylbenzamide

T/K	p/Pa	100 $\Delta p/p$	T/K	p/Pa	100 $\Delta p/p$	T/K	p/Pa	100 $\Delta p/p$[a]
				Crystalline Phase				
324.88	0.50	−0.9	334.80	1.52	0.4	344.79	4.26	−0.4
326.83	0.63	0.1	336.82	1.89	0.7	345.79	4.71	−0.5
328.93	0.80	0.4	338.85	2.35	1.1	346.80	5.28	0.9
330.82	0.98	−0.2	340.81	2.84	−0.3	347.77	5.75	−0.2
332.75	1.21	−0.2	342.75	3.48	0	348.76	6.31	−0.7
				Liquid Phase				
322.88	0.67	−0.8	346.77	5.47	0.5	370.59	31.48	−0.5
324.94	0.83	1.2	348.77	6.40	0.3	372.57	36.12	−0.1
326.92	0.99	0.4	350.75	7.53	1.0	374.56	40.95	−0.9
328.89	1.17	−1.0	352.74	8.61	−0.9	376.53	47.25	0.4
330.88	1.40	−1.0	354.74	10.13	0	378.51	53.25	−0.5
332.86	1.66	−1.6	356.70	11.68	−0.5	380.49	60.51	−0.4
334.86	2.01	0	358.72	13.59	−0.4	382.47	68.84	−0.1
336.84	2.41	0.9	360.66	15.72	0	384.46	78.04	0
338.82	2.84	0.5	362.68	18.12	−0.4	386.43	88.21	0.1
340.80	3.36	0.6	364.63	20.93	0.1	388.40	101.0	1.6
342.80	3.98	1.0	366.62	23.94	−0.5			
344.80	4.70	1.2	368.59	27.50	−0.3			

[a] $\Delta p = p - p_{\mathrm{calc}}$.

Table 5. Static Vapor-Pressure Results for *N*,*N*-Dimethylbenzamide

T/K	p/Pa	100 $\Delta p/p$	T/K	p/Pa	100 $\Delta p/p$	T/K	p/Pa	100 $\Delta p/p$[a]
				Crystalline Phase				
297.04	0.54	0.2	305.00	1.38	0.2	312.98	3.36	0.3
299.03	0.69	0.7	307.00	1.71	−1.1	314.98	4.18	0.6
301.02	0.86	−0.8	308.98	2.15	−0.4			
303.02	1.10	0.4	310.98	2.69	−0.1			
				Liquid Phase				
301.98	1.34	0.1	323.93	9.09	0.2	345.73	45.03	0.1
303.99	1.62	0.1	325.88	10.66	0.7	347.77	51.51	−0.2
305.97	1.95	0.2	327.91	12.39	−0.1	349.68	58.66	0.2
307.96	2.32	−0.6	329.85	14.39	0	351.75	66.97	0
310.43	2.89	−0.7	331.88	16.76	−0.1	353.64	75.71	0.1
312.30	3.43	−0.1	333.84	19.49	0.4	355.70	86.11	0
314.00	3.99	0.3	335.85	22.38	−0.6	357.62	97.22	0.2
316.00	4.72	−0.1	337.80	25.98	0.3	359.68	110.2	0
317.97	5.60	0.4	339.82	29.69	−0.8	361.66	124.4	0.2
319.95	6.58	0.1	341.77	34.32	0.1			
321.94	7.76	0.4	343.80	39.16	−0.8			

[a] $\Delta p = p - p_{\mathrm{calc}}$.

selected reference temperature ($\theta = 298.15$ K in this work), R is the molar gas constant (8.31447 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$), $\Delta_{\mathrm{cd}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}(\theta)$ is the difference in molar Gibbs energy between the gaseous and the crystalline or liquid phases (condensed phases) at the selected reference pressure. $\Delta_{\mathrm{cd}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\theta)$ is the difference in molar enthalpy between the gas and the condensed phases, and $\Delta_{\mathrm{cd}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}}(\theta)$ is the difference in molar heat capacity at constant pressure between the gaseous and the condensed phase. The results related to the small, medium, and large orifices are reported in SI, Table S3.

Static Vapor Pressures and Phase Diagrams. Tables 3 to 5 present the static vapor pressure results for the crystalline and liquid phases of the three studied compounds, including vapor pressure results of the undercooled liquids. The experimental results of the solid and liquid static vapor pressures were also fitted (independently) by the Clarke and Glew equation (eq 2). The results of the fittings are present in Table 6. The values of $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}}(\theta)$ inserted in eq 2 were estimated for the three studied compounds. For benzamide the value $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}}(\theta) = -23.8$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ was estimated from the molar heat capacity of crystalline benzamide $C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{cr}) = 153.8$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$,[6] using eq 3 proposed by Chickos et al.[7]

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}}(\theta) = -\{0.75 + 0.15C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{cr})\}\mathrm{J \cdot K^{-1} \cdot mol^{-1}} \tag{3}$$

For *N*,*N*-dimethylbenzamide, the value $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}}(\theta) = -30.7$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ was estimated from the value $C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{cr}) = 199.9$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$,[8] using again eq 3. The value $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}}(\theta) = -27.3$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ was estimated for *N*-methylbenzamide as the mean of the values of $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}}(\theta)$ estimated for benzamide and *N*,*N*-dimethylbenzamide. For the liquid phases of the studied compounds, the values $\Delta_{\mathrm{l}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K}) = -(96 \pm 10)$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, $\Delta_{\mathrm{l}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K}) = -(98 \pm 8)$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, and $\Delta_{\mathrm{l}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K}) = -(113 \pm 3)$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ were derived from the regression of the fittings of eq 2 to the liquid vapor-pressure results of benzamide, *N*-methylbenzamide, and *N*,*N*-dimethylbenzamide, respectively. The vapor-pressure results of both crystalline and liquid phases of the studied compounds yielded the phase diagrams presented in Figures 1 to 3. Literature vapor-pressure results are also presented in these figures.

For similar temperatures, the vapor pressures of crystalline benzamide measured through the static method are only about 5 % higher than those measured by the effusion method, and the enthalpies of sublimation derived from the two sets of data are in excellent agreement. The vapor-pressure results published by Aihara[1] for this compound are also close to the ones measured in this study but yield a value of $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})$, that is, about 5 $\mathrm{kJ \cdot mol^{-1}}$ lower than the one derived in this work. The vapor pressures of *N*-methylbenzamide published by Aihara[1] are higher than the values obtained in this study. The value $\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})$ derived from those vapor-pressure results is 1.34 $\mathrm{kJ \cdot mol^{-1}}$ lower than the value calculated from the vapor

Table 6. Parameters of Clarke and Glew Equation 2 Derived from Vapor-Pressure Results for Crystalline and Liquid Benzamide, *N*-Methylbenzamide, and *N*,*N*-Dimethylbenzamide ($p^0 = 10^5$ Pa)

phase	ΔT K	θ K	$\Delta^{g}_{cr,l}G^{0}_{m}(\theta)$ $kJ \cdot mol^{-1}$	$\Delta^{g}_{cr,l}H^{o}_{m}(\theta)$ $kJ \cdot mol^{-1}$	R^2	$-\Delta^{g}_{cr,l}C^{o}_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$	s^a
			Benzamide				
crystalline	345−394	298.15	42.08 ± 0.02	102.6 ± 0.1	1.0000	23.8[b]	0.007
		369.56[c]	27.78 ± 0.01	100.9 ± 0.1			
		399.17[d]	21.94 ± 0.01	100.2 ± 0.1			
		298.15[e]	42.32 ± 0.04	103.1 ± 0.4	0.9999		0.010
		298.15[f]	41.60 ± 0.10	97.7 ±1.0	0.9991		0.017
liquid[g]	380−438	298.15	37.16 ± 0.17	86.5 ± 1.2	1.0000	96 ± 10[h]	0.005
		409.32[c]	20.56 ± 0.01	75.8 ± 0.1			
		399.17[d]	21.94 ± 0.01	76.7 ± 0.1			
			N-Methylbenzamide				
crystalline	325−349	298.15	38.52 ± 0.02	101.0 ± 0.2	0.9999	27.3[b]	0.006
		336.82[c]	30.48 ± 0.04	99.9 ± 0.2			
		348.91[d]	27.99 ± 0.01	99.6 ± 0.2			
		298.15[f]	37.18 ± 0.02	86.3 ± 0.4	0.9998		0.009
liquid[g]	323−388	298.15	35.92 ± 0.04	84.9 ± 0.5	1.0000	98 ± 8[h]	0.008
		355.64[c]	27.00 ± 0.01	79.2 ± 0.1			
		348.91[d]	27.99 ± 0.01	79.9 ± 0.1			
			N,*N*-Dimethylbenzamide				
crystalline	297−315	298.15	29.74 ± 0.01	88.8 ±0.3	0.9999	30.7[b]	0.006
		306.01[c]	28.19 ± 0.01	88.6 ± 0.3			
		316.95[d]	26.04 ± 0.01	88.2 ± 0.3			
		298.15[i]	30.02 ± 0.01	89.6 ± 0.3	0.9999		0.006
liquid[g]	302−362	298.15	28.73 ± 0.01	72.5 ± 0.1	1.0000	113 ± 4[h]	0.004
		331.82[c]	23.99 ± 0.01	68.7 ± 0.1			
		316.95[d]	26.04 ± 0.02	70.4 ± 0.1			

[a] s is the standard deviation of the fit defined as $s = [(\sum_{i=1}^{n}(\ln p - \ln p_{calc})_i^2)/(n - m)]^{1/2}$ where n is the number of experimental points used in the fit and m is the number of adjustable parameters of Clarke and Glew eq 2. [b] Estimated value. [c] Mean temperature. [d] Temperature of the triple point. [e] Knudsen effusion (this work). [f] Ref 1. [g] Including supercooled liquid. [h] Adjustable parameter. [i] Ref 8.

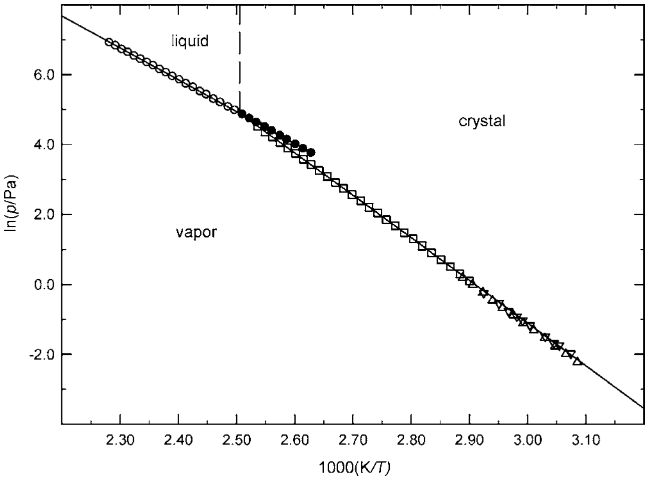


Figure 1. Phase diagram of benzamide. ○, static liquid vapor pressures; ●, undercooled liquid vapor pressures; □, static crystalline vapor pressures (this study); △, effusion vapor pressures (mean of small, medium, and large orifices results; this study); ▽, crystalline vapor pressures (ref 1). Triple-point coordinates: $T = 399.17$ K, $p = 135.7$ Pa.

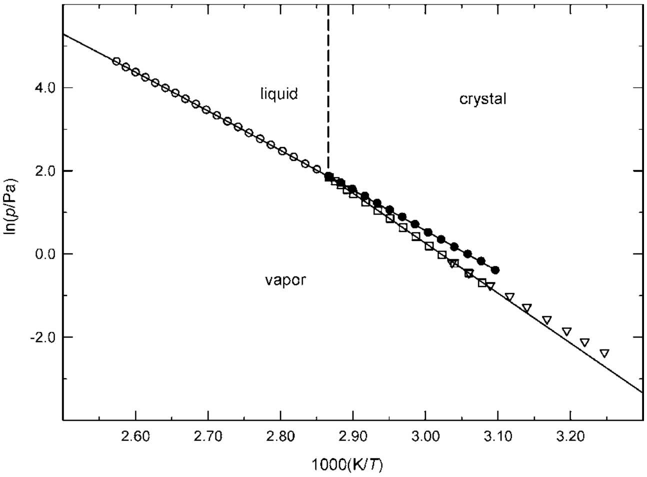


Figure 2. Phase diagram of *N*-methylbenzamide. ○, liquid vapor pressures; ●, undercooled liquid vapor pressures; □, crystalline vapor pressures (this study); ▽, crystalline vapor pressures (ref 1). Triple-point coordinates: $T = 348.91$ K, $p = 6.45$ Pa.

pressures measured in this study. Moreover the results of Aihara for this compound yield a value of $\Delta^{g}_{cr}H^{o}_{m}$(298.15 K) about 15 $kJ \cdot mol^{-1}$ lower than the value derived in this study.

For *N*,*N*-dimethylbenzamide, there is excellent agreement between the results published in the literature[8] and the ones derived in this study. As the best of our knowledge, there are no reported vapor pressures for the liquid phase of the studied compounds.

Triple Point and Fusion. Table 7 presents values of the triple-point coordinates and of the temperatures and enthalpies of fusion for the studied compounds. For benzamide, the temperature of the triple point is 2.1 K lower than the value of the temperature of fusion obtained through the DSC experiments and 3.8 K lower than the value published by Steele et al.[6] The enthalpy of fusion derived from the enthalpies of sublimation and of vaporization (presented in Table 6) is in excellent agreement with the value published by Steele et al.[6] and with the DSC results. For *N*-methylbenzamide the temperature of the triple point is 1.5 K higher than the DSC result but 3.1 K lower than the literature value.[9] The enthalpy of fusion derived from the vapor pressures is about 1 $kJ \cdot mol^{-1}$ higher than the value obtained from the DSC experiments. For *N*,*N*-dimethylbenzamide, the temperature of the triple point is in excellent agreement with DSC result and only 1 K higher than the literature result,[10] while the enthalpy of fusion derived from the vapor pressures is 3.6 $kJ \cdot mol^{-1}$ smaller than the value derived from the DSC experiments. The proximity between the

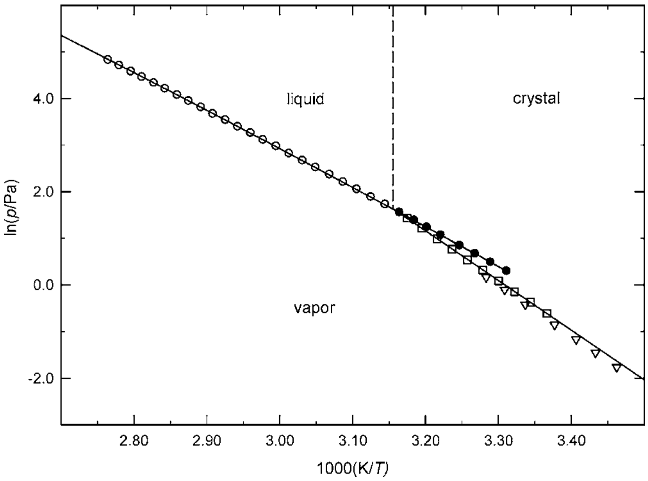


Figure 3. Phase diagram of *N*,*N*-dimethylbenzamide. ○, liquid vapor pressures; ●, undercooled liquid vapor pressures; □, crystalline vapor pressures (this study); ▽, crystalline vapor pressures (ref 8). Triple-point coordinates: $T = 316.95$ K, $p = 5.12$ Pa.

calorimetric values and the values derived indirectly from the vaporization and sublimation curves gives additional consistency to the results derived from the vapor-pressure study.

Hydrogen Bonds. According to the packing arrangements established for benzamide[11] and for *N*-methylbenzamide,[12] represented schematicly in Figure 4, there are two hydrogen bonds (NH···O) per molecule in the crystals of the former compound and just one in the latter. These hydrogen bonds have slightly different lengths (for benzamide, $l = 296$ pm inside the dimers and $l = 291$ pm between them; for *N*-methylbenzamide $l = 293$ pm). For *N*,*N*-dimethylbenzamide there are not any bonds of this type.

To calculate the hydrogen bond enthalpies in these crystals the following equations were used,

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\text{benzamide}) = A + 2(\Delta_{\mathrm{HB}}H)_{\mathrm{m}} \tag{4}$$

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(N\text{-methylbenzamide}) = A + \Delta_{\mathrm{HB}}H + B \tag{5}$$

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(N,N\text{-dimethylbenzamide}) = A + 2B \tag{6}$$

where $(\Delta_{\mathrm{HB}}H)_{\mathrm{m}}$ is the mean enthalpy of the two different hydrogen bonds in benzamide, $\Delta_{\mathrm{HB}}H$ is the enthalpy of the hydrogen bond in *N*-methylbenzamide, and B is the increment in the enthalpy of sublimation when a H atom, not involved in a hydrogen bonding, is replaced by CH_3 in the benzamide or in the *N*-methylbenzamide molecules.

Solving the equations simultaneously the following solution is achieved:

$$\Delta_{\mathrm{HB}}H = 12.2\ \mathrm{kJ\cdot mol^{-1}} + B \tag{7}$$

$$A = 102.6\ \mathrm{kJ\cdot mol^{-1}} - 2(\Delta_{\mathrm{HB}}H)_{\mathrm{m}} \tag{8}$$

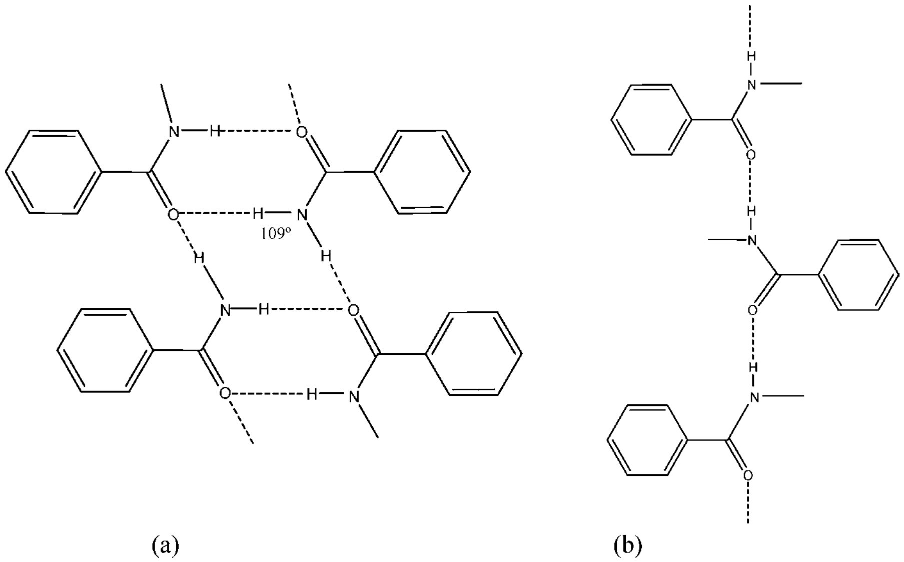
$$\Delta_{\mathrm{HB}}H - (\Delta_{\mathrm{HB}}H)_{\mathrm{m}} = 5.3\ \mathrm{kJ\cdot mol^{-1}} \tag{9}$$

Assuming the value $B = 8.2\ \mathrm{kJ\cdot mol^{-1}}$ that was estimated from the enthalpies of sublimation of several compounds, as it is shown in Table S4 of the SI, the following values are derived:

Table 7. Triple-Point Coordinates (*p*,*T*) and Temperature and Molar Enthalpy of Fusion of the Studied Compounds

compound	T_{tp} K	T_{fus} K	$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(T^{a})$ kJ·mol^{-1}	p_{tp} Pa	$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})$ kJ·mol^{-1}	method/reference
benzamide	–	401.34 ± 0.17	23.18 ± 0.05	–		DSC/this work
	399.17	–	23.5 ± 0.1	135.7	16.1 ± 1.2	static/this work
		403	23.76			6
N-methylbenzamide	–	347.41 ± 0.04	18.62 ± 0.20	–		DSC/this work
	348.91	–	19.6 ± 0.2	6.45	16.1 ± 0.5	static/this work
		352				9
N,*N*-dimethylbenzamide	–	316.90 ± 0.10	21.22 ± 0.10	–		DSC/this work
	316.95	–	17.6 ± 0.3	5.12	16.3 ± 0.3	static/this work
		315.9				10

[a] Temperature of fusion or temperature of the triple point.



(a) (b)

Figure 4. Schematic representation of the crystalline packing arrangements of (a) benzamide (adapted from ref 11) and (b) *N*-methylbenzamide (adapted from ref 12).

$A = 72.4$ kJ·mol^{-1}; $\Delta_{\mathrm{HB}}H = 20.4$ kJ·mol^{-1}; $(\Delta_{\mathrm{HB}}H)_{\mathrm{m}} = 15.1$ kJ·mol^{-1}. So, accordingly to eq 9 the enthalpy of the hydrogen bond in *N*-methylbenzamide is 5.3 kJ·mol^{-1} higher than the mean enthalpy of the hydrogen bondings in benzamide (independently of the value estimated for *B*). This result points out that the set of the two hydrogen bonds around the same nitrogen atom in benzamide (forming an angle of ca. 109°) is weaker than a set of two hydrogen bonds involving two different nitrogen atoms as in *N*-methylbenzamide. As this makes sense, our results for the enthalpies of hydrogen bonding in the studied compounds seem more consistent than those derived by Aihara,[1] $\Delta_{\mathrm{HB}}H = 16.7$ kJ·mol^{-1} and $(\Delta_{\mathrm{HB}}H)_{\mathrm{m}} = 18.2$ kJ·mol^{-1}.

Taking into account that the values of the enthalpies of fusion, at $T = 298.15$ K, derived for the three studied compounds are identical, it may be assumed that similar hydrogen bonds remain in the liquid phase for both benzamide and *N*-methylbenzamide. Therefore, solving a system of three equations similar to eqs 4, 5, and 6 (with the enthalpies of sublimation replaced by the enthalpies of vaporization, at $T = 298.15$ K, of the three studied compounds, presented in Table 6) yields the following solution:

$$\Delta_{\mathrm{HB}}H(\mathrm{liq}) = 12.4\ \mathrm{kJ \cdot mol^{-1}} + B' \qquad (10)$$

$$A' = 86.5\ \mathrm{kJ \cdot mol^{-1}} - 2\{\Delta_{\mathrm{HB}}H(\mathrm{liq})\}_{\mathrm{m}} \qquad (11)$$

$$\Delta_{\mathrm{HB}}H(\mathrm{liq}) - \{\Delta_{\mathrm{HB}}H(\mathrm{liq})\}_{\mathrm{m}} = 5.4\ \mathrm{kJ \cdot mol^{-1}} \qquad (12)$$

where B' is the increment in the enthalpy of vaporization when a H atom not involved in a hydrogen bonding is replaced by CH_3 in the benzamide or in the *N*-methylbenzamide molecules. From the group increments recommended by Domalski and Hearing[13] the value $B' = 5.4$ kJ·mol^{-1} is derived while Chickos et al.[14] predicted an increment $B' = 4.7$ kJ·mol^{-1} for the enthalpies of vaporization of hydrocarbons. Considering literature values from the enthalpies of vaporization of several compounds (as shown in Table S5 of the SI) the mean value $B' = 3.7$ kJ·mol^{-1} was also estimated. As the value predicted by Chickos et al. is close to the mean of the other two estimations, the value $B' = 4.7$ kJ·mol^{-1} was used to derive the following values: $A' = 63.1$ kJ·mol^{-1}; $\Delta_{\mathrm{HB}}H(\mathrm{liq}) = 17.1$ kJ·mol^{-1}; $\{\Delta_{\mathrm{HB}}H(\mathrm{liq})\}_{\mathrm{m}} = 11.7$ kJ·mol^{-1}. These results show that if the assumption about the number of hydrogen bonds in the liquid phase is correct than these hydrogen bonds are significantly weaker than the corresponding ones in the crystalline phase.

Supporting Information Available:

Detailed data of the effusion orifices of the Knudsen apparatus and the benzamide vapor-pressure results, the parameters of the Clausius−Clapeyron equation, standard molar enthalpies of sublimation, standard enthalpy and Gibbs energy of sublimation, and literature values for the enthalpy of sublimation and vaporization. This material is available free of charge via the Internet at http://pubs.acs.org.

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