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Vapor Pressures and Phase Diagrams of Two Methyl Esters of Substituted Benzoic Acids

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S *Supporting Information*

ABSTRACT: The vapor pressures of condensed phases of methyl *p*-methylbenzoate and methyl *p*-(dimethylamino)benzoate were measured in the temperature ranges (269.3 to 357.0) K and (325.0 to 390.4) K, respectively, using a static method. The Knudsen mass-loss effusion technique was also used to study the vapor pressures as function of temperature of the crystals of methyl *p*-(dimethylamino)benzoate in the pressure range (0.1 to 1) Pa. The results obtained for each compound enabled the determination of the standard molar entropies and enthalpies of sublimation and of vaporization at $T = 298.15$ K as well as phase diagram representations of the (p,T) experimental data. The temperatures and molar enthalpies of fusion were determined using differential scanning calorimetry and were compared with the values derived from the vapor pressure measurements. The enthalpies of the intermolecular hydrogen bonds O—H···O in the crystalline phase of the parent substituted benzoic acids were calculated.

INTRODUCTION

Vapor pressure is a key property often required for planning industrial processes and for environmental studies. Vapor pressure measurements have also been recently used to determine enthalpies of hydrogen bonding,[1,2] which provides the strongest intermolecular forces between molecules in organic molecular crystals and hence strongly influences the packing arrangements. The OH···O bonding is the most familiar of the hydrogen bonds and has been widely explored since they occur in several different classes of compounds including those related to biochemical processes like carbohydrates, aminoacids, peptides, purines, pyrimidines, nucleosides, and so forth. A thermodynamic study of the sublimation of selected esters of benzoic acids provides a way to determine the enthalpies of intermolecular hydrogen bonds OH···O in the parent acids with known sublimation enthalpies, which we aim to achieve. Also, the measurement of the vapor pressures of the two esters studied in the present work, in both crystalline and liquid phases, enabled the determination of relevant thermodynamic properties of their phase transitions.

EXPERIMENTAL SECTION

Materials. Methyl *p*-methylbenzoate (CAS Registry No. 99-75-2) and methyl *p*-(dimethylamino)benzoate (CAS Registry No. 1202-25-1), were commercially obtained and were further purified by sublimation under reduced pressure prior to the experimental measurements. The final purities were checked by gas chromatography (GC) using an Agilent 4890D gas chromatograph equipped with a HP-5 column, cross-linked, with 5 % diphenyl and 95 % dimethylpolysiloxane (15 m × 0.530 mm i.d. × 1.5 μm film thickness) and a flame ionization detector, using nitrogen as the carrier gas. The initial and final purities of the samples are presented in Table 1.

Differential Scanning Calorimetry. The thermal behavior and the determination of the temperatures and enthalpies of fusion of the purified samples were conducted by differential scanning calorimetry (Setaram DSC 141). The calibration of the power scale of the calorimeter was performed using high-purity indium (mass fraction >0.99999), and 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.[3] The measurements were made in sealed aluminum crucibles and in nitrogen atmosphere. For the experimental determinations, five samples each weighing ≈ 6 mg were scanned from $T = 298$ K to about 20 K above their melting points using a heating rate of $(3.3 \cdot 10^{-2})$ K·s^{-1}. The crucibles and the samples of compounds were weighed with a sensitivity of $\pm\ 1 \cdot 10^{-7}$ g on a Mettler UMT2 microbalance. No crystalline transitions were detected between the temperature 298 K and the temperature of fusion of the compounds studied. The onset temperatures of fusion, T_{fus}, and the enthalpies of fusion, $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\text{o}}(T_{\text{fus}})$, were computed from the DSC thermograms and are presented in Table 5 where the uncertainties assigned are the standard deviation of the mean.

Vapor Pressure Measurements. The vapor pressures of the condensed phases of the two compounds were measured at different temperatures by means of a static apparatus based on capacitance diaphragm gauges that was previously described in detail.[4] This equipment can operate with two capacitance diaphragm absolute gauges (MKS Instruments, Inc.) working

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Table 1. Source, Purification, and Analysis Details of the Samples

chemical name	source	initial mole fraction purity	purification method	final mole fraction purity	analysis method
methyl *p*-methylbenzoate	Alfa Aesar	0.993	sublimation	0.999	GC[a]
methyl *p*-(dimethylamino)benzoate	Alfa Aesar	0.997	sublimation	0.999	GC[a]

[a] Gas−liquid chromatography.

Table 2. Static Vapor Pressure Results for Methyl *p*-Methylbenzoate[a]

T/K	p/Pa	$100\ \Delta p/p$	T/K	p/Pa	$100\ \Delta p/p$	T/K	p/Pa	$100\ \Delta p/p^b$
				Crystalline Phase				
269.27	0.40	0.1	281.08	1.84	0.2	293.04	7.45	−0.8
271.21	0.52	0.2	283.07	2.35	0.3	295.02	9.39	0.2
273.18	0.67	−0.4	285.08	3.00	0.6	297.03	11.67	−0.2
275.19	0.87	−0.4	287.05	3.77	0.1	299.02	14.51	−0.1
277.14	1.12	−0.2	289.04	4.75	−0.1	300.98	17.95	0.2
279.16	1.45	0.2	291.04	5.99	0.1			
				Liquid Phase				
293.03	10.66	0.0	312.95	50.65	−0.1	332.84	193.4	0.9
295.08	12.70	0.3	314.97	58.15	−0.7	334.91	216.2	−0.7
297.05	14.98	0.5	316.99	67.35	−0.3	336.82	245.4	0.4
299.04	17.55	0.1	318.90	76.85	−0.3	338.88	274.8	−0.6
301.03	20.57	0.1	320.95	89.45	0.9	340.75	310.0	0.5
303.00	24.04	0.1	322.94	100.9	−0.5	342.80	346.9	−0.2
305.03	27.84	−0.9	324.92	117.1	1.2	344.71	388.4	0.2
306.98	32.42	−0.6	326.96	132.0	−0.1	346.77	435.3	0.0
308.97	38.25	1.0	328.85	151.0	1.2	348.75	484.0	−0.4
310.97	43.40	−1.1	330.92	168.9	−0.7	357.05	772.0	1.1

[a] Estimated uncertainties are 0.01 K for the temperature, [0.01 + 0.0025 (p/Pa)] Pa for static pressures below 130 Pa (measured through gauge 1), [0.1 + 0.0025 (p/Pa)] Pa for the other static pressures (measured through gauge 2), and 0.01 Pa for the effusion pressures. [b] $\Delta p = p - p_{\mathrm{calc}}$.

at self-controlled constant temperatures: gauge I—Baratron 631A01TBEH (T_{gauge} = 423 K) that allows measuring pressures in the range (0.4 to 133) Pa and in the temperature range from (253 to 413) K and gauge II—Baratron 631A11TBFP (T_{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 by a platinum resistance thermometer (PRT) Pt100 class 1/10 DIN (in a four-wire connection) that was calibrated by comparison with a standard PRT (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. The uncertainty in the vapor pressure measurements increases linearly with the pressure; it is adequately described by the expressions $\sigma(p/\mathrm{Pa}) = 0.01 + 0.0025\ (p/\mathrm{Pa})$ for gauge 1 and $\sigma(p/\mathrm{Pa}) = 0.1 + 0.0025\ (p/\mathrm{Pa})$ for gauge 2.

The vapor pressures of the crystalline sample of methyl *p*-(dimethylamino)benzoate were also measured using the Knudsen mass-loss effusion technique. This apparatus enables the simultaneous operation of nine aluminum effusion cells with three different effusion orifice diameters, contained in cylindrical holes inside three temperature-controlled aluminum blocks. Each aluminum block is kept at a constant temperature, different from the other two blocks, and contains three effusion cells with orifices of different areas: one "small" ($A_o \approx 0.5\ \mathrm{mm}^2$: series A), one "medium" ($A_o \approx 0.8\ \mathrm{mm}^2$: series B), and one "large" ($A_o \approx 1.1\ \mathrm{mm}^2$: series C). The measuring procedure and the detailed description of the apparatus have been reported as well as the experimental results obtained during its testing by measuring reference compounds (benzoic acid, phenanthrene, anthracene, benzanthrone, and 1,3,5-triphenylbenzene).[5] In each effusion experiment, in a system evacuated to a pressure near $1 \cdot 10^{-4}$ Pa, the loss of mass Δm of the samples, during a convenient effusion time period t, is determined by weighing the effusion cells to ± $1 \cdot 10^{-5}$ g before and after the effusion period. The vapor pressure p of the crystalline sample contained in each effusion cell is calculated by the equation

$$p = (m/A_o w_o t)(2\pi RT/M)^{1/2} \tag{1}$$

where T is the temperature of the effusion experiment, measured with an accuracy of ± 0.01 K, A_o is the area of the effusion orifice, R is the gas constant (R = 8.314472 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$), M is the molar mass of the compound assumed monomeric, and w_o is the Clausing probability factor. The accuracy of the measured

Table 3. Static and Effusion Vapor Pressure Results for Methyl *p*-(Dimethylamino)benzoate[a]

T	p		T	p		T	p	
K	Pa	$100\ \Delta p/p$	K	Pa	$100\ \Delta p/p$	K	Pa	$100\ \Delta p/p$[b]
Crystalline Phase (Knudsen Effusion)								
311.12	0.082	1.8	319.18	0.211	−0.7	329.11	0.662	1.0
313.19	0.104	0.1	323.12	0.332	−1.0	331.17	0.829	1.0
315.17	0.131	−0.8	325.18	0.421	−0.6	333.16	1.019	0.2
317.11	0.166	−0.3	327.16	0.525	−0.7			
Crystalline Phase (Static)								
324.96	0.43	−1.9	340.86	2.46	1.2	356.72	11.68	1.8
326.93	0.53	−2.2	342.81	2.98	0.5	358.69	14.03	1.8
328.93	0.68	−0.5	344.83	3.65	0.4	360.68	16.58	0.4
330.90	0.84	−0.4	346.78	4.47	1.2	362.67	19.87	0.5
332.91	1.05	0.0	348.79	5.42	0.7	364.65	23.18	−1.9
334.88	1.30	0.2	350.75	6.55	0.6	366.61	27.25	−3.0
336.89	1.61	0.3	352.74	7.99	1.4	368.66	32.55	−3.1
338.85	1.99	0.9	354.73	9.60	0.8			
Liquid Phase (Static)								
352.78	11.05	−0.2	366.67	29.28	0.1	380.52	70.58	0.0
354.77	12.76	−0.3	368.66	33.41	0.2	382.50	79.72	0.2
356.75	14.75	0.0	370.64	37.97	0.0	384.49	89.49	−0.1
358.73	16.97	0.0	372.62	43.21	0.2	386.42	100.6	0.3
360.72	19.53	0.1	374.62	48.85	−0.3	388.46	112.6	−0.4
362.70	22.36	0.0	376.56	55.53	0.4	390.44	125.9	−0.5
364.68	25.63	0.2	378.53	62.70	0.3			

[a] Estimated uncertainties are 0.01 K for the temperature, $[0.01 + 0.0025\ (p/\mathrm{Pa})]$ Pa for the static pressures, and 0.01 Pa for the effusion pressures. [b] $\Delta p = p - p_{\mathrm{calc}}$.

Table 4. Standard (p^0 = 0.1 MPa) Molar Properties of Sublimation Derived from the Fitting of the Clarke and Glew Equation to the Experimental *p*,*T* Results

	ΔT	θ	$\Delta_{\mathrm{cr,l}}^{\mathrm{g}}G_{\mathrm{m}}^{\mathrm{o}}(\theta)$	$\Delta_{\mathrm{cr,l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(\theta)$	$\Delta_{\mathrm{cr,l}}^{\mathrm{g}}S_{\mathrm{m}}^{\mathrm{o}}$		$-\Delta_{\mathrm{cr,l}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}}$	
phase	K	K	$\mathrm{kJ\cdot mol^{-1}}$	$\mathrm{kJ\cdot mol^{-1}}$	$\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	R^2	$\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	s[a]
Methyl *p*-Methylbenzoate								
crystalline	269.3 to 301.0	298.15	22.14 ± 0.01	80.22 ± 0.06	194.8 ± 0.2	1.0000	30.6[c]	0.003
		285.12[b]		80.62 ± 0.05				
		305.94[d]		80.01 ± 0.05				
liquid[e]	293.0 to 357.0	298.15	21.62 ± 0.01	59.84 ± 0.18	128.2 ± 0.6	1.0000	74.6 ± 7.5[f]	0.007
		325.04[b]		57.84 ± 0.06				
		305.94[d]		59.26 ± 0.06				
Methyl *p*-(Dimethylamino)benzoate								
crystalline	325.0 to 368.7	298.15	38.87 ± 0.03	100.9 ± 0.2	208.0 ± 0.7	0.9999	39[c]	0.015
		346.81[b]		99.0 ± 0.2				
		368.35[d]		98.1 ± 0.2				
		298.15[g]	38.95 ± 0.03	100.1 ± 0.3	205.1 ± 1.0	0.9999		0.010
liquid[e]	352.8 to 390.4	298.15	34.73 ± 0.01	81.0 ± 0.1	155.2 ± 0.3	1.0000	94.9 ± 5.8[f]	0.005
		371.61[b]		74.0 ± 0.1				
		368.35[d]		74.3 ± 0.1				

[a] s is the standard deviation of the fit defined as $s = [(\sum_{i=1}^{n}(\ln p - \ln p_{\mathrm{calc}})_i^2/(n-m))]^{1/2}$ 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] Mean temperature. [c] Estimated value. [d] Temperature of triple point. [e] Including supercooled liquid. [f] Adjustable parameter. [g] Knudsen effusion (this work).

pressures is estimated to be better than ± 0.01 Pa. The areas and the Clausing factors of each effusion orifice, made in platinum foil of 0.0125 mm thickness, are given in the Supporting Information (Table S1).

Table 5. Triple-Point Coordinates (p,T), Temperature, and Molar Enthalpy of Fusion of the Two Compounds Studied

compound	T_{tp}	$T_{fus.}$	$\Delta_{cr}^{l}H_{m}^{o}(T^{a})$	p_{tp}	$\Delta_{cr}^{l}H_{m}^{o}(298.15\ K)$	method/reference
	K	K	$kJ\cdot mol^{-1}$	Pa	$kJ\cdot mol^{-1}$	
methyl *p*-methylbenzoate		305.09 ± 0.19	20.2 ± 0.4			DSC/this work
	305.94		20.8 ± 0.1	30.1	20.4 ± 0.2	static/this work
		306.5	20.78 ± 0.02			8, 11
		306.3				10
methyl *p*-(dimethylamino)benzoate		371.29 ± 0.05	23.4 ± 0.1			DSC/this work
	368.35		23.8 ± 0.2	32.7	19.9 ± 0.2	static/this work
		371.7	26.07			11, 12

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

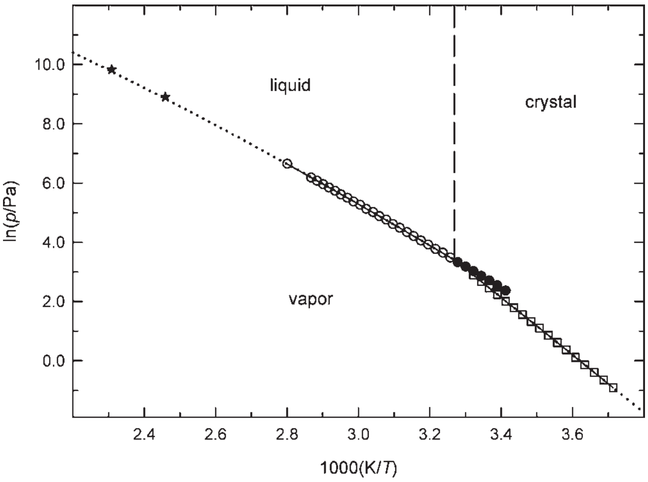

Figure 1. Phase diagram of methyl *p*-methylbenzoate. ○, static liquid vapor pressures; ●, undercooled liquid vapor pressures; □, static crystalline vapor pressures; ★, literature vapor pressures.[10] Triple-point coordinates $T = 305.94$ K, $p = 30.1$ Pa.

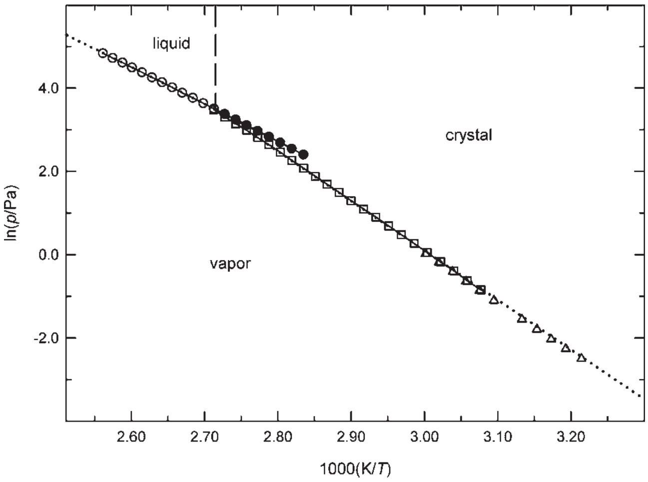

Figure 2. Phase diagram of methyl *p*-(dimethylamino)benzoate. ○, static liquid vapor pressures; ●, undercooled liquid vapor pressures; □, static crystalline vapor pressures; △, effusion vapor pressures (mean of small, medium, and large orifice results). Triple-point coordinates $T = 368.35$ K, $p = 32.7$ Pa.

RESULTS AND DISCUSSION

Static and Effusion Vapor Pressures. Table 2 presents the vapor pressure results measured using the static method in the crystalline and the liquid (both stable and undercooled) phases, for the methyl *p*-methylbenzoate. Table 3 lists the mean pressures derived from the Knudsen effusion results at several temperatures. The detailed experimental results obtained from each effusion cell at each studied temperature are summarized in Table S2 (Supporting Information). The static vapor pressure results for the crystalline and liquid phases of the methyl *p*-(dimethylamino)benzoate, including vapor pressures results of the undercooled liquid, are also listed in Table 3. The experimental data of the solid and liquid vapor pressures were fitted (independently) by the truncated form of the Clarke and Glew equation (eq 2),[6]

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

where p is the vapor pressure at the temperature T, p° is a selected reference pressure ($p^{\circ} = 10^{5}$ Pa in this work), θ is a selected reference temperature ($\theta = 298.15$ K in this work), and $\Delta_{cd}^{g}G_{m}^{o}(\theta)$ is the difference in molar Gibbs energy between the gaseous and the crystalline or liquid phases (condensed phases) at the selected reference pressure. $\Delta_{cd}^{g}H_{m}^{o}(\theta)$ is the difference in molar enthalpy between the gas and the condensed phases, and $\Delta_{cd}^{g}C_{p,m}^{o}(\theta)$ is the difference in molar heat capacity at constant pressure between the gaseous and the condensed phase. The results of the fittings are presented in Table 4. The results of $\Delta_{l}^{g}C_{p,m}^{o}(298.15\ K)$, presented in Table 4, were derived directly from the regression of eq 2 to the liquid vapor pressure–temperature data over the (64 and 38) K temperature interval for methyl *p*-methylbenzoate and methyl *p*-(dimethylamino)benzoate, respectively. The values of $\Delta_{cr}^{g}C_{p,m}^{o}(\theta)$ in eq 2 were estimated for the two compounds using eq 3 proposed by Chickos et al.[7]

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

The following values were inserted in eq 3: methyl *p*-methylbenzoate, $C_{p,m}^{o}(g)(cr) = 199.12\ J\cdot K^{-1}\cdot mol^{-1}$,[8] and methyl

Table 6. Enthalpies of the Intermolecular Hydrogen Bond OH···O in Crystalline Benzoic Acids

	$\Delta_{\text{HB}}H$(crystal)
compound	$\text{kJ}\cdot\text{mol}^{-1}$
benzoic acid	26.7
p-methylbenzoic acid	26.6
p-(dimethylamino)benzoic acid	27.6
mean	27.0

p-(dimethylamino)benzoate, $C^{\text{o}}_{p,\text{m}}(\text{g})(\text{cr}) = 254.23\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (derived using group contribution values recommended by Domalsky and Hearing[9]).

Figures 1 and 2 represent the pressure−temperature phase diagrams for methyl *p*-methylbenzoate and methyl *p*-(dimethylamino)benzoate, respectively. The phase diagram represented in Figure 1 includes two vapor pressure results calculated in the present study using the Antoine equation presented in literature:[10] T = 406.69 K (lower limit of applicability), $p = 7.35\cdot10^{3}$ Pa; T = 433.15 K (upper limit of applicability), $p = 18.6\cdot10^{3}$ Pa. These values are higher than the pressures derived from extrapolation of our vapor pressure equation to those temperatures by, respectively, 6 % and 7 %. To the best of our knowledge, there are no other reported values for vapor pressures of the compounds studied. The static crystalline vapor pressure of methyl *p*-(dimethylamino)benzoate at the temperature 298.15 K exceed the vapor pressure measured by the effusion method in 3 %, and the enthalpies of sublimation derived from the two different techniques for this compound agree within 0.8 %. This agreement also validates the assumption of absence of dimerization in the gas phase: The effusion vapor pressures calculated using eq 1 depend on the molar mass of the effusing vapor, while those measured using the static method are independent of the molar mass.

Triple Points and Fusion. Table 5 lists the values of the temperatures and enthalpies of fusion derived from the DSC. This table also presents the temperature and pressure of the triple point determined from the vapor pressure measurements and the enthalpies of fusion derived from the enthalpies of vaporization and of sublimation, at the triple point temperature. Small discrepancies between the temperature of the triple point, derived from the intersection of the liquid and crystal vapor pressure curves, and the temperature of fusion, derived calorimetrically, are usually observed. This is normally a consequence of the proximity of the slopes of the two intersecting curves. For methyl *p*-methylbenzoate, the temperature of the triple point is 0.85 K higher than the value of the temperature of fusion obtained through the calorimetric experiments and about 0.5 K lower than the mean of the two literature results.[8,10,11] The enthalpy of fusion derived from the static vapor pressures is 3 % higher than the value obtained from DSC analysis, and it equals within the uncertainty the literature value.[8,11] The temperature of fusion of methyl *p*-(dimethylamino)benzoate, obtained by calorimetric analysis, is 2.94 K higher than the value determined by the static measurements. The enthalpy of fusion obtained indirectly from the vaporization and sublimation enthalpies is in good agreement with the DSC results but outside the mutual uncertainties. The temperature of fusion reported in literature for this compound is about 2 K lower.[11,12] The proximity between the values derived indirectly from the vapor pressure curves with the calorimetric ones gives strong consistency to the results derived from the vapor pressure study.

Hydrogen Bonds in the Crystalline Packing of Benzoic Acids. Most benzoic acids dimerize in the crystalline phase, connected by two OH···O intermolecular hydrogen bonds. The determination of the enthalpy of intermolecular hydrogen bond OH···O in benzoic acid, *p*-methylbenzoic acid, and *p*-(dimethylamino)benzoic acid was carried out using a similar approach to that used before for determining the intermolecular hydrogen bonds NH···O in benzamide and in *N*-methylbenzamide.[1]

Benzoic Acid. According to the crystal structure of benzoic acid,[13] there is one OH···O bond per molecule with a length of 264 pm. The other intermolecular approach distances are over 300 pm.[13] As the parent ester—methyl benzoate—does not form any hydrogen bond, the following equations can be used to calculate the enthalpy of each intermolecular hydrogen bond in benzoic acid,

$$\Delta^{\text{g}}_{\text{cr}}H^{\text{o}}_{\text{m}}(\text{acid}) = A + \Delta_{\text{HB}}H \tag{4}$$

$$\Delta^{\text{g}}_{\text{cr}}H^{\text{o}}_{\text{m}}(\text{parent ester}) = A + B \tag{5}$$

where A represents the contribution of all intermolecular interactions (with exception of those originated by hydrogen bonding) to the enthalpy of sublimation, $\Delta_{\text{HB}}H$ is the enthalpy of the hydrogen bond per molecule of benzoic acid, and B is the increment in the enthalpy of sublimation of a crystalline compound when a hydrogen atom, not involved in a hydrogen bonding, is replaced by a methyl group. Solving the above equations, the following solution is achieved:

$$\Delta_{\text{HB}}H = \Delta^{\text{g}}_{\text{cr}}H^{\text{o}}_{\text{m}}(\text{acid}) - \Delta^{\text{g}}_{\text{cr}}H^{\text{o}}_{\text{m}}(\text{parent ester}) + \text{B} \tag{6}$$

The enthalpy of sublimation of benzoic acid was selected from literature as $\Delta^{\text{g}}_{\text{cr}}H_{\text{m}}(298.15\ \text{K}) = 90.2\ \text{kJ}\cdot\text{mol}^{-1}$.[14] The enthalpy of sublimation of benzoate $\Delta^{\text{g}}_{\text{cr}}H^{\text{o}}_{\text{m}}$ (298.15 K) = 71.7 $\text{kJ}\cdot\text{mol}^{-1}$ was calculated by adding the enthalpy of vaporization $\Delta^{\text{l}}_{\text{cr}}H^{\text{o}}_{\text{m}}$ (298.15 K) = (55.57 ± 0.04) $\text{kJ}\cdot\text{mol}^{-1}$[15] to the enthalpy of fusion $\Delta^{l}_{\text{cr}}H^{\text{o}}_{\text{m}}$ (298.15 K) = 16.1 $\text{kJ}\cdot\text{mol}^{-1}$. The latter result was derived from the value $\Delta^{\text{l}}_{\text{cr}}H^{\text{o}}_{\text{m}}$ (261 K) = 13.9 $\text{kJ}\cdot\text{mol}^{-1}$[16] using the value $\{C^{\text{o}}_{p,\text{m}}(\text{g})(\text{l}) - C^{\text{o}}_{p,\text{m}}(\text{g})(\text{cr})\} = 59.05\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ calculated from the values $C^{\text{o}}_{p,\text{m}}(\text{g})(\text{l})$ (benzoate) = 222.01 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $C^{\text{o}}_{p,\text{m}}(\text{g})(\text{cr})$ (benzoate) = 162.96 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ estimated using a method of group additivity suggested by Domalsky and Hearing.[9] The value B = 8.2 $\text{kJ}\cdot\text{mol}^{-1}$ was estimated as before[1] from the enthalpies of sublimation of several compounds presented in the Supporting Information (Table S3). Inserting this value in eq 6, the enthalpy of each intermolecular hydrogen bond in benzoic acid was calculated as $\Delta_{\text{HB}}H = 26.7\ \text{kJ}\cdot\text{mol}^{-1}$.

***p*-Methylbenzoic Acid.** The crystalline packing of *p*-methylbenzoic acid shows one hydrogen bond OH···O, per molecule, with l = 263 pm. The lengths of the other intermolecular contacts are higher than 347 pm.[17] Using eq 6, the enthalpy of the hydrogen bond in *p*-methylbenzoic acid was calculated as $\Delta_{\text{HB}}H$ = 26.6 $\text{kJ}\cdot\text{mol}^{-1}$ inserting the values $\Delta^{\text{g}}_{\text{cr}}H_{\text{m}}{}^{\text{o}}(298.15\ \text{K}) = 98.6$ $\text{kJ}\cdot\text{mol}^{-1}$ for *p*-methylbenzoic acid[14,18] and $\Delta^{\text{g}}_{\text{cr}}H^{\text{o}}_{\text{m}}(298.15\ \text{K}) = 80.2\ \text{kJ}\cdot\text{mol}^{-1}$, determined in this work, for methyl *p*-methylbenzoate.

***p*-(Dimethylamino)benzoic Acid.** Taking into account the crystal structure of *p*-(dimethylamino)benzoic acid, there is also one hydrogen bond OH···O, per molecule, with 262 pm in length. The distances of the other intermolecular contacts ranges from 350 pm to about 404 pm.[19] Equation 6 was used to calculate the $\Delta_{\mathrm{HB}}H$ = 27.6 kJ·mol^{-1} considering the values $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) = 120.3 kJ·mol^{-1} for *p*-(dimethylamino)benzoic acid[14] and $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) = 100.9 kJ·mol^{-1} calculated in the present study for methyl *p*-(dimethylamino)benzoate.

The enthalpies of the intermolecular hydrogen bonds in the crystalline phase of benzoic acids calculated from the parent esters are summarized in Table 6. These results may be compared with the enthalpies of OH···O hydrogen bonds calculated by Aihara[20] for the crystalline phases of *p*-formylphenol, 30 kJ·mol^{-1}, *p*-acetylphenol, 27 kJ·mol^{-1}, and *p*-methoxyphenol, 26 kJ·mol^{-1}. The latter two results are close to the values derived in this work for the hydrogen bonds of the three considered benzoic acids.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Detailed data of the effusion orifices (area and Clausing factors) of the Knudsen apparatus and vapor pressure results related to the small, medium, and large effusion orifices for the methyl *p*-(dimethylamino)benzoate and literature values for the increment in the enthalpy of sublimation when an H atom not involved in a hydrogen bonding is replaced by CH_3 in different molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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