

# Vapour pressures, enthalpies and entropies of sublimation of *para* substituted benzoic acids

Manuel J. S. Monte · Luís M. N. B. F. Santos ·  
José M. S. Fonseca · Carlos A. D. Sousa

Portuguese Special Chapter

Received: 15 January 2009 / Accepted: 30 March 2009 / Published online: 12 January 2010

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**Abstract** The vapour pressures of six *para*-substituted benzoic acids were measured using the Knudsen effusion method within the pressure range (0.1–1 Pa) in the following temperature intervals: 4-hydroxybenzoic acid (365.09–387.28) K; 4-cyanobenzoic acid (355.14–373.28) K; 4-(methylamino)benzoic acid (359.12–381.29) K; 4-(dimethylamino)benzoic acid (369.29–391.01) K; 4-(acetylamino)benzoic acid (423.10–443.12) K; 4-acetoxybenzoic acid (351.28–373.27) K. From the temperature dependence of the vapour pressure, the standard molar enthalpy, entropy and Gibbs energy of sublimation, at the temperature 298.15 K, were derived for each of the studied compounds using estimated values of the heat capacity differences between the gaseous and the crystalline phases. Equations for estimating the vapour pressure of *para* substituted benzoic acids at the temperature of 298.15 K are proposed.

**Keywords** Vapour pressure · Knudsen effusion · Heat capacity · Enthalpy of sublimation · Entropy of sublimation · Benzoic acids · 4-Hydroxybenzoic acid · 4-Cyanobenzoic acid · 4-(Methylamino)benzoic acid · 4-(Dimethylamino)benzoic acid · 4-(Acetylamino)benzoic acid · 4-Acetoxybenzoic acid

## Introduction

The vapour pressure of a pure substance is a key physical property that is required for several thermodynamic calculations related mainly with thermochemistry, chemical engineering and environmental studies. Most published data of vapour pressures are for volatile substances for which there are many accurate results. The measurement of vapour pressures of low volatile substances, however, is technically difficult and the accuracy of published results is often poor. Many hazard substances are very low volatile solids that present vapour pressures at ambient temperatures smaller than 1  $\mu$ Pa. The knowledge of vapour pressure data for these substances is crucial for evaluation of their fate in the environment.

Our research group has been quite involved in the study of volatility of solid organic compounds. Correlations between the enthalpy of sublimation and the temperature of sublimation at a reference pressure, or between the enthalpy of sublimation and the standard Gibbs energy of sublimation at 298.15 K, have been derived [1–7], with the aim of finding accurate estimations of sublimation vapour pressures for low volatile organic compounds. Although the variation of sublimation vapour pressure with the temperature is nowadays the most used experimental method to determine enthalpy of sublimation, this important thermodynamic property may be determined without measuring vapour pressures—directly, using calorimetry, or indirectly, calculating the difference between the enthalpy of formation in the gas phase (which may be estimated by computational approaches or using group enthalpic contributions) and the enthalpy of formation of the crystalline phase (which is normally determined from combustion calorimetry). Since the measurement of

M. J. S. Monte (✉) · L. M. N. B. F. Santos ·  
J. M. S. Fonseca · C. A. D. Sousa  
Department of Chemistry, Faculty of Science, Centro de  
Investigação em Química, University of Porto, Rua do Campo  
Alegre, 687, 4169-007 Porto, Portugal  
e-mail: mjmonte@fc.up.pt

very small vapour pressures is technically very difficult, methods for estimating vapour pressures from values of enthalpy of sublimation would be very useful.

In this study, it was decided to investigate how correlations between standard Gibbs energy of sublimation (which is a measure of the vapour pressure at a reference temperature) and enthalpy of sublimation apply to a series of *para* substituted benzoic acids. Therefore, we collected available literature data for these compounds and decided to perform a thermodynamic study on the sublimation of other six *para* substituted benzoic acids.

## Experimental

### Compounds and purity control

All the compounds studied in this study were obtained commercially from Aldrich Chemical Co. with the following assessed molar purities: 4-hydroxybenzoic acid (CAS n. 99-96-7), 99.8%, 4-cyanobenzoic acid (CAS n. 619-65-8), 99.0%, 4-(methylamino)benzoic acid (CAS n. 10541-83-0), 97.8%, 4-(dimethylamino)benzoic acid (CAS n. 619-84-1), 99.7%, 4-(acetylamino)benzoic acid (CAS n. 556-08-1), 98%, 4-acetoxybenzoic acid (CAS n. 2345-34-8), 98.6%. All the compounds were purified by sublimation under reduced pressure ( $p = 1$  Pa) previously to the experimental study. Purity of each compound was further checked by differential scanning calorimetry which was also used to verify if any phase transition occurs between 298.15 K and the temperature of fusion.

### Differential scanning calorimetry

The enthalpy and the temperature of fusion of the sublimed samples (hermetically sealed in steel crucibles) were measured using a power compensated differential scanning calorimeter, Setaram DSC 141, under a heating rate of  $3.3 \times 10^{-2} \text{ K s}^{-1}$ . 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 [8]: naphthalene, benzoic acid and indium. For each compound, at least four independent runs were performed. Mean results and standard deviations of the temperatures (observed at the onset of the calorimetric peaks) of fusion,  $T_{\text{fus}}$ , and of the molar enthalpies of fusion,  $\Delta_{\text{cr}}^1 H_{\text{m}}^{\circ}(T_{\text{fus}})$  are presented in Table 1 together with the mass fractions of impurity,  $x$ , calculated through a fractional fusion technique [9]. This table also presents the temperature of fusion of other *para* substituted benzoic acids, benzoic acid and benzene as these data were used together with values

**Table 1** Enthalpies of fusion,  $\Delta_{\text{cr}}^1 H_{\text{m}}^{\circ}(T_{\text{fus}})$ , and molar fraction of impurities,  $x$ , of the studied compounds

Compound	$10^3 x$	$T_{\text{fusion}}/\text{K}$	$\Delta_{\text{cr}}^1 H_{\text{m}}^{\circ}/\text{kJ mol}^{-1}$	References
HOBA	0.5	$489.4 \pm 0.1$	$32.5 \pm 0.1$	This study
CNBA	0.4	$495.4 \pm 0.1$	$31.8 \pm 0.1$	This study
MABA	0.6	$435.9 \pm 0.2$	$21.0 \pm 0.1$	This study
DMABA	3.8	$512.5 \pm 0.2$	$34.1 \pm 0.1$	This study
AABA	0.5	$531.7 \pm 0.2$	$42.4 \pm 0.1$	This study
ACOBA	0.7	$464.8 \pm 0.2$	$30.5 \pm 0.1$	This study
BA		395.52		[10]
FBA		456		[11]
CIBA		$512.5 \pm 0.2$		[12]
BrBA		$526.3 \pm 0.4$		[12]
IBA		$543.7 \pm 0.2$		[13]
MBA		$452.3 \pm 0.2$		[14]
ABA		461.4		[15]
MOBA		$455.3 \pm 0.2$		[10]
NBA		512.4		[15]
MOCBA		$492.54 \pm 0.54$		[7]
Benzene		$278.67 \pm 0.01$		[16]

Temperatures of fusion,  $T_{\text{fusion}}$ , of the studied and other compounds  
*HOBA* 4-hydroxybenzoic acid, *CNBA* 4-cyanobenzoic acid, *MABA* 4-(methylamino)benzoic acid, *DMABA* 4-(dimethylamino)benzoic acid, *AABA* 4-(acetylamino)benzoic acid, *ACOBA* 4-acetoxybenzoic acid, *BA* benzoic acid, *FBA* 4-fluorobenzoic acid, *CIBA* 4-chlorobenzoic acid, *BrBA* 4-bromobenzoic acid, *IBA* 4-iodobenzoic acid, *MBA* 4-methylbenzoic acid, *ABA* 4-aminobenzoic acid, *MOBA* 4-methoxybenzoic acid, *NBA* 4-nitrobenzoic acid, *MOCBA* 4-methoxycarbonylbenzoic acid

of enthalpy of sublimation to develop correlations to estimate vapour pressures. Crystal I–crystal II transition phases were observed at the temperature ( $410.3 \pm 0.1$ ) K for 4-(methylamino)benzoic acid ( $\Delta_{\text{cr}}^{\text{crII}} H_{\text{m}} = 3.6 \pm 0.1 \text{ kJ mol}^{-1}$ ) and at the temperature ( $324.7 \pm 0.2$ ) K for

**Table 2** Areas and Clausing factors of the effusion orifices

Orifice	$A_{\text{o}}/\text{mm}^2$	$w_{\text{o}}$
Small orifices		
A1	0.502	0.988
A2	0.499	0.988
A3	0.497	0.988
Medium orifices		
B4	0.774	0.991
B5	0.783	0.991
B6	0.773	0.991
Large orifices		
C7	1.116	0.992
C8	1.125	0.992
C9	1.150	0.992

$w_{\text{o}} = \{1 + (3/8r)\}^{-1}$ , where  $l$  is the length of the effusion orifice ( $l = 0.0125$  mm) and  $r$  is its radius

**Table 3** Effusion results for the studied compounds

<i>T</i> /K	<i>t</i> /s	Orifices	<i>m</i> /mg			<i>p</i> /Pa		
			<i>M</i> <sub>S</sub>	<i>M</i> <sub>M</sub>	<i>M</i> <sub>L</sub>	<i>P</i> <sub>S</sub>	<i>P</i> <sub>M</sub>	<i>P</i> <sub>L</sub>
4-Hydroxybenzoic acid								
365.09	11797	A1-B4-C7	1.70	2.72	3.78	0.108	0.112	0.108
367.29	11797	A3-B6-C9	2.18	3.30	5.92	0.140	0.136	0.135
369.23	11797	A2-B5-C8	2.66	4.19	4.87	0.171	0.171	0.168
371.08	21961	A1-B4-C7	5.97	9.33	13.00	0.205	0.208	0.200
373.22	21961	A2-B5-C8	7.42	11.63	16.41	0.257	0.256	0.251
375.28	21961	A3-B6-C9	9.12	14.06	20.48	0.319	0.315	0.308
377.29	17086	A3-B6-C9	8.70	13.37	19.43	0.392	0.386	0.377
379.22	17086	A2-B5-C8	10.50	16.58	23.12	0.472	0.474	0.459
381.07	17086	A1-B4-C7	12.66	19.65	27.39	0.566	0.570	0.550
383.06	10744	A1-B4-C7	9.45	15.12	21.08	0.674	0.699	0.674
385.21	10744	A2-B5-C8	11.91	18.70	26.17	0.857	0.856	0.833
387.28	10744	A3-B6-C9	14.40	22.26	32.32	1.045	1.036	1.009
4-Cyanobenzoic acid								
355.14	24888	A1-B4-C7	5.90	9.20	13.07	0.170	0.171	0.168
357.22	24888	A2-B5-C8	7.34	11.46	16.21	0.213	0.211	0.208
359.28	24888	A3-B6-C9	9.04	13.91	20.57	0.264	0.261	0.259
361.27	23305	A3-B6-C9	10.34	15.79	23.44	0.324	0.317	0.316
363.24	23305	A2-B5-C8	12.58	19.58	27.59	0.393	0.389	0.381
365.14	23305	A1-B4-C7	15.15	23.34	33.19	0.471	0.471	0.463
367.28	10006	A3-B6-C9	7.96	12.21	18.08	0.585	0.576	0.572
369.24	10006	A2-B5-C8	9.64	15.01	21.15	0.707	0.700	0.685
371.13	10006	A1-B4-C7	11.55	17.81	25.16	0.844	0.843	0.824
373.28	12228	A3-B6-C9	17.31	26.53	38.88	1.050	1.032	1.015
4-(Methylamino)benzoic acid								
359.12	26346	A1-B4-C7	3.43	5.19	7.35	0.092	0.091	0.089
361.23	26346	A2-B5-C8	4.35	6.63	9.38	0.118	0.115	0.113
363.29	26346	A3-B6-C9	5.26	8.20	12.25	0.144	0.144	0.144
365.28	22762	A3-B6-C9		8.89	13.20		0.181	0.181
367.23	22762	A2-B5-C8		10.83	15.55		0.218	0.218
369.13	22762	A1-B4-C7	8.68	13.44	18.80	0.274	0.275	0.266
371.29	16731	A3-B6-C9	8.03	12.24	18.34	0.350	0.342	0.344
373.23	16731	A2-B5-C8	9.81	15.35	21.35	0.427	0.425	0.410
375.12	16731	A1-B4-C7	11.95	18.38	25.85	0.518	0.516	0.502
377.12	11857	A1-B4-C7	10.38	16.07	22.60	0.636	0.639	0.621
379.22	11857	A2-B5-C8	12.85	16.66	27.98	0.795		0.765
381.29	11857	A3-B6-C9	15.86	24.16	36.01	0.989	0.966	0.966
4-(Dimethylamino)benzoic acid								
369.29	28177	A3-B6-C9	7.09	11.01	15.59	0.120	0.119	0.114
371.20	28177	A2-B5-C8	5.83	9.35	12.98	0.144	0.147	0.141
373.06	28177	A1-B4-C7	4.85	7.50	10.72	0.174	0.175	0.172
375.07	20775	A1-B4-C7	6.45	9.91	14.08	0.215	0.214	0.211
377.20	20775	A2-B5-C8	7.96	12.35	17.41	0.268	0.265	0.259
379.29	20775	A3-B6-C9	9.58	14.85	21.40	0.325	0.323	0.313
381.07	20042	A1-B4-C7	11.01	17.12	24.17	0.384	0.387	0.378
383.21	20042	A2-B5-C8		20.95	29.65		0.469	0.461
385.28	20042	A3-B6-C9	16.54	25.24	36.36	0.587	0.574	0.555

**Table 3** continued

<i>T</i> /K	<i>t</i> /s	Orifices	<i>m</i> /mg			<i>p</i> /Pa		
			<i>M</i> <sub>S</sub>	<i>M</i> <sub>M</sub>	<i>M</i> <sub>L</sub>	<i>P</i> <sub>S</sub>	<i>P</i> <sub>M</sub>	<i>P</i> <sub>L</sub>
387.28	10367	A3-B6-C9	10.31	15.86	22.79	0.709	0.699	0.674
389.17	10367	A2-B5-C8	12.41	19.40	27.02	0.851	0.846	0.819
391.01	10367	A1-B4-C7	14.66	22.56	31.87	1.001	0.999	0.976
4-(Acetylamino)benzoic acid								
423.10	24517	A1-B4-C7	5.81	8.87	12.78	0.168	0.166	0.165
425.22	24517	A2-B5-C8		11.11	15.20		0.206	0.196
427.27	24517	A3-B6-C9	8.76	13.30	19.03	0.257	0.250	0.240
429.10	18078	A1-B4-C7	7.68	11.30	16.30	0.303	0.289	0.288
431.22	18078	A2-B5-C8		13.99	19.44		0.354	0.341
433.28	18078	A3-B6-C9	11.07	16.96	24.06	0.443	0.436	0.415
435.28	11936	A3-B6-C9	8.96	13.76	19.86	0.545	0.536	0.520
437.23	11936	A3-B6-C9		16.46	23.07		0.635	0.618
439.17	11936	A2-B5-C8	12.71	19.33	27.47	0.767	0.756	0.744
441.29	9169	A2-B5-C8	11.45	17.37		0.913	0.888	
443.12	9169	A1-B4-C7	13.41	20.09	28.63	1.059	1.028	1.014
4-Acetoxybenzoic acid								
351.28	29791	A3-B6-C9	5.03	7.72	11.40	0.110	0.108	0.107
353.23	29791	A2-B5-C8	6.24	9.73	13.83	0.136	0.135	0.133
355.13	29791	A1-B4-C7	7.65	11.83	16.82	0.166	0.166	0.164
357.27	23204	A3-B6-C9	7.44	11.45	16.93	0.210	0.207	0.206
359.23	23204	A2-B5-C8	9.22	14.27	20.26	0.260	0.256	0.252
361.13	23204	A1-B4-C7	11.12	17.32	24.75	0.312	0.315	0.312
363.13	15684	A1-B4-C7	9.23	14.25	20.39	0.385	0.385	0.381
365.24	15684	A2-B5-C8	11.60	17.77	25.28	0.488	0.475	0.470
367.28	15684	A3-B6-C9	14.10	21.68	31.83	0.598	0.589	0.581
369.13	10779	A1-B4-C7	11.68	18.13	25.70	0.714	0.718	0.705
371.22	10779	A2-B5-C8	14.52	22.52	31.78	0.895	0.883	0.866
373.27	10779	A3-B6-C9	17.62	27.25	39.69	1.096	1.086	1.062

Results related to the small (A1, A2, A3), medium (B4, B5, B6) and large (C7, C8, C9) effusion orifices are denoted, respectively, by the subscripts *S*, *M* and *L*

4-acetoxybenzoic acid ( $\Delta_{\text{cr}}^{\text{rll}}H_{\text{m}} = 1.5 \pm 0.1 \text{ kJ mol}^{-1}$ ). For the other studied compounds no phase transitions were detected between the temperature 298.15 K and the temperature of fusion.

#### Vapour pressures measurements

The vapour pressures of each crystalline compound were measured at several temperatures using a Knudsen effusion apparatus enabling the simultaneous operation of nine effusion cells at three different temperatures. The detailed description of this apparatus and the results obtained by measuring vapour pressures between 0.1 and 1 Pa of benzoic acid, phenanthrene, anthracene, benzanthrone and 1,3,5-triphenylbenzene were published before [17]. Both the measured vapour pressures and the derived enthalpies

of sublimation were in excellent agreement with literature results and recommended values for those compounds. The nine effusion cells are contained in cylindrical holes inside three aluminium blocks. During an effusion experiment, each aluminium 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” ( $A_{\text{o}} \approx 0.5 \text{ mm}^2$ ; series A), one “medium” ( $A_{\text{o}} \approx 0.8 \text{ mm}^2$ ; series B) and one “large” ( $A_{\text{o}} \approx 1.1 \text{ mm}^2$ ; series C). The exact areas and Clausing factors of each used effusion orifice in platinum foil of 0.0125 mm thickness are given in Table 2.

For the temperature *T*, the vapour 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

vapour,  $R$  is the gas constant,  $A_o$  is the area of the effusion orifice and  $w_o$  is the respective Clausing factor.

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

## Results

Table 3 presents, for the studied compounds, the experimental results obtained from each effusion cell at each studied temperature as well as the global results obtained for each compound from all the three effusion cells.

Table 4 presents for the three series of effusion orifices and for the global treatment of all the ( $p, T$ ) data obtained for each studied compound, the detailed parameters of the Clausius–Clapeyron equation,  $\ln(p/\text{Pa}) = a - b(K/T)$ , where  $a$  is a constant and  $b = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle)/R$ , and the

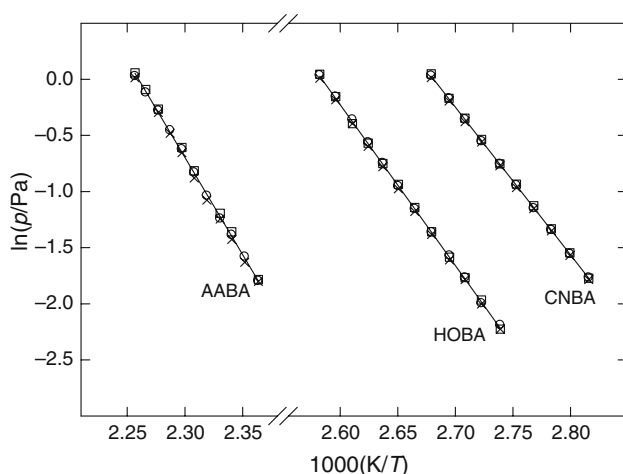
standard molar enthalpies of sublimation at the mean temperature of the experiments  $T = \langle T \rangle$ . The equilibrium pressure at this temperature  $p(\langle T \rangle)$  and the entropies of sublimation at equilibrium conditions,  $\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}\{\langle T \rangle, p(\langle T \rangle)\} = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle)/(\langle T \rangle)$ , are also presented. The plots of  $\ln(p/\text{Pa})$  versus  $1/T$  for the six studied compounds are presented in Figs. 1 and 2.

In order to derive, at the reference temperature 298.15 K, the standard molar enthalpy of sublimation,  $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\theta)$ , and the standard molar Gibbs energy of sublimation,  $\Delta_{\text{cr}}^{\text{g}} G_{\text{m}}^{\circ}(\theta)$ , the experimental results of the vapour pressures were also fitted by the Clarke and Glew Eq. 2 [18].

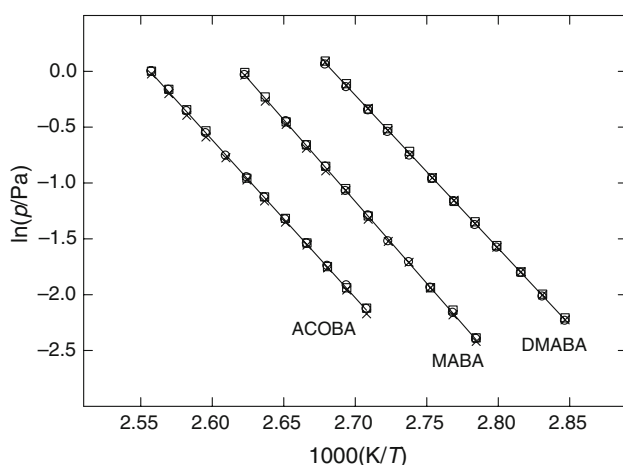
$$R \cdot \ln\left(\frac{p}{p^{\circ}}\right) = -\frac{\Delta_{\text{cr}}^{\text{g}} G_{\text{m}}^{\circ}(\theta)}{\theta} + \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\theta) \left(\frac{1}{\theta} - \frac{1}{T}\right) + \Delta_{\text{cr}}^{\text{g}} C_{\text{p,m}}^{\circ}(\theta) \left[\left(\frac{\theta}{T}\right)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

**Table 4** Experimental results for the studied compounds where  $a$  and  $b$  are from Clausius–Clapeyron equation  $\ln(p/\text{Pa}) = a - b(K/T)$ , and  $b = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle)/R$ ;  $R = 8.31472 \text{ J K}^{-1} \text{ mol}^{-1}$

Effusion orifices	$a$	$b$	$\langle T \rangle/\text{K}$	$p(\langle T \rangle)/\text{Pa}$	$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle)/\text{kJ mol}^{-1}$	$\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}\{\langle T \rangle, p(\langle T \rangle)\}/\text{J K}^{-1} \text{ mol}^{-1}$	$R^2$
4-Hydroxybenzoic acid							
A	$37.05 \pm 0.17$	$14335 \pm 62$		0.348	$119.2 \pm 0.5$		0.9998
B	$37.03 \pm 0.18$	$14328 \pm 68$		0.348	$119.1 \pm 0.6$		0.9998
C	$36.87 \pm 0.10$	$14275 \pm 39$		0.341	$118.7 \pm 0.3$		0.9999
Global	$36.98 \pm 0.14$	$14313 \pm 53$	376.2	0.344	$119.0 \pm 0.4$	$316.3 \pm 1.1$	0.9995
4-Cyanobenzoic acid							
A	$35.42 \pm 0.11$	$13207 \pm 42$		0.430	$109.8 \pm 0.4$		0.9999
B	$35.28 \pm 0.08$	$13159 \pm 29$		0.427	$109.4 \pm 0.2$		1.0000
C	$35.13 \pm 0.09$	$13109 \pm 32$		0.421	$109.0 \pm 0.3$		1.0000
Global	$35.28 \pm 0.13$	$13158 \pm 47$	364.2	0.428	$109.4 \pm 0.4$	$300.4 \pm 1.3$	0.9996
4-(Methylamino)benzoic acid							
A	$38.34 \pm 0.15$	$14627 \pm 56$		0.303	$121.6 \pm 0.5$		0.9999
B	$38.39 \pm 0.14$	$14648 \pm 51$		0.311	$121.8 \pm 0.4$		0.9999
C	$38.22 \pm 0.19$	$14591 \pm 71$		0.306	$121.3 \pm 0.6$		0.9998
Global	$38.32 \pm 0.13$	$14628 \pm 50$	370.3	0.306	$121.6 \pm 0.4$	$328.4 \pm 1.1$	0.9996
4-(Dimethylamino)benzoic acid							
A	$36.29 \pm 0.12$	$14188 \pm 47$		0.358	$118.0 \pm 0.4$		0.9999
B	$36.00 \pm 0.14$	$14080 \pm 54$		0.356	$117.1 \pm 0.5$		0.9999
C	$36.03 \pm 0.18$	$14103 \pm 68$		0.345	$117.2 \pm 0.6$		0.9998
Global	$36.10 \pm 0.16$	$14120 \pm 62$	380.2	0.354	$117.4 \pm 0.5$	$308.8 \pm 1.3$	0.9994
4-(Acetylamino)benzoic acid							
A	$38.99 \pm 0.29$	$17245 \pm 127$		0.437	$143.4 \pm 1.1$		0.9996
B	$38.99 \pm 0.37$	$17256 \pm 159$		0.426	$143.5 \pm 1.3$		0.9992
C	$39.25 \pm 0.42$	$17377 \pm 182$		0.418	$144.5 \pm 1.5$		0.9990
Global	$39.20 \pm 0.31$	$17345 \pm 134$	433.1	0.428	$144.2 \pm 1.1$	$325.0 \pm 1.3$	0.9982
4-Acetoxybenzoic acid							
A	$36.81 \pm 0.13$	$13710 \pm 47$		0.356	$114.0 \pm 0.4$		0.9999
B	$36.82 \pm 0.10$	$13718 \pm 35$		0.352	$114.1 \pm 0.3$		0.9999
C	$36.65 \pm 0.07$	$13660 \pm 25$		0.349	$113.6 \pm 0.2$		1.0000
Global	$36.76 \pm 0.10$	$13696 \pm 6$	362.3	0.352	$113.9 \pm 0.3$	$314.4 \pm 0.8$	0.9998



**Fig. 1** Plots of  $\ln p$  vs.  $1/T$  for 4-(acetylamino)benzoic acid (AABA), 4-hydroxybenzoic acid (HOBA) and 4-cyanobenzoic acid (CNBA). Open square, small effusion orifices; circle, medium effusion orifices; times, large effusion orifices



**Fig. 2** Plots of  $\ln p$  vs.  $1/T$  for 4-acetoxybenzoic acid (ACOBA), 4-(methylamino)benzoic acid (MABA) and 4-(dimethylamino)benzoic acid (DMABA). Open square, small effusion orifices; circle, medium effusion orifices; times, large effusion orifices

where  $p$  is the vapour pressure at the temperature  $T$ ,  $p^\circ$  is a selected reference pressure ( $p^\circ = 10^5$  Pa in this study),  $\theta$  is a selected reference temperature ( $\theta = 298.15$  K in this study),  $R$  is the molar gas constant and  $\Delta_{\text{cr}}^{\text{g}}C_{\text{p,m}}^\circ(\theta)$  is the difference between the gaseous and the crystalline phase in molar heat capacity at constant pressure. This equation was also used to derive the standard molar Gibbs energy of sublimation and the standard molar enthalpy of sublimation of the other compounds presented in Tables 1, 5 and 6 using values of vapour pressures presented in literature and the molar heat capacity differences presented in Table 5. The thermodynamic parameters derived from Eq. 2 and the standard molar entropy of sublimation, calculated as  $\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}^\circ(\theta) = [\{\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^\circ(\theta) - \Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^\circ(\theta)\}/\theta]$ , are also presented in this table as well as the respective standard

deviations. For benzene and for 4-aminobenzoic acid the vapour pressures presented in literature are smoothed values obtained from adjustment equations considering  $\Delta_{\text{cr}}^{\text{g}}C_{\text{p,m}}^\circ = 0$ , and so it was not possible to assign experimental uncertainties to the values of  $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^\circ$  calculated through Eq. 2 for these two compounds.

With the exception of benzene, the values of the molar heat capacity of the gaseous phase,  $C_{\text{p,m}}^\circ(\text{g})$ , at the temperature 298.15 K, for the compounds presented in Table 5, were calculated in this study using computational chemistry. The geometry optimizations, as well as the fundamental vibrational frequency calculations, were performed using density functional theory (DFT) with the hybrid exchange correlation functional B3LYP at the 6-311++G(d,p) level of theory. The frequencies were scaled using the scale factor of 0.9688 [19] and the heat capacities in the gaseous state were determined for all the compounds using the scaled vibrational frequency calculations. All the theoretical calculations were performed using the Gaussian 03 software package [20]. Since the molar heat capacity of the crystalline phase,  $C_{\text{p,m}}^\circ(\text{cr})$ , at the temperature 298.15 K, was known for only five of the compounds presented in the table, we estimated the heat capacity differences, from  $C_{\text{p,m}}^\circ(\text{g})$ , using Eq. 3 which is a rearrangement of Eq. 4 proposed by Chickos et al. [21] for estimation of  $\{C_{\text{p,m}}^\circ(\text{g}) - C_{\text{p,m}}^\circ(\text{cr})\}$  at the temperature 298.15 K, from  $C_{\text{p,m}}^\circ(\text{cr})$  values:

$$\Delta_{\text{cr}}^{\text{g}}C_{\text{p,m}}^\circ(\theta)/\text{JK}^{-1}\text{mol}^{-1} = -\{0.9 + 0.176 C_{\text{p,m}}^\circ(\text{g})\} \quad (3)$$

$$\Delta_{\text{cr}}^{\text{g}}C_{\text{p,m}}^\circ(\theta)/\text{JK}^{-1}\text{mol}^{-1} = -\{0.75 + 0.15 C_{\text{p,m}}^\circ(\text{cr})\}. \quad (4)$$

The estimated  $\Delta_{\text{cr}}^{\text{g}}C_{\text{p,m}}^\circ$  values presented in Table 5 are in reasonable agreement with the available experimental values which were always the ones selected to insert in Eq. 2. The largest discrepancy is observed for 4-nitrobenzoic acid.

## Discussion

To the best of our knowledge, there are not published vapour pressure for five of the studied compounds. For 4-hydroxybenzoic acid there are two published values for the enthalpy of sublimation, differing from each other about  $6 \text{ kJ mol}^{-1}$  at the temperature 298.15 K, but only one of those values was derived from vapour pressure measurements. Sabbah and Le [30] presented the calorimetric value  $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^\circ(T = 298.15 \text{ K}) = (114.1 \pm 0.7) \text{ kJ mol}^{-1}$  while Davis and Jones [31] determined the value  $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^\circ(T = 415.3 \text{ K}) = (116.1 \pm 0.4) \text{ kJ mol}^{-1}$ . Adjusting Eq. 2 to the vapour pressures measured by Davis and Jones, we calculated the values  $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^\circ(T = 298.15 \text{ K}) = (119.8 \pm 0.5) \text{ kJ mol}^{-1}$  and  $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^\circ(T = 298.15 \text{ K}) = (55.6 \pm 0.1) \text{ kJ mol}^{-1}$  (using the estimated value  $\Delta_{\text{cr}}^{\text{g}}C_{\text{p,m}}^\circ = -27 \text{ JK}^{-1}\text{mol}^{-1}$ ) which are in

**Table 5** Heat capacities and standard ( $p^\circ = 0.1$  MPa) molar enthalpy, entropy and Gibbs energies of sublimation, at  $T = 298.15$  K, of benzene, benzoic acid and *para* substituted benzoic acids

Compound	$C_{p,m}^\circ/(g)JK^{-1}mol^{-1}$	$C_{p,m}^\circ(cr)/JK^{-1}mol^{-1}$	$\Delta_{cr,p,m}^\circ C_{p,m}^\circ/JK^{-1}mol^{-1}$ (experimental)	$\Delta_{cr,p,m}^\circ C_{p,m}^\circ/JK^{-1}mol^{-1}$ (estimated)	$\Delta_{cr}^\circ H_m^\circ/kJmol^{-1}$	$\Delta_{cr}^\circ S_m^\circ/JK^{-1}mol^{-1}$	$\Delta_{cr}^\circ G_m^\circ/kJmol^{-1}$
HOBA	147 <sup>a</sup>			-27	121.1 ± 0.4 <sup>a</sup>	218.0 ± 1.4 <sup>a</sup>	56.1 ± 0.1 <sup>a</sup>
CNBA	152 <sup>a</sup>			-28	111.2 ± 0.4 <sup>a</sup>	202.9 ± 1.4 <sup>a</sup>	50.7 ± 0.1 <sup>a</sup>
MABA (crI)	174 <sup>a</sup>			-32	123.9 ± 0.4 <sup>a</sup>	230.1 ± 1.4 <sup>a</sup>	55.3 ± 0.1 <sup>a</sup>
DMABA	194 <sup>a</sup>			-35	120.3 ± 0.5 <sup>a</sup>	213.0 ± 1.7 <sup>a</sup>	56.8 ± 0.1 <sup>a</sup>
AABA	198 <sup>a</sup>			-35	148.9 ± 1.1 <sup>a</sup>	243.2 ± 3.8 <sup>a</sup>	76.4 ± 0.3 <sup>a</sup>
ACOA (crII)	195 <sup>a</sup>			-35	116.1 ± 0.3 <sup>a</sup>	216.7 ± 1.1 <sup>a</sup>	51.5 ± 0.1 <sup>a</sup>
BA	125 <sup>a</sup>	146.8 <sup>c</sup>	-22	(-23)	90.2 ± 0.5 <sup>e</sup>	188.7 ± 1.7 <sup>e</sup>	33.95 ± 0.02 <sup>e</sup>
BA					90.8 ± 0.1 <sup>f</sup>	190.6 ± 0.3 <sup>f</sup>	33.98 ± 0.01 <sup>f</sup>
MBA	149 <sup>a</sup>	169.0 <sup>d</sup>	-20	(-27)	97.6 ± 0.5 <sup>g</sup>	192.9 ± 1.7 <sup>g</sup>	40.1 ± 0.1 <sup>g</sup>
FBA	139 <sup>a</sup>			-25	92.8 ± 0.8 <sup>h</sup>	187.5 ± 2.8 <sup>h</sup>	36.9 ± 0.2 <sup>h</sup>
CIBA	143 <sup>a</sup>	167.8 <sup>d</sup>	-25	(-26)	104.5 ± 0.5 <sup>i</sup>	197.2 ± 1.7 <sup>i</sup>	45.7 ± 0.1 <sup>i</sup>
BrBA	145 <sup>a</sup>			-26	108.9 ± 0.5 <sup>j</sup>	201.2 ± 1.7 <sup>j</sup>	48.9 ± 0.1 <sup>j</sup>
IBA				-26 <sup>A</sup>	112.9 ± 0.5 <sup>j</sup>	202.2 ± 1.7 <sup>j</sup>	52.6 ± 0.1 <sup>j</sup>
ABA	153 <sup>a</sup>	177.8 <sup>d</sup>	-25	(-28)	115.1 ± 1	205.9 <sup>k</sup>	53.7 <sup>k</sup>
MOBA	167 <sup>a</sup>			-30	111.2 ± 0.6 <sup>l</sup>	212.0 ± 2.0 <sup>l</sup>	48.0 ± 0.1 <sup>l</sup>
NBA	164 <sup>a</sup>	180.3 <sup>d</sup>	-16	(-30)	116.6 ± 0.6 <sup>m</sup>	210.0 ± 2.0 <sup>m</sup>	54.0 ± 0.1 <sup>m</sup>
MOCBA	192 <sup>a</sup>			-35	123.5 ± 0.5 <sup>n</sup>	228.4 ± 1.7 <sup>n</sup>	55.4 ± 0.1 <sup>n</sup>
Benzene	82.4 <sup>b</sup>			-15.4	50.0 ± 2 <sup>o</sup>	160.1 <sup>o</sup>	2.27 <sup>o</sup>

<sup>a</sup> This study; <sup>b</sup> [22]; <sup>c</sup> [23]; <sup>d</sup> [15]; <sup>e-o</sup> The values presented in this table were calculated through Eq. 2 from the vapour pressures presented in the following references: <sup>e</sup> [17]; <sup>f</sup> [24]; <sup>g</sup> [14]; <sup>h</sup> [25]; <sup>i</sup> [12]; <sup>j</sup> [13]; <sup>k</sup> [26]; <sup>l</sup> [27]; <sup>m</sup> [28]; <sup>n</sup> [7]; <sup>o</sup> [29]

<sup>A</sup> Estimated value accordingly to the value of  $\Delta_{cr}^\circ C_{p,m}^\circ$  for the other 4-halobenzoic acids. Note: values of  $\Delta_{cr}^\circ C_{p,m}^\circ$  inside parenthesis were not selected

**Table 6** Vapour pressures at  $T = 298.15$  K calculated by inserting in Eq. 8 the values of  $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}$  calculated using Eqs. 2, 5, 6 and 7

Compound	$p^{\circ}$ (Eq. 2)/ Pa	$p^{\circ}$ (Eq. 5)/ Pa	$p^{\circ}$ (Eq. 6)/ Pa	$p^{\circ}$ (Eq. 7)/ Pa
HOBA	$1.5 \times 10^{-5}$			$1.3 \times 10^{-5}$
CNBA	$1.3 \times 10^{-4}$	$1.4 \times 10^{-4}$		$1.6 \times 10^{-4}$
MABA (crI)	$2.0 \times 10^{-5}$		$1.2 \times 10^{-5}$	$1.3 \times 10^{-5}$
DMABA	$1.1 \times 10^{-5}$	$7.8 \times 10^{-6}$		$1.2 \times 10^{-5}$
AABA	$4.1 \times 10^{-9}$		$5.6 \times 10^{-9}$	$4.9 \times 10^{-9}$
ACOB (crII)	$9.5 \times 10^{-5}$		$1.3 \times 10^{-4}$	$6.8 \times 10^{-5}$
BA	$1.1 \times 10^{-1a}$	$9.6 \times 10^{-2}$		$1.5 \times 10^{-1}$
MBA	$9.4 \times 10^{-3}$	$1.0 \times 10^{-2}$		$1.0 \times 10^{-2}$
FBA	$3.4 \times 10^{-2}$	$4.6 \times 10^{-2}$		$3.5 \times 10^{-2}$
CIBA	$9.9 \times 10^{-4}$	$1.1 \times 10^{-3}$		$7.2 \times 10^{-4}$
BrBA	$2.7 \times 10^{-4}$	$2.9 \times 10^{-4}$		$1.9 \times 10^{-4}$
IBA	$6.1 \times 10^{-5}$	$8.1 \times 10^{-5}$		$5.1 \times 10^{-5}$
ABA	$3.9 \times 10^{-5}$	$4.0 \times 10^{-5}$		$6.9 \times 10^{-5}$
MOBA	$3.9 \times 10^{-4}$		$5.8 \times 10^{-4}$	$2.7 \times 10^{-4}$
NBA	$3.5 \times 10^{-5}$	$2.5 \times 10^{-5}$		$3.0 \times 10^{-5}$
MOCBA	$2.0 \times 10^{-5}$		$1.3 \times 10^{-5}$	$6.6 \times 10^{-6}$
Benzene <sup>b</sup>	$4.0 \times 10^4$	$3.4 \times 10^4$		$3.2 \times 10^4$

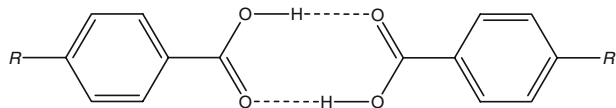
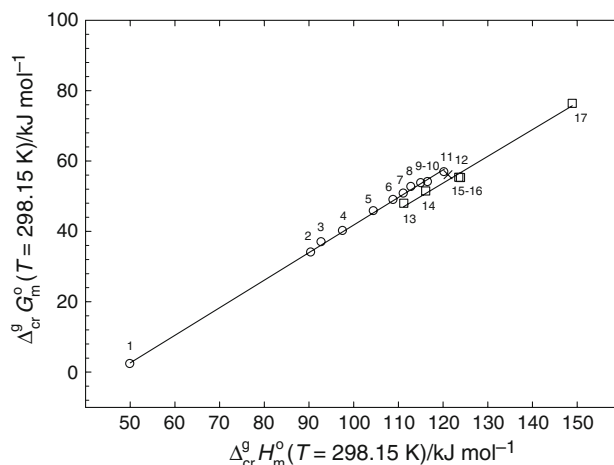
<sup>a</sup> Calculated from the mean of the values of  $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}$  presented for benzoic acid in Table 5

<sup>b</sup> Since benzene is liquid at 298.15 K, these values refer to the hypothetical sublimation pressure at this temperature

reasonable agreement with the results derived from the vapour pressures measured in the present study.

Similarly to other carboxylic acids, *para* substituted benzoic acids dimerize in the crystalline phase as presented in Fig. 3, where  $R$  represents the substituent group.

Leiserowitz [32] observed that the crystalline package of the carboxylic acids formed by symmetric molecules is characterised by an identical intramolecular environment about the carbonyl and hydroxyl oxygen atoms, which enables two equivalent orientations of the carboxyl dimers, mutually indistinguishable. The higher degree of orientational disorder of the crystalline symmetric carboxyl dimers explain the smaller values of entropy of sublimation of the *para*-substituted halobenzoic acids (symmetric molecules) when compared with the *ortho* and *meta* isomers [12] yielding to lower volatility of the *para* isomers. For other *para*-substituted benzoic acids, the symmetry of

**Fig. 3** Representation of the dimers presented in the crystalline package of *para* substituted benzoic acid, where  $R$  represents the substituent**Fig. 4** Plot of  $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}(T = 298.15 \text{ K}) = f\{\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(T = 298.15 \text{ K})\}$  for the compounds with symmetric molecules (circle) and for the compounds with asymmetric molecules (open square). 1, benzene; 2, benzoic acid; 3, FBA; 4, MBA; 5, CIBA; 6, BrBA; 7, CNBA; 8, IBA; 9, ABA; 10, NBA; 11, DMABA; 12, HOBA (times); 13, MOBA; 14, ACOBA; 15, MOCBA; 16, MABA; 17, AABA

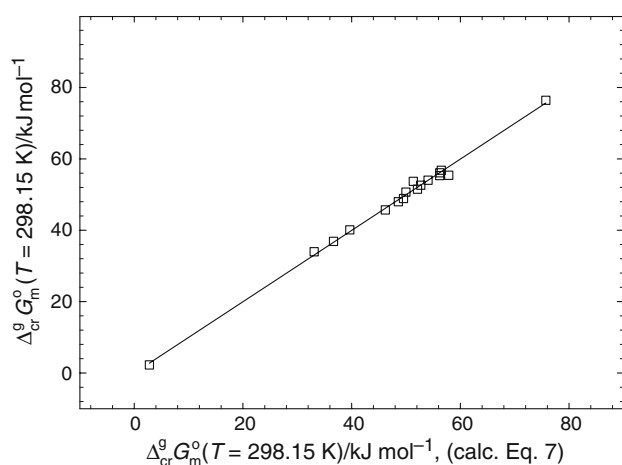
the molecules depends on the substituent group being or not symmetric. Therefore, it was expected that the entropy of sublimation of those compounds would be influenced by the degree of symmetry of the substituent. In fact, two distinct straight lines are observed in Fig. 4 representing the plotting  $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}(T = 298.15 \text{ K}) = f\{\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(T = 298.15 \text{ K})\}$ . One for the results of the compounds containing symmetric substituent groups  $R$ , Eq. 5, which includes also the results of benzoic acid and of benzene, and another for the results of the compounds containing asymmetric substituent groups ( $R =$  acetamido, acethylamino, acetoxy, methoxy and methoxycarbonyl), Eq. 6. Since the stable phase of benzene at the temperature of 298.15 K is the liquid phase, the results for this compound refers to a hypothetical crystalline phase.

$$\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}(T = 298.15 \text{ K}) = -(36.5 \pm 0.9) + (0.783 \pm 0.009)\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(T = 298.15 \text{ K}); R^2 = 0.9988 \quad (5)$$

$$\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}(T = 298.15 \text{ K}) = -(37.5 \pm 5.5) + (0.76 \pm 0.04)\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(T = 298.15 \text{ K}); R^2 = 0.9901. \quad (6)$$

For similar values of  $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(T = 298.15 \text{ K})$ , the values of  $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}(T = 298.15 \text{ K})$  for the compounds with symmetric groups  $R$  are about  $4 \text{ kJ mol}^{-1}$  higher than those with asymmetric substituents. The results related to 4-hydroxybenzoic acid were not included in the data used to derive any of the two correlations due to the fact that the dimers are held together in the crystals by hydrogen bonds formed between the phenolic groups [33]—the point representing the results





**Fig. 5** Plot of  $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}(T = 298.15 \text{ K}) = f \{ \Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}(T = 298.15 \text{ K})$ , calculated through Eq. 7} for benzene, benzoic acid and *para* substituted benzoic acids

for this compound seems to be positioned between the two straight lines presented in Fig. 4.

In order to derive a unique correlation to estimate  $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}(T = 298.15 \text{ K})$  independently of the degree of the orientational disorder presented in the crystalline package of the considered molecules, the temperature of fusion was included as a second independent variable. This correlation, Eq. 7, presented in Fig. 5, adjusts very well ( $R^2 = 0.9964$ ) to most of the results of the considered compounds containing either symmetric or asymmetric molecules, including 4-hydroxybenzoic acid.

$$\begin{aligned} \Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}(T = 298.15 \text{ K}) = & -(39.4 \pm 1.8) \\ & + (0.65 \pm 0.02)\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(T = 298.15 \text{ K}) \\ & + (0.035 \pm 0.006)T_{\text{fusion}}. \end{aligned} \quad (7)$$

Table 6 presents the values of the sublimation vapour pressure, at  $T = 298.15 \text{ K}$ , calculated inserting in Eq. 8, where  $R$  is the gas constant, the values of  $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}(T = 298.15 \text{ K})$  derived by Eq. 2 and estimated by Eqs. 5, 6 and 7.

$$\ln(p/10^5 \text{ Pa}) = -\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}(T = 298.15 \text{ K})/298.15R. \quad (8)$$

Comparing the values of the pressures calculated using Eq. 2 with the values calculated using the proposed Eq. 7, we conclude that Eq. 7 may be used, together with Eq. 8, to estimate with reasonable accuracy vapour pressures of *para*-substituted benzoic acids, independently of the degree of symmetry of the substituent.

**Acknowledgements** Thanks are due to Fundação para a Ciência e Tecnologia (FCT) Lisbon, Portugal, for financial support given to Centro de Investigação em Química of University of Porto and to the Project POCTI/QUI/43144/2001 which was also financed through FEDER.

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