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Thermodynamic Study of 4-*n*-Alkyloxybenzoic Acids

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The Knudsen mass-loss effusion technique was used for measuring the vapor pressures at different temperatures of the following 4-*n*-alkyloxybenzoic acids: 4-methoxybenzoic acid, between (340 and 362) K; 4-ethoxybenzoic acid, between (349 and 373) K; 4-propoxybenzoic acid, between (345 and 365) K; 4-butoxybenzoic acid, between (351 and 373) K; 4-pentyloxybenzoic acid, between (355 and 377) K; 4-hexyloxybenzoic acid, between (363 and 379) K; 4-heptyloxybenzoic acid, between (355 and 361) K; and 4-octyloxybenzoic acid, between (363 and 372) K. From the temperature dependence of the vapor pressure of each crystalline compound, the standard ($p^o = 10^5$ Pa) molar enthalpies and Gibbs energies of sublimation, at $T = 298.15$ K, were derived. Differential scanning calorimetry was used in the study of phase transitions between condensed phases. The measured thermodynamic properties are compared with the results obtained on a previous similar study concerning the 4-*n*-alkylbenzoic acids series.

Introduction

Our research group has been investigating the volatility of different aromatic carboxylic acids[1−11] with the aim of understanding the factors that contribute to the observed volatilities. An important part of this study is concerned with substituted benzoic acids.[4−11] In this work, we decided to perform a thermodynamic study on the sublimation of eight 4-*n*-alkyloxybenzoic acids, from 4-methoxybenzoic acid to 4-octyloxybenzoic acid, to compare the results with those obtained from a similar study on the 4-*n*-alkylbenzoic acids.[8]

Several 4-*n*-alkyloxybenzoic acids present liquid crystal phases, as first observed by Bradfield and Jones in 1929 during purification of synthesized 4-propoxybenzoic and 4-butoxybenzoic acids.[12] The fact that 4-propoxybenzoic acid was, by that time, the simplest molecular structure to yield a mesomorphic form (explained by the authors on the assumption of self-association of the molecules) lead to subsequent works[13−15] where other compounds of the series were studied and their liquid crystal properties were related with structural assumptions. During subsequent years, other authors have studied the phase transitions on this series of compounds.[16−18] 4-Methoxybenzoic acid was also the subject of several calorimetric studies and has been proposed for a reference material in calorimetry.[19−22]

Some of the compounds studied in this work present antituberculotic activity, with emphasis for 4-pentyloxybenzoic acid, which shows relevant antimycobacterial activity comparable with that of commercial antituberculotics when tested in vitro.[23]

Experimental Section

Materials. All the compounds studied in this work are commercial products from Aldrich Chemical Co.: 4-methoxybenzoic acid (MetOBA; CAS no. 100-09-4); 4-ethoxybenzoic acid (EtOBA; CAS no. 619-86-3); 4-propoxybenzoic acid (PropOBA; CAS no. 5438-19-7); 4-butoxybenzoic acid (ButOBA; CAS no. 1498-96-0); 4-pentyloxybenzoic acid (PentOBA; CAS no. 15872-41-0); 4-hexyloxybenzoic acid (HexOBA; CAS no. 1142-39-8); 4-heptyloxybenzoic acid (HeptOBA; CAS no. 15872-42-1), and 4-octyloxybenzoic acid (OctOBA; CAS no. 2493-84-7). Previously to the experimental study, samples of all the compounds were purified by repeated sublimation under reduced pressure ($p = 1$ Pa), except the sample of 4-ethoxybenzoic acid which was purified by zone melting. The final molar purity of all isomers was assessed through a fractional fusion technique[24] as being better than 99.9 %.

Differential Scanning Calorimetry. DSC was used for measuring the temperatures and enthalpies of transitions between condensed phases. The experiments were made in hermetically sealed steel crucibles using a power compensated differential scanning calorimeter, SETARAM model DSC 141, under a heating rate of $2\ \mathrm{K \cdot min^{-1}}$, from 295 K up to a temperature higher than the temperature of isotropization of each compound. The calibration of the power scale of the calorimeter was performed using high-purity indium (mass fraction > 99.999 %). 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.[25] For each compound, at least three independent runs were performed.

Vapor Pressure Measurements. A mass-loss Knudsen-effusion apparatus which enables the simultaneous operation of nine effusion cells, contained in cylindrical holes inside three temperature-controlled aluminum blocks, was used to measure the vapor pressure of the purified crystalline samples of each of the eight 4-*n*-alkyloxybenzoic acids at different temperatures. During an effusion experiment, each aluminum block is kept at a constant temperature (different from the temperature of the other two blocks) and contains three effusion cells with effusion 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 temperature of each block is measured using a platinum resistance thermometer Pt100 class

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Table 1. Areas and Clausing Factors of the Effusion Orifices[a]

	orifice	A_o/mm^2	w_o
small orifices	A_1	0.502	0.988
	A_2	0.499	0.988
	A_3	0.497	0.988
medium orifices	B_4	0.774	0.991
	B_5	0.783	0.991
	B_6	0.773	0.991
large orifices	C_7	1.116	0.992
	C_8	1.125	0.992
	C_9	1.150	0.992

[a] $w_o = \{1 + (3l/8r)\}^{-1}$, where l is the length of the effusion orifice ($l = 0.0125$ mm) and r is its radius.

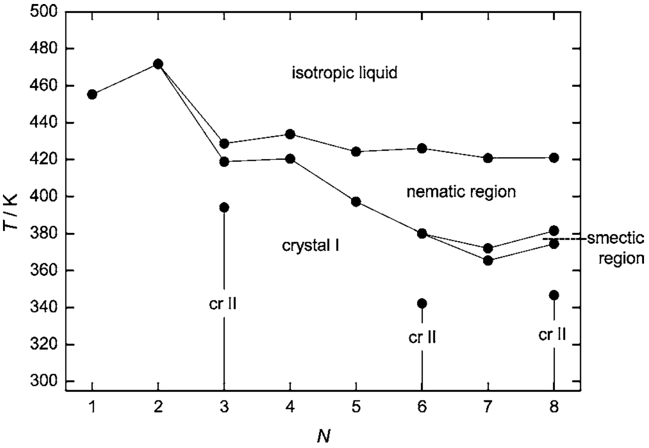

Figure 1. Phase transition temperatures for the series of 4-*n*-alkyloxybenzoic acids. *N* stands for the number of carbons in the aliphatic chain (e.g., $N = 1$ for the 4-methoxybenzoic acid).

1/10 DIN (in a four wire connection) previously calibrated by comparison with an SPRT (25 Ω; Tinsley, 5187A). The detailed description of this apparatus and the results obtained by measuring vapor pressures between (0.1 and 1) Pa of benzoic acid, phenanthrene, anthracene, benzanthrone, and 1,3,5-triphenylbenzene were previously published.[26] Both the measured vapor pressures and the derived enthalpies of sublimation were in excellent agreement with literature results and recommended values for those compounds.

For the effusion experiments, 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 accuracy of ± 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 exact areas and Clausing factors of each used effusion orifice in platinum discs of 0.0125 mm thickness are given in Table 1. All the platinum discs were commercially obtained from Goodfellow Cambridge Limited, which also measured the diameter of the effusion orifices and the thickness of the disks. The results were confirmed in our research group using a calibrated microscope. The accuracy of the measured pressures is estimated to be better than ± 0.01 Pa.

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

Results and Discussion

Differential Scanning Calorimetry. The results for the transition temperatures (observed at the onset of the calorimetric peaks) are presented in Table 2, together with values found in the literature and in Figure 1. It should be noticed that the lines presented in the plots have no physical meaning and are intended to help the visualization of the liquid crystal behavior of this series of compounds. The molar enthalpies of the transitions between condensed phases are also presented in Table 2. All the scannings were performed from the temperature 295 K up

Table 2. Temperatures and Molar Enthalpies of the Transitions between Condensed Phases of the Studied Compounds

	MetOBA		EtOBA		PropOBA		ButOBA		PentOBA		HexOBA		HeptOBA		OctOBA		
	T	$(\Delta_\alpha^\beta H_m)$	T	$(\Delta_\alpha^\beta H_m)$	T	$(\Delta_\alpha^\beta H_m)$	T	$(\Delta_\alpha^\beta H_m)$	T	$(\Delta_\alpha^\beta H_m)$	T	$(\Delta_\alpha^\beta H_m)$	T	$(\Delta_\alpha^\beta H_m)$	T	$(\Delta_\alpha^\beta H_m)$	
$\alpha \rightarrow \beta$ transition	K	(kJ·mol^{-1})	K	(kJ·mol^{-1})	K	(kJ·mol^{-1})	K	(kJ·mol^{-1})	K	(kJ·mo^{-1})	K	(kJ·mol^{-1})	K	(kJ·mol^{-1})	K	(kJ·mol^{-1})	ref
crystal−crystal					394.1	8.08					342.2	5.95			346.7	17.87	this work
					389								363		345		14
					394	8.0					348	6.7			348	18.0	17
crystal−smectic													365.4	27.59	374.5	11.57	this work
													365		374		15, 16
													367	19.3	374	10.9	17
crystal−nematic					418.8	17.03	420.4	19.55	397.2	22.04	380.0						this work
					418		420		397		378						15, 16
					419.7	16.7	420.7	18.8	398	21.8	380						17
							420.9	19.1									18
crystal−isotropic	455.3	28.97	471.8	35.07													this work
	457		469														15
	457																17
	457.8	28.4	475.8	29.7													18
	456.7	28.33															19
	456.5	29.72															20
	456.55																21
	456.12																22
smectic−nematic													372.1	1.94	381.6	1.38	this work
													371		381		15, 16
													373	10.9	381	1.3	17
nematic−isotropic					428.7	27.19	433.7	2.77	424.2	2.16	426.1	3.16	420.8	2.11	421.0	1.38	this work
					427		433		424		426		419		420		15, 16
					426.7	27.2	432	2.9	422	2.1	426	3.3	420	2.5	419	2.5	17

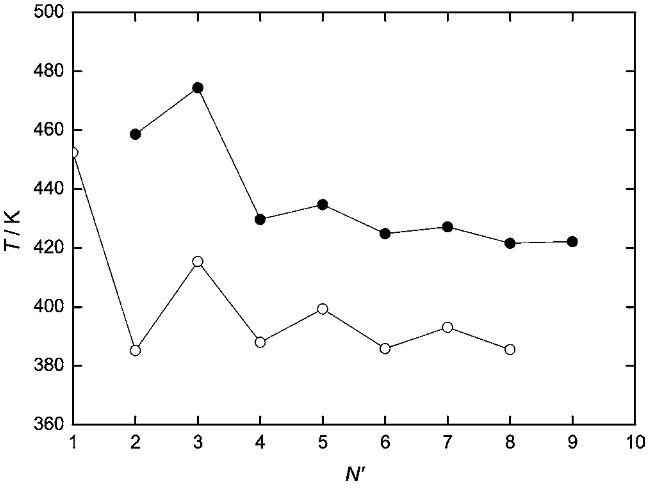

Figure 2. Temperatures of isotropization of the 4-*n*-alkyloxybenzoic acids and of the 4-*n*-alkylbenzoic acids.[8] N' represents the number of carbons (N) in the alkylic chain for the 4-*n*-alkylbenzoic acids, and $N' = N + 1$ for the 4-*n*-alkyloxybenzoic acids (e.g., $N' = 2$ for 4-ethylbenzoic acid and for 4-methoxybenzoic acid).

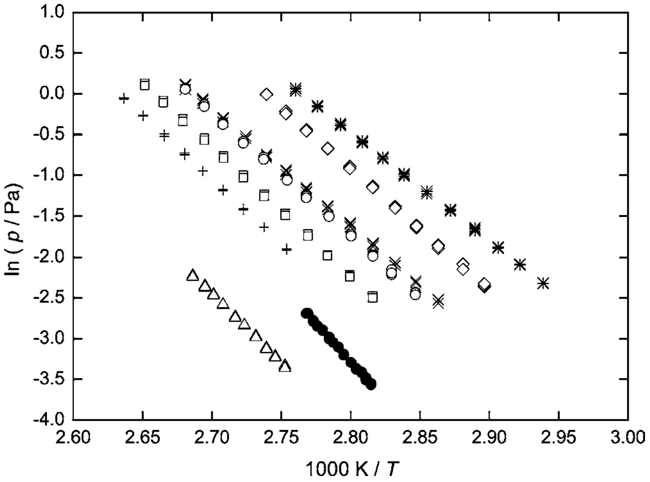

Figure 3. Plots of ln p against $1/T$ for the series of 4-*n*-alkyloxybenzoic acids. $\ast$, 4-methoxybenzoic acid; $\times$, 4-ethoxybenzoic acid; ◇, 4-propoxybenzoic acid; ○, 4-butoxybenzoic acid; □, 4-pentyloxybenzoic acid; $+$, 4-hexyloxybenzoic acid; ●, 4-heptyloxybenzoic acid; Δ, 4-octyloxybenzoic acid.

to a temperature higher than the temperature of isotropization. It was not possible within this work to characterize the structure of the liquid crystal phases. The existence of smectic and nematic phases was therefore assumed as proposed in previous works on the same compounds,[14,17] in which the authors performed observations under a microscope using polarized light.

In general, the agreement of our results with literature ones is very good—most of the differences are smaller than 1 K for the transition temperatures and smaller than 1 kJ·mol^{-1} for the transition enthalpies. Exceptions to this agreement are the results for 4-heptyloxybenzoic acid related to the enthalpies of the transitions of crystal−smectic phase and smectic−nematic phases. While for the former transition the value obtained was 8 kJ·mol^{-1} lower than the value published by Herbert,[17] for the smectic−nematic transition the value derived in this work was 9 kJ·mol^{-1} higher than the result reported by this author. However, considering the sum of the enthalpies of these two phase transitions, the difference between the values reported by Herbert[17] and the present results is only 1 kJ·mol^{-1}.

A similar study was previously performed for a series of 4-*n*-alkylbenzoic acids,[8] with some of these compounds showing liquid crystal properties as well. An interesting relation was found when comparing the temperatures of isotropization for both series of compounds, as presented in Figure 2. The comparison between the temperatures of isotropization of the compounds with similar length of the aliphatic chain and belonging to each of the two series shows that: the 4-*n*-alkyloxybenzoic acids present higher temperatures of isotropization; the differences between those temperatures diminish with the size of the chain, appearing to stabilize around $\Delta T =$ 35 K for the heaviest compounds considered in this work; and for 4-*n*-alkylbenzoic acids, an odd−even effect is observed. This effect is less pronounced for the 4-*n*-alkyloxybenzoic acids. While for 4-*n*-alkylbenzoic acids the highest temperatures of isotropization are observed for odd numbers of carbons in the alkylic chain, for the series of 4-*n*-alkyloxybenzoic acids, the highest temperatures of isotropization are observed for an even number of carbons.

Vapor Pressure Measurements. Table 3 presents, for all the 4-*n*-alkyloxybenzoic acids studied, the experimental results related to each effusion cell at each studied temperature. For each temperature, results obtained using the different effusion orifices are equal within 0.01 Pa, showing that the measured pressures are nearly independent of the orifice size of the used orifices. The plots of ln(p/Pa) versus $1/T$ for the seven compounds studied are shown in Figure 3, where it is easily seen that the vapor pressures of 4-ethoxybenzoic acid are much lower than expected when compared with the pressures of its neighbors in the series. This may be due to the behavior of the temperature of fusion (odd−even effect) of the smallest members of the two series of compounds, as shown in Figure 3, and its consequence in the volatility of these compounds, as shown in Figure 5.

Table 4 presents for the three series of effusion orifices the detailed parameters of the Clausius−Clapeyron equation, $\ln(p/\text{Pa}) = a - b(\text{K}/T)$, where a is a constant and $b = \Delta_{cr}{}^{g}H_m{}^{o}(\langle T\rangle)/R$, and the standard molar enthalpies of sublimation at the mean temperature of the experiments $T = \langle T\rangle$. For each compound, these parameters are also presented for the global treatment of all the (p,T) data. This treatment of results yields values similar to the results derived from the average of the pressures measured using each effusion orifice.

The values of the standard molar enthalpy, entropy, and Gibbs energy of sublimation at the reference temperature $\theta = 298.15$ K were derived fitting the experimental results of the vapor pressures by the Clarke and Glew equation (eq 2).[27]

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

where p is the vapor pressure at the temperature T; p^{0} is a selected reference pressure ($p^{o} = 10^{5}$ Pa in this work); R is the molar gas constant; and $\Delta_{cr}^{g}C_{p,m}^{o}(\theta)$ is the difference in molar heat capacity at constant pressure between the gaseous and the crystalline phase. For 4-hexyloxybenzoic acid and 4-octyloxybenzoic acid, the studied crystalline phase (cr I) differs from the phase stable at 298.15 K (cr II). The thermodynamic parameters of sublimation for this crystalline phase (cr II) were derived taking into account the enthalpies of the crystal−crystal transitions measured by DSC, according to eq 3, based on the

Table 3. Effusion Results for the Studied Compounds[a]

				m/mg			p/mPa	
T/K	t/s	orifices	m_S	m_M	m_L	p_S	p_M	p_L
			4-methoxybenzoic acid					
340.29	28347	$A_3-B_6-C_9$	3.99	6.25	9.26	98.0	98.4	97.9
342.24	28347	$A_2-B_5-C_8$	5.02	7.93	11.47	123	124	124
344.10	28347	$A_1-B_4-C_7$	6.18	9.67	13.86	151	153	152
346.07	23372	$A_1-B_4-C_7$	6.27	10.01	14.20	186	193	189
348.20	23372	$A_2-B_5-C_8$	8.07	12.62	17.89	242	241	237
350.29	23372	$A_3-B_6-C_9$	10.00	15.51	22.55	302	301	293
352.29	18234	$A_3-B_6-C_9$	9.68	14.90	21.75	376	371	364
354.20	18234	$A_2-B_5-C_8$	11.85	18.66	26.34	459	460	451
356.07	18234	$A_1-B_4-C_7$	14.34	22.46	31.71	554	562	549
358.07	13283	$A_1-B_4-C_7$	12.84	20.22	28.41	683	697	677
360.21	13283	$A_2-B_5-C_8$	16.18	25.26	35.85	868	862	850
362.29	13283	$A_3-B_6-C_9$	19.79	30.68	44.43	1071	1064	1034
			4-ethoxybenzoic acid					
349.27	28978	$A_3-B_6-C_9$	3.44	5.34	7.65	80.1	79.8	76.7
351.26	28978	$A_2-B_5-C_8$	4.35	6.84	9.63	101	101	99
353.11	28978	$A_1-B_4-C_7$	5.48	8.42	11.76	127	126	122
355.11	21711	$A_1-B_4-C_7$	5.15	7.87	11.07	160	158	154
357.19	21711	$A_2-B_5-C_8$	6.56	10.12	14.15	205	201	196
359.27	21711	$A_3-B_6-C_9$	8.00	12.32	17.80	252	249	242
361.27	16388	$A_3-B_6-C_9$	7.54	11.53	16.59	316	310	299
363.18	16388	$A_2-B_5-C_8$	9.41	14.54	20.15	393	386	372
365.07	16388	$A_1-B_4-C_7$	11.45	17.39	24.57	477	469	459
367.06	11745	$A_1-B_4-C_7$	10.24	15.74	22.10	596	594	577
369.28	10775	$A_3-B_6-C_9$	11.59	17.86	25.49	747	738	707
371.28	11745	$A_3-B_6-C_9$	15.89	24.20	34.80	942	919	887
373.04	10775	$A_1-B_4-C_7$	17.48	26.67	36.70	1119	1106	1053
			4-propoxybenzoic acid					
345.26	10093	$A_2-B_5-C_8$	1.48	2.36	3.48	94.0	95.3	97.7
347.10	25786	$A_1-B_4-C_7$	5.01	7.74	10.49	124	124	117
349.27	17459	$A_3-B_6-C_9$	4.05	6.57	9.65	150	156	154
351.20	17459	$A_2-B_5-C_8$	5.22	8.45	12.00	193	199	196
353.08	17459	$A_1-B_4-C_7$	6.64	10.50	14.86	245	251	246
355.12	14346	$A_1-B_4-C_7$	7.15	10.95	15.71	322	320	317
357.24	14346	$A_2-B_5-C_8$	9.02	14.16	19.89	410	409	400
359.26	14346	$A_3-B_6-C_9$	11.25	17.57	25.89	516	516	511
361.27	10160	$A_3-B_6-C_9$	9.82	15.49	22.78	637	644	636
363.20	10160	$A_2-B_5-C_8$	12.45	19.67	27.43	806	810	785
365.05	10160	$A_1-B_4-C_7$	15.38	23.78		992	994	
			4-butoxybenzoic acid					
351.28	37417	$A_3-B_6-C_9$	5.25	8.11	11.80	87.9	87.0	85.0
353.40	37417	$A_2-B_5-C_8$	6.96	10.28	15.10	116	109	111
355.10	37417	$A_1-B_4-C_7$	8.30	12.88	18.31	138	139	137
357.11	22732	$A_1-B_4-C_7$	6.47	10.00	14.18	178	178	175
359.14	22732	$A_2-B_5-C_8$		12.62	18.12		222	222
361.27	22732	$A_3-B_6-C_9$	10.26	15.87	23.18	287	284	279
363.07	19273	$A_1-B_4-C_7$	10.70	16.68	23.66	349	353	346
365.32	19273	$A_2-B_5-C_8$	13.61	21.86	30.70	448	458	447
367.28	19273	$A_3-B_6-C_9$	16.81	26.23	38.12	558	559	545
369.28	14596	$A_3-B_6-C_9$	16.04	24.71	36.19	706	697	685
371.14	14596	$A_2-B_5-C_8$	20.06	31.32	44.12	880	874	855
373.03	14596	$A_1-B_4-C_7$	24.35	37.91	54.02	1064	1074	1059
			4-pentyloxybenzoic acid					
355.12	31896	$A_1-B_4-C_7$	4.38	6.89	9.69	82.5	84.1	81.9
357.24	31896	$A_2-B_5-C_8$	5.75	8.95	12.65	109	108	106
359.27	31896	$A_3-B_6-C_9$	7.21	11.32	16.67	138	139	138
361.11	25714	$A_1-B_4-C_7$	7.60	11.73	16.50	179	179	174
363.24	25714	$A_2-B_5-C_8$	9.71	15.22	21.36	231	230	225
365.28	25714	$A_3-B_6-C_9$	12.17	18.87	27.52	292	290	284
367.28	18744	$A_3-B_6-C_9$	11.18	17.35	25.09	369	367	356
369.24	18744	$A_2-B_5-C_8$	14.16	22.28	31.17	466	466	453
371.10	18744	$A_1-B_4-C_7$	17.54	27.22	38.44	575	578	565
373.27	15820	$A_3-B_6-C_9$	18.64	28.92	41.93	735	731	711
375.23	15820	$A_2-B_5-C_8$	23.36	36.76	51.56	918	919	896
377.10	15820	$A_1-B_4-C_7$	29.00	44.82	63.19	1135	1137	1110
			4-hexyloxybenzoic acid					
363.13	27624	$A_1-B_4-C_7$	6.94		15.75	148		150
365.29	27624	$A_2-B_5-C_8$	9.04	14.28	20.48	194	195	195
367.28	27624	$A_3-B_6-C_9$	11.31	17.61	25.82	245	245	241
369.28	19491	$A_3-B_6-C_9$	10.05	15.71	22.98	309	310	304
371.27	19491	$A_2-B_5-C_8$	12.60	19.89	28.50	387	388	387
373.10	19491	$A_1-B_4-C_7$	15.34	24.44	34.61	469	485	475

Table 3. Continued

			m/mg			p/mPa		
T/K	t/s	orifices	m_S	m_M	m_L	p_S	p_M	p_L
375.12	11948	$A_1-B_4-C_7$	11.79	18.78	26.44	590	609	593
377.29	11948	$A_2-B_5-C_8$	15.06	23.90	34.10	760	768	761
379.28	11948	$A_3-B_6-C_9$	18.57	29.24	42.85	945	954	939
			4-heptyloxybenzoic acid					
355.28	40720	$A_3-B_6-C_9$	2.05	3.14	4.67	28.7	28.2	28.2
355.73	40720	$A_2-B_5-C_8$	2.14	3.47	4.99	29.9	30.8	30.8
356.11	26507	$A_1-B_4-C_7$	1.53	2.37	3.44	32.6	32.7	32.9
356.60	40720	$A_1-B_4-C_7$		3.83	5.48		34.5	34.1
357.10	26210	$A_1-B_4-C_7$			3.83			37.1
357.78	25365	$A_3-B_6-C_9$	1.82	2.81	4.23	41.1	40.7	41.1
358.28	26154	$A_3-B_6-C_9$	2.05		4.75	44.9		44.8
358.75	25365	$A_2-B_5-C_8$	2.11	3.32		47.5	47.5	
359.11	25365	$A_1-B_4-C_7$	2.23	3.49	4.94	49.9	50.6	49.6
359.72	26154	$A_2-B_5-C_8$	2.53	3.94	5.72	55.3	54.8	55.2
360.23	26210	$A_2-B_5-C_8$	2.65	4.16	6.05	57.8	57.7	58.3
360.59	26154	$A_1-B_4-C_7$	2.85	4.41	6.29	62.0	62.1	61.3
361.10	27432	$A_1-B_4-C_7$		5.02	7.27		67.5	67.6
361.28	26210	$A_3-B_6-C_9$	3.08	4.80		67.7	67.6	
			4-octyloxybenzoic acid					
363.28	28229	$A_3-B_6-C_9$	1.74	2.81	4.06	34.6	35.8	34.7
364.22	28229	$A_2-B_5-C_8$	1.99	3.19	4.50	39.4	40.2	39.4
365.07	28072	$A_1-B_4-C_7$	2.22	3.47	4.93	44.0	44.5	43.8
366.07	28426	$A_1-B_4-C_7$	2.60	4.05	5.75	50.9	51.4	50.5
367.20	28426	$A_2-B_5-C_8$	2.95	4.63	6.74	58.2	58.1	58.8
368.08	28229	$A_1-B_4-C_7$	3.24	5.08	7.24	64.1	65.1	64.2
369.29	27948	$A_3-B_6-C_9$	3.69	5.84	8.68	74.7	75.8	75.6
370.20	27948	$A_2-B_5-C_8$	4.24	6.70	9.49	85.4	85.9	84.5
371.06	27948	$A_1-B_4-C_7$	4.64	7.33	10.46	93.0	95.2	94.1
372.28	28426	$A_3-B_6-C_9$	5.41		12.37	108		106

[a] Results related to the small (A_1, A_2, A_3), medium (B_4, B_5, B_6), and large (C_7, C_8, C_9) effusion orifices are denoted, respectively, by the subscripts S, M, and L.

assumption that the values of $C_{p,\mathrm{m}}^{\circ}(\mathrm{cr})$ do not differ significantly for both crystalline phases

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{0}(\text{cr II, 298.15 K}) = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{0}(\text{cr I, 298.15 K}) + \Delta_{\mathrm{cr\ II}}^{\mathrm{cr\ I}}H_{\mathrm{m}}(T_{\mathrm{tr}}) \quad (3)$$

Under equilibrium conditions, for the crystal−crystal transition, $\Delta_{\mathrm{cr\ II}}^{\mathrm{cr\ I}}G_{\mathrm{m}} = 0$, so $\Delta_{\mathrm{cr\ II}}^{\mathrm{cr\ I}}S_{\mathrm{m}}$ was calculated dividing $\Delta_{\mathrm{cr\ II}}^{\mathrm{cr\ I}}H_{\mathrm{m}}$ by the transition temperature, T_{tr}. Considering that the entropy of the crystal−crystal transition does not change significantly with the pressure and assuming once again a similar value of $C_{p,\mathrm{m}}^{\circ}(\mathrm{cr})$for the two crystalline phases, then $\Delta_{\mathrm{cr\ II}}^{\mathrm{cr\ I}}S_{\mathrm{m}}(T_{\mathrm{tr}})$ will not differ from $\Delta_{\mathrm{cr\ II}}^{\mathrm{cr\ I}}S_{\mathrm{m}}^{0}$ (298.15 K). So, the value of $\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}^{0}$ (cr II, 298.15 K) was calculated as

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}^{0}(\text{cr II, 298.15 K}) = \Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}^{0}(\text{cr I, 298.15 K}) + \Delta_{\mathrm{cr\ II}}^{\mathrm{cr\ I}}S_{\mathrm{m}}(T_{\mathrm{tr}}) \quad (4)$$

and $\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{0}$ (cr II, 298.15 K) was calculated as

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{0}(\text{cr II, 298.15 K}) = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{0}(\text{cr II, 298.15 K}) - 298.15\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}^{0}(\text{cr II, 298.15 K}) \quad (5)$$

The values of $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\circ}(\theta)$ used in eq 2 were calculated from values of $C_{p,\mathrm{m}}^{\circ}(\mathrm{cr})$ and $C_{p,\mathrm{m}}^{\circ}(\mathrm{g})$ estimated by group contribution using values recommended by Domalski and Hearing[28] for the method originally developed by Benson for the gas phase.[29] As not all the values of the contributing groups are available in both phases, we used as a starting point values of $C_{p,\mathrm{m}}^{\circ}(\mathrm{cr})$ and $C_{p,\mathrm{m}}^{\circ}(\mathrm{g})$ for benzoic acid.[11,30] The estimations of $C_{p,\mathrm{m}}^{\circ}(\mathrm{cr})$ and $C_{p,\mathrm{m}}^{\circ}(\mathrm{g})$ were based on those values and convenient addition and subtraction of group contributions, according to the following expressions where the Benson notation is used.[29]

$$C_{p,\mathrm{m}}^{0}(\text{4-methoxybenzoic ac.}) = C_{p,\mathrm{m}}^{0}(\text{benzoic ac.}) - C_{p,\mathrm{m}}^{0}\{\mathbf{C_B}\text{-(H)(C}_{\mathrm{B}})_2\} + C_{p,\mathrm{m}}^{0}\{\mathbf{C_B}\text{-(O)(C}_{\mathrm{B}})_2\} + C_{p,\mathrm{m}}^{0}\{\mathbf{O}\text{-(C)(C}_{\mathrm{B}})\} + C_{p,\mathrm{m}}^{0}\{\mathbf{C}\text{-(H)}_3\text{(O)}\} \quad (6)$$

$$C_{p,\mathrm{m}}^{0}(\text{4-ethoxybenzoic ac.}) = C_{p,\mathrm{m}}^{0}(\text{4-methoxybenzoic ac.}) - C_{p,\mathrm{m}}^{0}\{\mathbf{C}\text{-(H)}_3\text{(O)}\} + C_{p,\mathrm{m}}^{0}\{\mathbf{C}\text{-(H)}_2\text{(O)(C)}\} + C_{p,\mathrm{m}}^{0}\{\mathbf{C}\text{-(H)}_3\text{(C)}\} \quad (7)$$

For the other compounds studied, the heat capacity values were estimated from the results derived for the 4-ethoxybenzoic acid, by adding the contribution $C_{p,\mathrm{m}}^{0}\{\text{C-(H)}_2\text{(C)}_2\}$ for each methylene group added to the aliphatic chain. Domalski and Hearing[28] noted that 90 % of the results of heat capacity of condensed phases estimated using their group contribution method have an uncertainty better than ± 8 J·K^{-1}·mol^{-1}. We took this value as a measure of the uncertainty of the values estimated in the present work for both solid and gaseous heat capacity, which yielded an estimated uncertainty of ± 11 J·K^{-1}·mol^{-1} for $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\circ}$.

Table 5 presents the standard thermodynamic properties of sublimation at 298.15 K for the crystalline phases of the compounds studied, together with values for the 4-*n*-alkylbenzoic acids calculated from vapor pressure values published in a previous work[8] and values calculated from the vapor pressures found in the literature for 4-methoxybenzoic acid.[31] All the literature values were recalculated using the heat capacity differences presented in Table 5, which were estimated using a group method similar to the one described above. For 4-propyl,

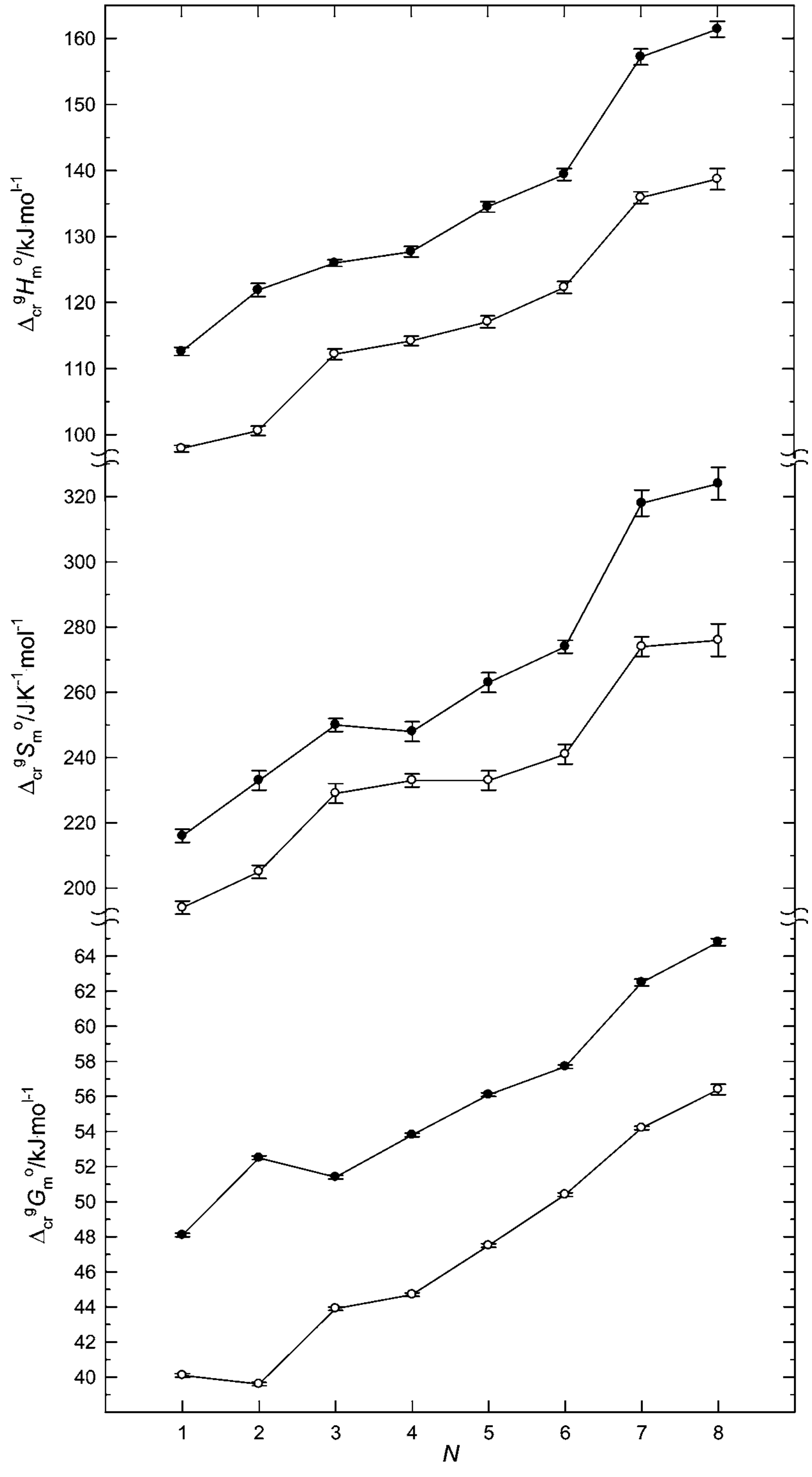

Figure 4. Standard molar enthalpy, entropy, and Gibbs energy of sublimation at $T = 298.15$ K of 4-*n*-alkyloxybenzoic acids and 4-*n*-alkylbenzoic acids as functions of the number of carbons in the aliphatic chain, *N*. ●, 4-*n*-alkyloxybenzoic acids; ○, 4-*n*-alkylbenzoic acids.

4-butyl, 4-heptyl, and 4-octyl benzoic acids, the thermodynamic parameters of the stable phases at the temperature 298.15 K were derived using the schemes described above (eq 3 to eq 5).

Figure 4 presents values of the thermodynamic parameters of sublimation as functions of the number of carbons in the aliphatic chain, for the stable crystalline phases at $T = 298.15$ K. As previously referred, the increase in the enthalpy of sublimation with the length of the chain is relatively regular in both 4-*n*-alkyloxybenzoic and 4-*n*-alkylbenzoic acids, being about 3 to 5 kJ·mol^{-1} per methylene group added to the chain. The main exceptions are the difference $\Delta[\Delta_{cr}^{g}H_{m}^{o}(298.15\ \mathrm{K})] =$ 17.8 kJ·mol^{-1} between 4-heptyloxybenzoic acid and 4-hexyloxybenzoic acid (II) and the difference $\Delta[\Delta_{cr}^{g}H_{m}^{o}(298.15\ \mathrm{K})] =$ 13.6 kJ·mol^{-1} between 4-heptylbenzoic acid (II) and 4-hexylbenzoic acid. Similar observations can be done for the values of $\Delta_{cr}^{g}S_{m}^{0}(298.15\ \mathrm{K})$. Furthermore, it seems that the influence of the oxyl group in these thermodynamic properties is independent of the length of the aliphatic chain since for both the enthalpies and the entropies there is a noticeable parallelism between the two series. The variation of $\Delta_{cr}^{g}G_{m}^{0}(298.15\ \mathrm{K})$ with the number of atoms of carbon in the aliphatic chain is somewhat more regular, with the exception of the value for 4-ethoxybenzoic

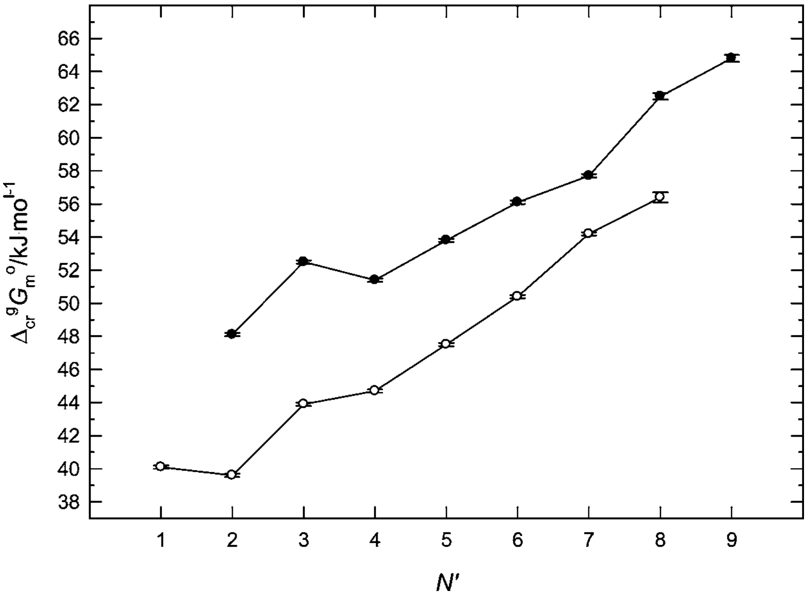

Figure 5. Standard molar Gibbs energy of sublimation at $T = 298.15$ K of 4-*n*-alkyloxybenzoic acids and 4-*n*-alkylbenzoic acids as functions of the number of carbons in the aliphatic chain, *N'*. ●, 4-*n*-alkyloxybenzoic acids; ○, 4-*n*-alkylbenzoic acids. *N'* represents the number of carbons (*N*) in the alkylic chain for the 4-*n*-alkylbenzoic acids, and $N' = N+1$ for the 4-*n*-alkyloxybenzoic acids (e.g., $N' = 2$ for 4-ethylbenzoic acid and for 4-methoxybenzoic acid).

Table 4. Experimental Results for the Studied Compounds Where *a* and *b* Are from the Clausius−Clapeyron Equation $\ln(p/\text{Pa}) = a - b(\text{K}/T)$ and $b = \Delta_{cr}^{g}H_m^{o}(\langle T\rangle)/R$

				$\langle T\rangle$	$\Delta_{cr}^{g}H_m^{o}(\langle T\rangle)$
effusion orifices	*a*	*b*	r^2	K	kJ·mol^{-1}
4-methoxybenzoic acid					
S	37.01 ± 0.12	13385 ± 43	0.9999		111.3 ± 0.4
M	36.82 ± 0.10	13316 ± 36	0.9999		110.7 ± 0.3
L	36.46 ± 0.13	13196 ± 45	0.9999		109.7 ± 0.4
global	36.76 ± 0.10	13299 ± 35	0.9998	351.29	110.6 ± 0.3
4-ethoxybenzoic acid					
S	38.77 ± 0.12	14422 ± 45	0.9999		119.9 ± 0.4
M	38.60 ± 0.11	14363 ± 40	0.9999		119.4 ± 0.3
L	38.39 ± 0.15	14298 ± 55	0.9998		118.9 ± 0.5
global	38.59 ± 0.17	14361 ± 61	0.9993	361.15	119.4 ± 0.5
4-propoxybenzoic acid					
S	41.01 ± 0.37	14974 ± 133	0.9993		124.5 ± 1.1
M	40.68 ± 0.18	14854 ± 63	0.9998		123.5 ± 0.5
L	40.48 ± 0.24	14787 ± 84	0.9997		122.9 ± 0.7
global	40.77 ± 0.18	14887 ± 62	0.9995	355.16	123.8 ± 0.5
4-butoxybenzoic acid					
S	40.23 ± 0.18	14984 ± 67	0.9998		124.6 ± 0.6
M	40.67 ± 0.20	15145 ± 74	0.9998		125.9 ± 0.6
L	40.40 ± 0.17	15053 ± 61	0.9998		125.2 ± 0.5
global	40.44 ± 0.13	15063 ± 47	0.9997	362.16	125.2 ± 0.4
4-pentyloxybenzoic acid					
S	42.34 ± 0.16	15918 ± 59	0.9999		132.3 ± 0.5
M	42.24 ± 0.14	15881 ± 50	0.9999		132.0 ± 0.4
L	42.11 ± 0.12	15840 ± 45	0.9999		131.7 ± 0.4
global	42.23 ± 0.13	15880 ± 46	0.9997	366.11	132.0 ± 0.4
4-hexyloxybenzoic acid					
S	41.34 ± 0.19	15703 ± 71	0.9999		130.6 ± 0.6
M	41.60 ± 0.18	15793 ± 65	0.9999		131.3 ± 0.5
L	41.28 ± 0.18	15678 ± 66	0.9999		130.4 ± 0.6
global	41.43 ± 0.14	15733 ± 50	0.9998	371.20	130.8 ± 0.4
4-heptyloxybenzoic acid					
S	48.79 ± 0.57	18598 ± 205	0.9986		154.6 ± 1.7
M	48.94 ± 0.58	18652 ± 208	0.9987		155.1 ± 1.7
L	49.16 ± 0.68	18729 ± 244	0.9983		155.7 ± 2.0
global	48.96 ± 0.33	18659 ± 118	0.9985	358.28	155.1 ± 1.0
4-octyloxybenzoic acid					
S	43.58 ± 0.42	17049 ± 156	0.9993		141.8 ± 1.3
M	43.38 ± 0.36	16969 ± 132	0.9996		141.1 ± 1.1
L	43.38 ± 0.51	16975 ± 189	0.9990		141.1 ± 1.6
global	43.37 ± 0.30	16971 ± 111	0.9989	367.78	141.1 ± 0.9

Table 5. Standard Thermodynamic Properties of Sublimation at $T = 298.15$ K of the 4-*n*-Alkyloxybenzoic Acids Studied in this Work and of the 4-*n*-Alkylbenzoic Acids[a]

	$\Delta_{cr}^{g}H_m^{o}$	$\Delta_{cr}^{g}S_m^{o}$	$\Delta_{cr}^{g}G_m^{o}$	$\Delta_{cr}^{g}C_{p,m}^{o}$
compound	kJ·mol^{-1}	J·K^{-1}·mol^{-1}	kJ·mol^{-1}	J·K^{-1}·mol^{-1}
4-methoxybenzoic acid	112.6 ± 0.6	216 ± 2	48.1 ± 0.1	–38 ± 11
4-methoxybenzoic acid[b]	111.6 ± 0.8	213 ± 3	48.0 ± 0.1	–38 ± 11
4-ethoxybenzoic acid	121.9 ± 1.0	233 ± 3	52.5 ± 0.1	–40 ± 11
4-propoxybenzoic acid (cr II)	126.0 ± 0.5	250 ± 2	51.4 ± 0.1	–39 ± 11
4-butoxybenzoic acid	127.7 ± 0.8	248 ± 3	53.8 ± 0.1	–38 ± 11
4-pentyloxybenzoic acid	134.5 ± 0.8	263 ± 3	56.1 ± 0.1	–37 ± 11
4-hexyloxybenzoic acid (cr II)	139.4 ± 0.9	274 ± 2	57.7 ± 0.1	–36 ± 11
4-hexyloxybenzoic acid (cr I)[c]	133.4 ± 0.9	256 ± 2	56.9 ± 0.1	–36 ± 11
4-heptyloxybenzoic acid	157.2 ± 1.2	318 ± 4	62.5 ± 0.2	–35 ± 11
4-octyloxybenzoic acid (cr II)	161.4 ± 1.2	324 ± 5	64.8 ± 0.2	–34 ± 11
4-octyloxybenzoic acid (cr I)[c]	143.5 ± 1.2	272 ± 5	62.4 ± 0.2	–34 ± 11
4-methylbenzoic acid[d]	97.9 ± 0.5	194 ± 2	40.1 ± 0.1	–30 ± 11
4-ethylbenzoic acid[d]	100.6 ± 0.7	205 ± 2	39.6 ± 0.1	–40 ± 11
4-propylbenzoic acid(II)[e]	112.2 ± 0.8	229 ± 3	43.9 ± 0.1	–47 ± 11
4-propylbenzoic acid (I)[d]	108.2 ± 0.8	218 ± 3	43.8 ± 0.1	–47 ± 11
4-butylbenzoic acid (II)[e]	114.2 ± 0.7	233 ± 2	44.7 ± 0.1	–46 ± 11
4-butylbenzoic acid (I)[d]	109.5 ± 0.7	218 ± 2	44.4 ± 0.1	–46 ± 11
4-pentylbenzoic acid[d]	117.1 ± 0.9	233 ± 3	47.5 ± 0.1	–45 ± 11
4-hexylbenzoic acid[d]	122.3 ± 0.9	241 ± 3	50.4 ± 0.1	–43 ± 11
4-heptylbenzoic acid (II)[e]	135.9 ± 0.9	274 ± 3	54.2 ± 0.1	–42 ± 11
4-heptylbenzoic acid (I)[d]	128.5 ± 0.9	251 ± 3	53.7 ± 0.1	–42 ± 11
4-octylbenzoic acid (II)[e]	138.7 ± 1.6	276 ± 5	56.4 ± 0.3	–41 ± 11
4-octylbenzoic acid (I)[d]	133.3 ± 1.6	258 ± 5	56.3 ± 0.3	–41 ± 11

[a] $\Delta_{cr}^{g}H_m^{o}$(298.15 K) and $\Delta_{cr}^{g}G_m^{o}$(298.15 K) were derived from Clarke Glew eq 2 considering the reference pressure $p^\circ = 0.1$ MPa and the heat capacity differences presented in this Table. [b] Values calculated in this work from the experimental vapor pressures reported in the literature.[31] [c] Values refer to the phase studied in this work, not stable at 298.15 K. [d] Values calculated in this work from the experimental vapor pressures reported in the literature,[8] using the values of heat capacity differences presented in this table. [e] Values calculated in this work from the experimental vapor pressures and the crystal−crystal transition results reported in the literature.[8]

acid. The volatility of this compound is considerably lower than expected when considering the trend inside the series—its standard molar Gibbs energy of sublimation is higher than that of the next compound of this series, 4-propoxybenzoic acid. Comparing the two series of compounds, the parallelism in the values of $\Delta_{cr}^{g}G_m^{0}$(298.15 K) is again noteworthy. With exception for the two compounds with $N = 2$, the difference between the two series is almost constantly around 8 $\mathrm{kJ\cdot mol^{-1}}$. In Figure 5, the values of $\Delta_{\mathrm{cr}}^{\mathrm{g}}G_{\mathrm{m}}^{0}$(298.15 K) are shifted in N in the same way as in Figure 2, enhancing what seems to be the influence of the temperature of fusion in the volatility of the lower members of both series of compounds, as has been discussed before for other *para*-substituted benzoic acids.[11]

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