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## Thermodynamic properties of isomeric iso-butoxybenzoic acids: Experimental and theoretical study



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## 1. Introduction

Alkoxybenzoic acids have become an object of recent increasing interest due to their new applications. They are used as flavoring substances and preservatives of fragrance in cosmetic formulations [1]. As some of them are natural products, they are good candidates for pharmaceutical co-crystals [1]. Several alkoxybenzoic acids and their derivatives reveal biological activity as inhibitors of phosphodiesterase [2]. The majority of the papers on alkoxybenzoic acids deals with *n*-alkoxy derivatives. It is due to their liquid crystal properties. Esters of these compounds with triethanolamine were found to be discotic mesogens [3]. It is noteworthy that these compounds easily form mixed supramolecular liquid crystals induced by hydrogen bonding which have a much wider mesophase range than their individual components [4,5]. For all the isomers of methoxybenzoic acid molecular and crystal structures have been determined by X-ray diffraction method [2,6]. The investigated compounds form

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## ABSTRACT

Standard ( $p^{\circ} = 0.1$  MPa) molar enthalpies of formation at the temperature T = 298.15 K of the 2-, 3-, and 4iso-butoxybenzoic acids were measured using the combustion calorimetry. Standard molar enthalpies of vaporization and sublimation were derived from the vapor pressure temperature dependencies measured by the transpiration method. Molar enthalpies of the solid state phase transitions were measured by the DSC. Thermodynamic data on alkoxy substituted benzoic acids available in the literature were collected and combined with own experimental results. This data set on alkoxybenzoic acids was evaluated by using quantum-chemical and group-additivity methods.

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dimeric molecules with a moderately strong intermolecular hydrogen bonds. Several polymorphs have been observed due to the flexibility of the molecule [1]. Thermochemistry of the methoxy substituted benzoic acids has been evaluated recently [7]. The molar enthalpy of formation and sublimation on benzoic acids with the *n*-alkoxy-substituents were also reported [8,9]. The lack of the data for branched alkoxy-substituted benzoic acids was the reason to investigate the iso-butoxy benzoic acids (see Fig. 1) in the present paper.

The new results together with the thermochemical data on alkoxybenzoic acid available in the literature (see Table 1) have been checked for internal consistency using the quantum chemical and the group-additivity methods.

## 2. Materials and methods

## 2.1. Materials

Samples of iso-butoxybenzoic acids were synthesized from the commercially available bromo-iso-butoxybenzenes according to a general procedure given on Fig. 2. Necessary details are given below for each isomer as follows.

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Compounds	St.	$\Delta_c H_m^o$	$\Delta_f H_m^o(\mathrm{cr})$	$\Delta^{\rm g}_{\rm cr} H^o_m$	$\Delta_1^{\mathrm{g}} H_m^o$	$\Delta_{f}H_{m}^{o}(\mathrm{liq})$	$\Delta_{f}H_{m}^{o}(g)$	
2-Iso-butoxy-	liq	$-5715.1 \pm 1.6$	-	-	$95.6\pm0.6$	$-614.3\pm2.2$	$-518.7\pm2.3$	
3-Iso-butoxy-	cr	$-5678.4 \pm 2.6$	$-651.0 \pm 3.0$	$120.7 \pm 1.4^{b}$	$99.2\pm0.9$	$-629.5 \pm 3.2^{\circ}$	$-530.3 \pm 3.3$	
4-Iso-butoxy-	cr	$-5672.8 \pm 1.7$	$-656.6 \pm 2.2$	$119.0\pm0.6$	$104.1 \pm 2.1^{b}$	$-641.7 \pm 3.0^{\circ}$	$-537.6 \pm 2.3$	
4-Etoxy-	cr	-	$-605.5 \pm 1.8$ [9]	$121.8 \pm 1.1^{b}$	$95.5\pm2.8^{b}$	$-579.2 \pm 3.2^{\circ}$	$-483.7\pm2.1$	
4-Butoxy-	cr	-	$-647.1 \pm 2.5$ [9]	$123.2 \pm 1.0$	$108.8 \pm 2.6^{b}$	$-632.7 \pm 3.5^{\circ}$	$-523.9\pm2.7$	
4-Octyloxy-	cr	-	$-767.9 \pm 3.9$ [9]	$159.6\pm2.6^{b}$	$126.7\pm3.8^{b}$	$-745.0\pm4.8^{c}$	$-608.3\pm4.7$	

Thermochemical data at  $T = 298.15 \text{ K} (p^\circ = 0.1 \text{ MPa})$  for alkoxybenzoic acids (in kJ mol<sup>-1</sup>)<sup>a</sup>

<sup>a</sup> Uncertainties correspond to expanded uncertainties of the mean (0.95 confidence level).

<sup>b</sup> From Table 3.

Table 1

<sup>c</sup> Calculated from the experimental  $\Delta_f H_m^o$  (cr)-values (this table) and the sum of the solid state phase transitions with enthalpies  $\sum \Delta_{\alpha}^{\beta} H_m^o$  values from Table 3.

4-Iso-butoxybenzoic acid. A solution of 4-bromophenyl-iso-butyl ether (40.0 g, 0.175 mol) in diethyl ether was added dropwise to a solution of *n*-butyllithium (0.183 mol) in dry diethyl ether (200 ml) and dry tetrahydrofuran (THF) (20 ml) at -70 °C. The temperature did not exceed -65 °C. After completion of the addition the mixture was stirred for one hour at -70 °C. The mixture was carefully poured on 140 g of dry ice in diethyl ether (100 ml). After completion of this step, 200 ml of water was added. The mixture was acidified to pH=6 with 3 M aq. HCl. The aqueous phase was extracted with ether (100 ml). The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure. Recrystallization from hexane yielded with 4iso-butoxybenzoic acid (15.03 g, 44.2%) as a white powder with the melting point of 139-141 °C (lit. 142 °C [10]. <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>): 7.00 (d, 2*H*), 7.96 (d, 2*H*), 2.04 (m, CH), 3.84 (d, CH<sub>2</sub>), 1.20 (d, CH<sub>3</sub>). 2- And 3-iso-butoxybenzoic acid were synthesized in similar manner.

2-Iso-butoxybenzoic acid. Colorless liquid. Crude product was distilled under reduced pressure at  $160 \circ C/20$  Torr (lit. 135–136  $\circ C/1$  Torr [11]. Yield 55%, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.01 (dd, 1*H*), 7.06 (ddd, 1*H*), 7.50 (ddd, 1*H*), 8.11 (ddd, 1*H*), 2.18 (m, CH), 3.98 (d, CH<sub>2</sub>), 1.50 (d, CH<sub>3</sub>).

3-*Iso-butoxybenzoic acid.* Yield 28.3%, melting point: 79–80 °C, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.11 (ddd, 1*H*), 7.37 (dd, 1*H*), 7.62 (dd, 1*H*), 7.70 (ddd, 1*H*), 2.11 (m, CH), 3.78 (d, CH<sub>2</sub>), 1.04 (d, CH<sub>3</sub>).

The products were re-crystalized or distilled under reduced pressure. No impurities (greater than 0.001 mass fractions) could be detected in samples used for the before the thermochemical measurements. The degree of purity was determined using the GC and the DSC methods. Provenance and purity of the compound prepared for thermochemical studies in this work are given in Table S1.



**Fig. 1.** Compounds studied in this work: 2-iso-butoxybenzoic acid, 3-iso-butoxybenzoic acid and 4-iso-butoxybenzoic acid.



Fig. 2. General procedure for synthesis of iso-butoxybenzoic acids.

## 2.2. Combustion calorimetry

Standard molar enthalpies of combustion of iso-butoxybenzoic acids were measured with an isoperibolic calorimeter with a static bomb and a stirred water bath. The detailed procedure has been described previously [12]. The liquid sample of the ortho-isomer was placed (under an inert atmosphere in a glove-box) in a polythene ampoule (Fa. NeoLab, Heidelberg, Germany). The neck of the ampoule was compressed with a special tweezers and was sealed outside the glove-box by heating of the neck in a close proximity to a glowing wire. Then, the container was placed in the crucible and was burned in oxygen at a pressure 3.04 MPa. The solid samples were pressed into pellets of mass  $\approx$ 700 mg, and were burned in oxygen with a mass of 1.00 g of water added to the bomb. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon but neither was detected. The energy equivalent of the calorimeter  $\varepsilon_{\rm calor}$  = 14816.0  $\pm$  0.7 J K  $^{-1}$  was determined with a standard reference sample of benzoic acid (sample SRM 39*i*, NIST). For the reduction of the data to standard conditions, conventional procedures [13] were used. Auxiliary data are collected in Table S2. Correction for nitric acid formation was based on titration with  $0.1 \text{ mol dm}^{-3}$  NaOH (aq). The residual water content 261.3 ppm in the liquid sample was determined by Karl Fischer titration before starting experiments and appropriate corrections have been made for combustion results. No discernable amount of moisture was detected in the solid samples. Primary results from combustion experiments are summarized in Tables S3–S5.

#### 2.3. Transpiration method. Vapor pressure measurements

Vapor pressures of iso-butoxybenzoic acids were measured using the transpiration method [14,15]. About 0.5 g of a solid sample was dissolved in acetonitrile and mixed with small glass beads in a glass beaker. Under vigorous stirring with spatula and gentle heating the solvent was removed from beaker producing glass beads covered uniformly with the sample. These covered glass beads were placed in a thermostatted U-shaped saturator. A well-defined nitrogen stream was passed through the saturator at a constant temperature ( $\pm$ 0.1 K), and the transported material was collected in a cold trap. The amount of condensed sample was determined by weighing with microbalances of 0.0001 g resolution. Material collected in the cold trap was systematically analyzed by the GC, but decomposition products were not detected.

The absolute vapor pressure  $p_i$  at each temperature  $T_i$  was calculated from the amount of the product collected within a definite period. Assuming validity of the Dalton's law applied to the nitrogen stream saturated with the substance *i*, values of  $p_i$  were calculated with Eq. (1):

$$p_i = \frac{m_i \times R \times T_a}{V \times M_i}; \quad V = V_{N_2} + V_i; \quad \left(V_{N_2} \gg V_i\right)$$
(1)

## Table 2

Absolute vapor pressures *p*, and standard vaporization/sublimation enthalpies, and vaporization/sublimation entropies of iso-butoxybenzoic acids obtained by the transpiration method.

T (K) <sup>a</sup>	<i>m</i> (mg) <sup>b</sup>	$V_{(N_2)} \left( dm^3 \right)^c$	$T_{\rm a}  ({\rm K})^{\rm d}$	Flow $(dm^3 h^{-1})$	<i>р</i> (Ра) <sup>е</sup>	u(p)(Pa)	$\Delta_1^{\mathrm{g}} H_m^o\left(\mathrm{kJ} \ \mathrm{mol}^{-1} ight)$	$\Delta_{l}^{g}S_{m}^{o}\left(J \ \mathrm{K}^{-1} \ \mathrm{mol}^{-1}\right)$
2-Iso-but	oxybenzoic acio	1; $\Delta_1^g H_m^o$ (298.15 K) = (	$(95.6 \pm 0.6)$ k	mol <sup>-1</sup>				
$\ln\left(p/p^{o}\right)$	$= \frac{381.0}{R} - \frac{126.6}{R \times (T)}$	$\frac{620.5}{(K)} - \frac{103.9}{R} \ln \left( \frac{T}{298.15} \right)$	)					
343.9	4.30	67.04	291.2	3.61	0.80	0.03	90.89	166.8
353.1	5.50	39.12	292.7	3.03	1.76	0.05	89.94	163.7
365.2	8.8 8.1	20.07	290.2	5.00	4.10	0.11	88.89	160.8
369.2	13.1	24.62	290.2	6.15	6.62	0.12	88.27	159.1
371.2	12.5	20.39	295.2	6.31	7.75	0.22	88.06	158.6
371.4	9.8	14.86	289.2	6.37	8.17	0.23	88.03	158.8
371.4	10.5	16.51	290.7	5.41	7.91	0.22	88.03	158.5
371.5	10.2	15.71	290.7	4.74	8.08	0.23	88.03	158.6
374.2	12.5	15.29	290.7	5.43	10.17	0.28	87.74	158.0
374.4	13.0	10.97	291.2	3.01 7.28	9.99	0.27	87.72 87.50	157.7
377.3	14.1	14.17	292.2	7.02	12.45	0.34	87.42	156.9
378.5	19.0	16.99	290.7	7.44	13.91	0.37	87.29	156.8
379.2	12.2	10.33	290.2	6.26	14.67	0.39	87.22	156.6
380.1	8.4	6.83	293.7	6.31	15.46	0.41	87.13	156.3
380.2	13.8	11.06	290.7	7.14	15.53	0.41	87.12	156.2
382.4	14.4	10.14	291.2	6.48	17.70	0.47	86.89	155.4
384.2	18.4	11.25	291.2	3.61	20.38	0.53	86.71	155.0
383.8 388.1	17.1	9.59	293.2	7.02	22.37	0.58	86.30	153.8
390.3	12.1	4 94	292.2	631	30.64	0.08	86.07	153.3
393.0	13.9	4.75	290.7	7.31	36.39	0.93	85.79	152.5
395.2	12.0	3.36	293.2	6.31	44.78	1.14	85.56	152.4
398.1	27.9	6.56	295.2	7.87	53.73	1.37	85.26	151.6
3-Iso-buto $\ln\left(p/p^o\right)$	$\left(\frac{389.0}{R} - \frac{130.2}{R\times(T)}\right) = \frac{389.0}{R} - \frac{130.2}{R\times(T)}$	d; $\Delta_1^g H_m^o(298.15 \text{ K}) = (\frac{18.5}{(\text{K})} - \frac{103.9}{R} \ln \left(\frac{T (\text{K})}{298.15}\right)$	$(99.2\pm0.9)$ kJ	mol <sup>-1</sup>				
354.8	16.1	125.5	294.2	3.18	1.62	0.05	93.36	171.4
356.2	21.3	148.2	294.2	5.00	1.81	0.05	93.21	171.0
357.4	13.5	84.13 65.76	294.2	5.77	2.02	0.06	93.09 92.87	170.6
361.2	22.6	101.20	294.2	4.00	2.81	0.08	92.69	169.5
363.0	22.3	87.84	294.2	5.06	3.20	0.08	92.50	168.7
364.2	20.2	71.10	294.2	3.99	3.58	0.09	92.38	168.5
365.7	16.0	49.62	294.2	6.49	4.06	0.11	92.22	168.1
368.3	14.6	36.81	290.2	6.92	4.93	0.13	91.95	167.2
370.9	12.5	26.12	293.2	7.43	6.01	0.18	91.69	166.4
3/2./	15.8	28.14	294.2	8.28	7.07	0.20	91.50	165.8
3753	173	25.94	294.2	8.01	8 71	0.22	91.40	165.4
378.2	17.5	20.06	294.2	5.60	10.99	0.30	90.92	164.6
380.1	21.5	20.91	295.2	4.50	13.00	0.35	90.73	164.3
382.7	16.9	13.48	294.2	8.34	15.79	0.42	90.46	163.6
4-Iso-but	oxybenzoic acio 	d (series I); $\Delta_{cr}^{g} H_{m}^{o}$ (298) $\frac{1}{100} = \frac{45.6}{10} \ln \left( \frac{T}{100} \right)$	8.15 K) = (119.0	$0\pm0.6)$ kJ mol <sup>-1</sup>				
368.2 <sup>f</sup>	$R = R \times (T)$	(K)) R (298.15) 1379	294.2	3 99	1 19	0.03	117 89	225.9
373.1 <sup>f</sup>	15.0	94.52	293.7	4.09	1.99	0.05	117.67	225.4
378.6 <sup>f</sup>	26.1	96.29	294.7	7.60	3.42	0.09	117.41	224.6
379.3 <sup>f</sup>	20.1	68.79	294.7	5.44	3.69	0.10	117.38	224.6
381.0 <sup>f</sup>	16.5	49.10	293.7	4.09	4.22	0.11	117.31	224.2
388.5 <sup>f</sup>	13.9	19.62	293.7	5.77	8.90	0.25	116.96	223.5
390.5 <sup>r</sup>	12.5	15.25	294.7	7.50	10.34	0.28	116.87	223.0
393.6 <sup>4</sup>	9.9	9.04	294.7	/.33	13.81	0.37	116.73	222.7
393.0° 393.7f	0.9 20 3	0.09 18.00	294.1 294.2	6.00	15.88 14.20	0.37	116.73	222.0 222.9
393.8 <sup>f</sup>	20.5 163	14 80	2937	8.30	13.84	0.37	116.72	222.5
395.2 <sup>f</sup>	13.3	10.27	291.7	5.76	16.17	0.43	116.66	222.6
396.9 <sup>f</sup>	13.0	8.36	294.7	7.60	19.61	0.52	116.58	222.8
397.4 <sup>f</sup>	9.1	5.59	291.7	5.59	20.32	0.53	116.56	222.6
398.6 <sup>f</sup>	13.2	7.78	292.7	7.18	21.26	0.56	116.50	222.0
399.0 <sup>f</sup>	2.3	1.23	291.7	1.37	23.36	0.61	116.49	222.5
399.9 <sup>1</sup>	23.9	12.45	293.7	8.30	24.13	0.63	116.44	222.0
402.6 <sup>r</sup>	31.0	12.11	293.7	8.55	32.18	0.83	116.32	222.1
403.2°	د.۲	3.19	294.7	1.30	32.83	0.85	116.29	221.8

## Table 2 (Continued)

<i>T</i> (K) <sup>a</sup>	<i>m</i> (mg) <sup>b</sup>	$V_{(N_2)} \left( dm^3 \right)^c$	$T_{\rm a}~({\rm K})^{\rm d}$	Flow $(dm^3 h^{-1})$	р (Ра) <sup>е</sup>	u(p) (Pa)	$\Delta_l^g H_m^o \left( kJ \ mol^{-1} \right)$	$\Delta_1^g S_m^o \left( J \ K^{-1} \ mol^{-1} \right)$
4-Iso-butox	ybenzoic acid (se	eries II)						
342.3 <sup>g</sup>	0.76	133.98	290.2	4.09	0.07	0.01	118.95	229.7
343.5 <sup>g</sup>	0.66	103.13	290.2	4.50	0.08	0.01	118.89	229.4
346.4 <sup>g</sup>	0.95	107.88	290.2	4.21	0.11	0.01	118.76	228.8
348.5 <sup>g</sup>	0.27	23.14	290.2	5.24	0.14	0.01	118.66	228.7
349.2 <sup>g</sup>	1.09	88.48	290.2	4.14	0.15	0.01	118.63	228.5
353.4 <sup>g</sup>	0.73	35.55	290.2	3.99	0.26	0.01	118.44	228.1
353.6 <sup>g</sup>	0.40	19.66	290.2	4.14	0.25	0.01	118.43	227.8
356.9 <sup>g</sup>	0.59	19.09	290.2	4.09	0.38	0.01	118.28	227.7
359.2 <sup>g</sup>	0.72	19.21	290.2	4.30	0.46	0.02	118.18	226.9
360.4 <sup>g</sup>	0.55	12.49	290.2	4.21	0.55	0.02	118.12	227.0
361.6 <sup>g</sup>	1.05	19.81	290.2	4.34	0.66	0.02	118.07	227.3
363.4 <sup>g</sup>	0.67	10.58	290.2	3.94	0.78	0.02	117.99	227.0
363.5 <sup>g</sup>	0.82	13.09	290.2	4.20	0.78	0.02	117.98	226.8
365.4 <sup>g</sup>	0.44	5.66	290.2	4.14	0.96	0.03	117.89	226.6
365.9 <sup>g</sup>	0.95	11.63	290.2	2.48	1.02	0.03	117.87	226.6
367.8 <sup>g</sup>	1.32	13.42	290.2	4.17	1.22	0.04	117.78	226.2
368.7 <sup>g</sup>	0.82	7.59	290.2	4.14	1.34	0.04	117.74	226.1
368.9 <sup>g</sup>	0.91	8.10	290.2	4.42	1.40	0.04	117.73	226.2
370.7 <sup>g</sup>	0.98	7.48	290.2	4.05	1.62	0.05	117.65	225.7
373.3 <sup>g</sup>	1.09	6.28	290.2	4.14	2.16	0.06	117.53	225.6
2-Methoxy	benzoic acid: $\Lambda^{g}$	$H^{0}(298.15 \text{ K}) = (106)$	3+09) kIm	ol <sup>-1</sup>				
$\ln\left(p/p^{\circ}\right)$	$=\frac{345.4}{R}-\frac{1116,657.1}{R\times(T(K))}$	$-\frac{34.7}{R}\ln\left(\frac{T}{298.15}\right)$	J±0.5) kj m	01				
342.4	9.5	157.0	294.7	4.18	0.98	0.03	104.78	210.1
346.2	10.6	113.3	295.9	3.97	1.52	0.04	104.65	210.0
350.3	17.1	125.3	295.9	4.17	2.21	0.06	104.50	209.2
348.2	6.0	53.78	295.9	3.97	1.81	0.05	104.58	209.6
352.2	24.7	147.2	295.9	6.07	2.72	0.07	104.44	209.2
354.3	16.3	76.00	295.9	6.00	3.47	0.09	104.36	209.2
356.2	20.8	80.40	295.9	6.00	4.19	0.11	104.30	209.0
358.9	21.0	62.62	292.2	4.04	5.36	0.14	104.20	208.5
361.4	16.6	39.46	295.9	6.07	6.80	0.20	104.12	208.3
363.2	29.6	58.90	295.9	6.00	8.13	0.23	104.06	208.2
366.2	9.9	14.83	291.7	5.23	10.64	0.29	103.95	207.8
367.9	30.1	37.90	290.7	2.93	12.62	0.34	103.89	207.8
371.5	14.0	13.10	295.9	5.50	17.28	0.46	103.77	207.3
				1				
4-Butoxybe	enzoic acid; $\Delta_{cr}^{g}H_{r}^{q}$	$n_n^{(298.15 \text{ K})} = (123.2)$	$\pm$ 1.0) kJ mol	-1				
$\ln\left(p/p^{o}\right)$	$=\frac{578.5}{R}-\frac{157,145.4}{Rx\cdot(T(K))}$	$-\frac{40.8}{R}\ln\left(\frac{1}{298.15}\right)$						
377.8	12.0	92.71	295.9	5.13	1.64	0.05	119.47	224.7
383.4	20.5	90.28	293.7	5.09	2.85	0.08	119.21	224.0
391.0	11.6	25.01	295.2	5.09	5.86	0.15	118.85	223.0
396.2	13.3	17.21	294.2	5.09	9.73	0.27	118.61	222.6
399.3	10.4	10.80	294.5	5.10	12.14	0.33	118.46	221.7
401.3	13.4	11.02	295.2	5.09	15.36	0.41	118.37	222.0
406.4	18.2	9.741	295.9	5.13	23.66	0.62	118.13	221.3
411.4	19.7	6.751	294.3	5.13	36.76	0.94	117.90	220.9
415.4	12.9	3.316	295.7	5.10	49.23	1.26	117.71	220.1
417.3	9.8	2.126	295.9	5.10	58.38	1.48	117.62	220.0
417.3	13.3	2.891	295.9	5.10	58.26	1.48	117.62	220.0

<sup>a</sup> Saturation temperature (u(T) = 0.1 K).

<sup>b</sup> Mass of transferred sample condensed at T = 293 K.

Volume of nitrogen  $(u(v) = 0.005 \text{ dm}^3)$  used to transfer m(u(m) = 0.0001 g) of the sample.

 $^{d}$  T<sub>a</sub> is the temperature of the soap bubble meter used for measurement of the gas flow.

<sup>e</sup> Vapor pressure at temperature *T*, calculated from the *m* and the residual vapor pressure at *T*=293 K calculated by an iteration procedure.

<sup>f</sup> Series I: the mass of the transported sample was determined by weighing of the cold trap.

<sup>g</sup> Series II: the mass of the transported sample was determined by GC.

where  $R = 8.314462 \text{ J K}^{-1} \text{ mol}^{-1}$ ;  $m_i$  is the mass of the transported compound,  $M_i$  is the molar mass of the compound, and  $V_i$ ; its volume contribution to the gaseous phase.  $V_{N_2}$  is the volume of the carrier gas and  $T_a$  is the temperature of the soap bubble meter used for measurement of the gas flow. The volume of the carrier gas  $V_{N_2}$  was determined from the flow rate and the time measurement. Experimental results are given in Tables 1 and 2. Accuracy of vapor pressures measured by the transpiration method is governed mostly by the reproducibility of the GC analysis as well as by the volume  $V_{N_2}$  determination [15]. The standard uncertainties (u) of the measured vapor pressures have been calculated to be: u(p (Pa)) = 0.025 + 0.025(p (Pa)) for p > 5 to 1000 Pa, u(p (Pa)) = 0.005 + 0.025(p (Pa)) for p < 5 Pa.

To validate system operation, the vapor pressure of benzoic acid was determined at p = (1 to 500) Pa. Experimental vapor pressure of benzoic acid obtained using the transpiration agreed with the results reported in the literature [16] to within (0.5 to 2.5) %. The system operation was also successfully tested (see Fig. S1) with measurements on the 2-methoxybenzoic acid, where reliable vapor pressures data are available from Knudsen effusion technique [17]. For validation of our uncertainty estimations we measured vapor pressures for series of *n*-alkanols [18] and aliphatic esters [14]

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Table	3

Compilation o	f experimental	data on enthal	pies of phase	transitions (	(in kJ mol−	<sup>1</sup> ).
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Compounds	T <sub>fus</sub> <sup>a</sup>	$\Delta_{258}^{T_{\mathrm{fus}}} H_m^{o\mathrm{a,b}}$	$\Delta_{298}^{T_{\rm fus}} H_m^{o c}$ At 298.15 K	$\Delta^{\rm g}_{ m cr} H^o_m$	$\Delta_1^{g} H_m^{o d}$
1	2	3	4	5	6
3-Iso-butoxybenzoic acid 4-Iso-butoxybenzoic acid 4-Ethoxybenzoic acid 4-Butoxybenzoic acid 4-Octyloxybenzoic acid	353.5° 415.3 471.8° [9] 433.7[9] 421.0[9]	$25.2 \pm 0.2$ $18.9 \pm 0.2$ $35.1 \pm 0.2 [9]$ $22.3 \pm 0.2 [9]$ $32.2 \pm 0.2 [9]$	$\begin{array}{c} 21.5 \pm 1.1 \\ 14.9 \pm 2.0^{\rm f} \\ 26.3 \pm 2.6 \\ 14.4 \pm 2.4 \\ 22.9 \pm 2.8 \end{array}$	$\begin{array}{c} 120.7 \pm 1.4^{i} \\ 119.0 \pm 0.6^{g} \\ 121.8 \pm 2.1^{h} \\ 123.2 \pm 1.0^{g,j} \\ 159.6 \pm 2.6^{h} \end{array}$	$\begin{array}{c} 99.2 \pm 0.9^{f} \\ 104.1 \pm 2.1 \\ 95.5 \pm 2.8 \\ 108.8 \pm 2.6 \\ 126.7 \pm 3.8 \end{array}$

<sup>a</sup> The uncertainty for melting and solid-solid phase transition temperatures u(T) = 0.5 K. The uncertainty for enthalpies of fusion and enthalpies of solid-solid phase transition  $u(\Delta_{l_T}^l H_m) = 0.2$  kJ mol<sup>-1</sup>.

<sup>b</sup> Sum of the enthalpy of fusion  $\Delta_{cr}^{l}H_{m}^{o}$  and the sum of enthalpies of the solid state phase transitions  $\sum \Delta_{\alpha}^{\beta}H_{m}^{o}$  (uncertainties of  $\Delta_{\alpha}^{\beta}H_{m}^{o}$  and  $\Delta_{cr}^{l}H_{m}^{o}$  were not reported in Ref. [9] and they were assessed in this work).

<sup>c</sup> Adjusted to the reference temperature according to Ref. [31].

<sup>d</sup> Difference between column 5 and column 4 in this table.

<sup>e</sup> No solid state phase transition prior to the melting was observed.

<sup>f</sup> Sum of the enthalpy of fusion  $\Delta_{\alpha}^{i}H_{m}^{\mu} = 18.9 \pm 0.2$  kJ mol<sup>-1</sup> and the enthalpy of the solid state phase transitions  $\Delta_{\alpha}^{\beta}H_{m}^{0} = 2.8 \pm 0.2$  kJ mol<sup>-1</sup> at 412.5 ± 0.5 K was adjusted to the reference temperature according to Ref. [31].

<sup>g</sup> From Table 2.

<sup>h</sup> Primary experimental vapor pressures reported in Ref. [9] were treated similar to our own results with Eqs. (3) and (4) and by using the  $\Delta_{s}^{IC}c_{n,m}$  values from Table S7.

<sup>i</sup> Calculated as sum of column 4 and 6 from this table.

<sup>j</sup> For comparison, experimental value  $\Delta_{cr}^{g} H_{m}^{o}(298.15 \text{ K}) = 127.8 \pm 1.0 \text{ kJ mol}^{-1}$  was reported in Ref. [9]. With the  $\Delta_{238}^{T} H_{m}^{o} = 14.4 \pm 2.4 \text{ kJ mol}^{-1}$  from column 4, the value  $\Delta_{g}^{g} H_{m}^{o}(298.15 \text{ K}) = 113.4 \pm 2.6 \text{ kJ mol}^{-1}$  was calculated.

where reliable data at p = (0.1 to 1000) Pa from different methods were available. It has turned out that vapor pressures of *n*-alkanols and esters derived from the transpiration method were comparable with the available high-precision data generally within (1 to 3) %. Experimental results from transpiration methods are collected in Table 2.

### 2.4. DSC. Enthalpies of the solid phase transitions measurements

The thermal behavior of solid samples of 3- and 4-isobutoxybenzoic acid was studied with a Metller Toledo 822. The instrument was standardized using indium metal with a mass fraction of 0.9999. The samples were hermetically sealed in 50 µL pans. The thermal behavior of the specimen was investigated during heating the sample with a rate of 10 K min<sup>-1</sup>. The DSC measurements were repeated in triplicate and values agreed within the experimental uncertainties  $u(\Delta_{cr}^{l}H_{m}) = 0.2 \text{ kJ mol}^{-1}$  for the enthalpy of fusion and u(T) = 0.5 K for the melting temperature. For the sample of 3-iso-butoxybenzoic acid only phase transition solid-liquid at 353.5 K was observed. For the sample of 4-isobutoxybenzoic acid also the solid-solid phase transition at 412.5 K was observed. The DSC results for benzoic acid derivatives are reported in Table 3. Uncertainties in the temperature adjustment of fusion enthalpies from  $T_{\rm fus}$  to the reference temperature were assumed to amount to 30% of the total adjustment [19].

## 2.5. Computational details

Quantum chemical calculations of benzoic acid derivatives were performed with the Gaussian 09 series software [20]. Energies of molecules were calculated using the G3MP2 method [21]. General computational details within this approach were reported elsewhere [22]. Enthalpies,  $H_{298}$ , of each compound were calculated according to standard thermodynamic procedures [23].

## 3. Results and discussion

## 3.1. Enthalpy of formation from the combustion calorimetry

Results of typical combustion experiments on 2-, 3-, and 4-isobutoxybenzoic acids are given in Tables S3–S5. The relative atomic masses used for the elements C, H, N and O were calculated as the mean of the bounds of the interval of the standard atomic weights recommended by the IUPAC commission in 2011 [24] for each of these elements. Values of the standard specific energies of combustion  $\Delta_c u^\circ$  are given in Table S6. They have been used to derive the standard molar enthalpies of combustion  $\Delta_c H_m^\circ$  and the standard molar enthalpies of formation in the liquid state  $\Delta_f H_m^\circ$  (1) or in the crystalline state  $\Delta_f H_m^\circ$ (cr) (see Table 1). Values of  $\Delta_c u^\circ$  and  $\Delta_f H_m^\circ$ refer to reaction:

$$C_{11}H_{14}O_3(lorcr) + 13O_2(g) = 11CO_2(g) + 7H_2O(l)$$
 (2)

The standard molar enthalpies of formation,  $\Delta_f H_m^0$ , of isobutoxybenzoic acids were calculated from the enthalpic balance according to Eq. (2) using standard molar enthalpies of formation of H<sub>2</sub>O (1) and CO<sub>2</sub> (g) recommended by CODATA [25]. Uncertainties related to combustion experiments were calculated according to the guidelines presented by Hubbard et al. [13] and by Olofsson [26]. The uncertainties of the standard molar energy of combustion correspond to expanded uncertainties of the mean (0.95 confidence level). The uncertainty assigned to the molar enthalpy of combustion and to the molar enthalpy of formation is twice the overall standard deviation and includes the uncertainties from calibration, from the combustion energies of the auxiliary materials, the uncertainties of the enthalpies of formation of the reaction products  $H_2O$  and  $CO_2$  [25], as well as the uncertainty due to the specific intervals of atomic masses reported by IUPAC [24]. The standard molar enthalpies of formation of all three isomers of the iso-butoxybenzoic acids (see Table 1) were measured for the first time.

### 3.2. Vapor pressures of iso-butoxybenzoic acids

Samples of 2- and 3-iso-butoxybenzoic acids were measured above their melting points. Vapor pressure for 4-iso-butoxybenzoic acid was measured over the crystalline sample. Temperature dependences of vapor pressures  $p_i$  measured for acids were fitted with the following equation [14]:

$$R \times \ln p_i = a + \frac{b}{T} + \Delta_l^g C_{p,m}^o \times \ln \left(\frac{T}{T_0}\right), \tag{3}$$

where *a* and *b* are adjustable parameters and  $\Delta_l^g C_{p,m}^o$  or  $(\Delta_{cr}^g C_{p,m}^o)$  is the difference of the molar heat capacities of the gaseous and the condensed phase, respectively.  $T_0$  appearing in Eq. (3) is an



Fig. 3. Optimized structures of 2-, 3- and 4-iso-butoxybenzoic acids obtained with the G3MP2 method.

#### Table 4

Comparison of the experimental and calculated by G3MP2 and GA gas-phase enthalpies of formation of alkoxybenzoic acids at T=298.15 K (in kJ mol<sup>-1</sup>).

Compounds	$\Delta_{f}H_{m}^{o}\left(\mathrm{g} ight)^{\mathrm{a}}\exp\left( \left( \mathrm{g}^{\mathrm{a}}\right) ^{\mathrm{a}}\right) $	$\Delta_{f}H_{m}^{o}(g) \operatorname{G3MP2}$	$arDelta^{ extbf{b}}$	$\Delta_{f}H_{m}^{o}\left( \mathbf{g} ight)$ add	$\Delta^{c}$
1	2	3	4	5	6
2-Methoxy-benzoic acid	$-431.9 \pm 1.2$ [7]	-437.8	5.9	_	_
3-Methoxy-benzoic acid	$-444.9 \pm 1.2$ [7]	-446.6	1.7	_	-
4-Methoxy-benzoic acid	$-449.5 \pm 1.4$ [7]	-452.3	2.8	_	-
2-iso-butoxybenzoic acid	$-518.7\pm2.3$	-524.5	5.3	-518.0	-0.7
3-iso-butoxybenzoic acid	$-530.3 \pm 3.3$	-532.6	2.3	-531.0	-0.7
4-iso-butoxybenzoic acid	$-537.6 \pm 2.3$	-538.0	0.4	-535.6	-2.0
4-Etoxybenzoic acid	$-483.7 \pm 2.1$	-483.3	-0.4	-485.8	2.1
4-Butoxybenzoic acid	$-523.9 \pm 2.7$	-527.1	3.2	-529.4	5.5
4-Octyloxybenzoic acid	$-608.3\pm4.7$	-609.4	1.1	-611.4	3.1

<sup>a</sup> From Table 1.

 $^{\rm b}\,$  Difference between columns 2 and 3 in this table.

<sup>c</sup> Difference between columns 2 and 5 in this table.

arbitrarily chosen reference temperature (which has been chosen to be *T* = 298.15 K) and *R* is the molar gas constant. Values of  $\Delta_l^g C_{p,m}^o$ or  $\Delta_{cr}^g C_{p,m}^o$  in Eq. (3) were calculated (see Table S7) according to the procedure developed by Chickos and Acree [27] based on the isobaric molar heat capacity  $C_{p,m}^o$  (l or cr, 298.15 K). The latter values were estimated by the group-additivity procedure [28]. Experimental vapor pressures measured by the transpiration method are given in Table 2.

# 3.3. Vaporization/sublimation enthalpies of iso-butoxybenoic acids

Vaporization enthalpies at temperature *T* were derived from the temperature dependence of vapor pressures using Eq. (4):

$$\Delta_l^g H_m^o(T) = -b + \Delta_l^g C_{p,m}^o \times T \tag{4}$$

Vaporization entropies at temperature *T* were also derived from the temperature dependence of vapor pressures using Eq. (5):

$$\Delta_1^{g} S_m^o(T) = \Delta_1^{g} H_m^o/T + R \ln \left( p_i/p^o \right)$$
<sup>(5)</sup>

Experimental absolute vapor pressures measured by the transpiration method, coefficients *a* and *b* of Eq. (3), as well as values of  $\Delta_I^g S_m^o(T)$  and  $\Delta_I^g H_m^o(T)$  are given in Table 2. Eqs. (3)–(5) are also valid for vapor pressure measurements over the solid sample giving the standard molar enthalpy of sublimation  $\Delta_{cr}^g H_m^o(T)$  and standard molar sublimation entropy  $\Delta_{cr}^g S_m^o(T)$ . Procedure for calculation of the combined uncertainties of the vaporization/sublimation enthalpies was described elsewhere [15,29]. It includes uncertainties from the transpiration experimental conditions, uncertainties in vapor pressure, and uncertainties in the temperature adjustment to *T* = 298.15 K. The standard molar enthalpies of sublimation or vaporization of all three isomers of iso-butoxybenzoic acids (see Tables 1 and 2) were measured for the first time.

In order to extend the temperature range of the 4-isobutoxybenzoic acid transpiration study possibly close to the reference temperature we have performed two independent sets of experiments with this compound. The first set of transpiration experiments was performed between 368.2 and 403.2 K as it was

described for all three isomers by weighing of the transported material collected in the cold trap accompanied with the GC analytic control of purity. From our experiences, about 8-20 mg of the collected material are essential for reliable measurements. Due to very low volatility of 4-iso-butoxybenzoic acid, experiments below 360 K become unreasonable time consuming in order to collect enough of sample for the weighing. In contrast, for the GC determination of the collected in the trap sample, already amount of 0.5-1 mg is usually sufficient. Thus, application of the GC for measurements of the mass m (see Eq. (1)) has allowed significantly extend the range toward lower temperatures of saturation. The second set of experiments with 4-iso-butoxybenzoic acid was performed in the range 342.3-373.3 K by using the GC analysis (external standard hexadecane) for determination of *m* in the cold trap. Experimental vapor pressures measured in the both sets are given in Table 2. Results from both series were consistent within 1-3% and they were treated together in order to develop coefficients of Eq. (3) (see Table 2) and the sublimation enthalpies (see Tables 1 and 2).

No values of enthalpies of vaporization/sublimation of the isobutoxybenzoic acids are available in the literature for comparison. For this reason, it is important to consider consistency of our new data for iso-butoxybenzoic acids in the context of the available in the literature data for isomeric methoxybenzoic acids [7], as well as with the recent systematic study of 4-*n*-alkoxybenzoic acids [9]. In the latter paper the sublimation enthalpies were measured by the Knudsen effusion method and adjusted to the reference temperature 298.15 K by using the Domalski and Hearing procedure [30]. In order to derive the consistent data set, the primary experimental vapor pressures reported in ref. [9] were treated in this work similar to our own results with Eqs. (3) and (4) and by using the Chickos and Acree procedure [27] with the  $\Delta_l^g C_{p,m}^o$ -values from Table S7. Enthalpies of sublimation of alkoxybenzoic acids derived in this way are listed in Tables 1 and 3.

### 3.4. Solid state phase transitions of 3- and 4-iso-butoxybenoic acids

It has turned out that volatility of the 3-iso-butoxybenzoic acid in the temperature range below the melting point of 353.5 K was too low in order to perform transpiration measurements in extended temperature range with a reasonable accuracy. In such cases we used to perform transpiration experiments above the melting point. The enthalpy of vaporization derived from vapor pressures temperature dependences according to Eqs. (3) and (4), combined with the DSC measured enthalpy of fusion,  $\Delta_{cr}^{l}H_{m}^{o}$ , provides the desired enthalpy of sublimation for the compound of interest. Enthalpies of fusion measured by the DSC are referenced to the melting temperature. In order to adjust these values to 298,15 K, the procedure established by Chickos and Acree [27] was applied. However, as reported by Fonseca et al. [9], the solid state phase transitions with enthalpies  $\sum \Delta_{\alpha}^{\beta} H_m^o$  are often observed for the alkoxybenzoic acids. For such compounds we calculated a total sum of solid state transition enthalpies,  $\Delta_{248}^{T_{\text{fus}}} H_m^o$ , as a sum of the enthalpy of fusion  $\Delta_{cr}^{l}H_{m}^{o}$  and  $\sum \Delta_{\alpha}^{\beta}H_{m}^{o}$ . We adjusted  $\Delta_{298}^{T_{fus}}H_{m}^{o}$  values to 298.15 K (see Table 3) according to recommendation by Chickos and Acree [31] in order derive values of  $\Delta_{cr}^{g}H_{m}^{o}(298.15 \text{ K})$  or  $\Delta_{1}^{g}H_{m}^{o}(298.15 \text{ K})$  of alkoxybenzoic acids listed in Table 3.

## 3.5. Experimental gas and liquid phase standard molar enthalpies of formation

Values of vaporization, sublimation, and solid phase transition enthalpies of alkoxybenzoic acids (Tables 1–3) can now be used together with the combustion calorimetry data, to yield the liquid phase,  $\Delta_f H_m^o$ (liq), and the gaseous standard enthalpies of formation,  $\Delta_f H_m^o$ (g) at 298.15 K. The resulting values are given in Table 1. These values can now be compared to the results from group-additivity procedure and those from the high-level quantum-chemical calculations.

## 4. Quantum chemical calculations

The modern high-level quantum-chemical (QC) calculations provide a valuable tool to test experimental and theoretical results for the mutual consistency [32,33]. We have used the composite method G3MP2 for calculation of the gaseous enthalpies of formation of alkoxybenzoic acids for comparison with the experimental data.

## 4.1. Theoretical gas phase standard molar enthalpies of formation of alkoxybenzoic acids

The optimized structures obtained for each of the isobutoxybenzoic acids are illustrated in Fig. 3.

The enthalpies  $H_{298}$  calculated for the alkoxybenzoic acid were converted to enthalpies of formation  $\Delta_f H_m^0(g, 298.15 \text{ K})$ using the conventional ring-conserved homodesmic reactions:(6)



## where $R_1$ and $R_2$ are alkoxy and carboxy substituents. Using enthalpies of reaction (6) participants calculated for benzoic acid derivatives by G3MP2 (see Table S8) together with the experimental enthalpies of formation, $\Delta_f H_m^0$ (g), for benzene, benzoic acid, and alkoxybenzenes (see Tables S8 and S9) the enthalpies of formation of all three iso-butoxybenzoic acids, as well as for available from Ref. [9] alkoxybenzoic acids were calculated (Table 4 column 3).

As it can be seen in Table 4, there is an overall good agreement (except for the *ortho*-substituted species) between theoretical

#### Table 5

Pairwise interactions of substituents on the benzene ring for di-substituted benzenes expressed as the enthalpy of reaction  $\Delta_r H_m^\circ$  (at 298.15 K, in kJ mol<sup>-1</sup>)<sup>a</sup>.

Compounds	$\Delta_r H_m^o$ (G3MP2)	$\Delta_r H^o_m({\rm G4})$	$\Delta_r H_m^o(\exp)$
2-Iso-butoxybenzoic acid	8.6	-	$16.9\pm3.8$
3-Iso-butoxybenzoic acid	0.5	-	$-5.3\pm4.3$
4-Iso-butoxybenzoic acid	-4.9	-	$2.0\pm3.7$
2-Methoxy-benzoic acid	9.9	9.8 [7]	15.8 ± 2.9 [7]
3-Methoxy-benzoic acid	1.1	1.2 [7]	$2.8\pm2.9\left[7\right]$
4-Methoxy-benzoic acid	-4.6	-4.7 [7]	-1.8 ± 3.0 [7]

<sup>a</sup> Reaction enthalpy  $\Delta_r H_m^0$  is ascribed to the reverse reaction (6).

and experimental data, particularly if the common uncertainties of about 2–4 kJ mol<sup>-1</sup> associated with the G3MP2 gas-phase enthalpies of formation are taken into account. This good agreement further reinforces the reliability of the experimental and theoretical results presented in this work.

The disagreement between the theoretical and the experimental values observed for *ortho*-substituted benzenes have already been observed in our previous study of the enthalpy of formation of 2-methoxybenzoic acid [7], as well as for 1,2-difluorobenzene [34]. In the current work we also observe the disagreement for 2-iso-butoxybenzoic acid. A systematic study of a series of 1,2di-substituted benzenes with the composite methods will help to reveal the reason in the future.

## 4.2. Pairwise interactions of substituents on the benzene ring

Pairwise interactions of substituents in the benzene ring belong to the basics of organic chemistry. Energetics of interplay of electron-donating and electron-accepting substituents in the ortho-, meta-, and para-position in the ring determine the mechanism of a chemical reaction. Having established a set of G3MP2 enthalpies  $H_{298}$  for iso-butoxybenzoic acids (see Table S8) we are able now to calculate effects of mutual interactions of carboxyl-group with the iso-butoxy-group on the benzene ring in the ortho-, meta-, and para-position (see Table 5). Similar to our recent results for the isomeric methoxybenzoic acids [7], only strong destabilization was observed for the ortho isomer. Mutual interactions in the meta position seems to be negligible within a few kJ mol<sup>-1</sup>. According to the G3MP2 calculations the para-isobutoxybenzoic acid is slightly stabilized about 5 kJ mol<sup>-1</sup>. It make oneself conspicuous, that G3MP2 derived pairwise interactions of methoxy- and iso-butoxy-substituents with the carboxyl-group are very similar. Also resulting interaction in methoxybenzoic calculated with the more sophisticated and time consuming G4method are indistinguishable from those from G3MP2 (see Table 5).



This fact can be considered as the manifestation of the internal consistency of the composite methods used in this work, except for the systematic deviations discussed for *ortho*-isomers above. The experimental *ortho* interactions of the methoxy- and isobutoxy substituent with the carboxyl (see Table 5 column 4) are remarkably similar, proving also the consistency of the experimental data sets. Experimental pairwise interactions in the *meta*- and

*para*-position of the alkoxy substituent are not large and hardly distinguishable within 3–4 kJ mol<sup>-1</sup> in agreement with the theoretical calculations.

## 4.3. Validation of thermochemical properties of alkoxybenzoic acids using the group-contribution method

In spite of the good agreement of the theoretical and experimental values for 3- and 4-iso-butoxybenzoic acids, quantum-chemical methods failed to prove our experimental data for the *ortho*-isomer. Following, another additional method have to be applied for validation of the experimental thermochemical results measured in this work. Good agreement of the experimental and theoretical gas-phase enthalpies of formation of the iso-butoxybenzoic acids shown in the previous chapter does not completely exclude a possible inconsistency in the vaporization enthalpies and in the liquid phase enthalpies,  $\Delta_f H^o_m$  (liq), which are constituted parts of the  $\Delta_f H^o_m$  (g).

Group-additivity methods (GA) are admittedly belong to complementary tools to assess consistency of experimental results [35,36]. One of the best flags to possible experimental errors is a large discrepancy between experimental and estimated values – especially if other, closely related compounds show no such discrepancy [36]. It is well established that enthalpies of vaporization, enthalpies of formation in the liquid and in the gas state obey the group additivity rules [37]. Application of the group additivity methods to sublimation enthalpies and solid state enthalpies of formation is possible [38] but less successful, because both the latter thermochemical properties include significant amount of the fusion enthalpy. For this reason, in this work we systematically derived the vaporization enthalpies and the liquid phase enthalpies of alkoxybenzoic acids from the experimental data in order to apply the GA procedure.

In order to assess consistency of the  $\Delta_f H_m^o(g, 298.15 \text{ K})$ ,  $\Delta_f H_m^o(\text{liq}, 298.15 \text{ K})$  as well as vaporization enthalpies  $\Delta_1^g H_m^o$  (298.15 K) of alkoxybenzoic acids, we applied in this work a simple group-additivity method based on the thermochemical properties of benzene and an appropriate substituted benzenes [15,34]. Experimental thermodynamic properties of benzene are well established and accurate [39]. Thus it reasonable to take this molecule as the starting point and exchange the H-atoms with the different substituents. Indeed, the difference between  $\Delta_f H_m^0$  (298.15 K) of methoxybenzene [33] and benzene [39] provides the increment  $\Delta H(H \rightarrow OCH_3) = -153.6 \text{ kJ mol}^{-1}$  for substitution of an H atom by the methoxy-group in the benzene ring. Likewise, applying the same procedure for the benzoic acid and benzene yields the increment  $\Delta H(H \rightarrow COOH) = -378.4 \text{ kJ mol}^{-1}$ [7]. Introduction of the methoxy and carboxyl substituents into the benzene ring produces three additional increments [7]: (ortho  $CH_3O-COOH$ ) = 15.8 kJ mol<sup>-1</sup>, (*meta*  $CH_3O-COOH$ ) = 2.8 kJ mol<sup>-1</sup>, and  $(para CH_3O-COOH) = -1.8 \text{ kJ mol}^{-1}$ , which are taking into account the pairwise interactions of substituents on the benzene ring (see Table 6). These pairwise interactions were calculated (e.g. for vaporization enthalpy) as the difference between the experimental vaporization enthalpy of an appropriate methoxybenzoic acid [7] and the sum:  $\Delta_1^{g} H_m^0$  (298.15 K, benzene) +  $\Delta H(H \rightarrow OCH_3)$  +  $\Delta H(H \rightarrow COOH)$ . The quantities of contributions from pairwise interactions to the vaporization enthalpy (see Tables 5 and 6), are not large (except for orthodestabilization) but they are significant for prediction vaporization enthalpies of poly-substituted benzenes.

In our recent study we measured, collected, and evaluated available thermochemical data on methoxybenzoic acids [7]. We have reconcile data from numerous experimental studies and recommended a data set of the benchmark quality for the *ortho-, meta*, and

#### Table 6

Parameters for the calculation of enthalpies of vaporization and enthalpies of formation of substituted benzenes at 298.15 K (in kJ mol<sup>-1</sup>)<sup>a</sup>.

Parameters	${\it \Delta}_{ m f} H^\circ_m({ m g})$	$\Delta_1^{g} H_m^\circ$	$\Delta_{\mathrm{f}} H^{\circ}_m(\mathrm{liq})$
Benzene [39]	82.9	33.9	49.0
$\Delta H(H \rightarrow CH_3O)$	-153.6	12.5	-166.1
$\Delta H(H \rightarrow COOH)$	-378.4	41.9	-420.4
ortho (CH <sub>3</sub> O-COOH)	15.8	-2.2	19.3
meta (CH₃O—COOH)	2.8	2.2	2.1
para (CH <sub>3</sub> O-COOH)	-1.8	3.4	-2.7
C(C)(H) <sub>3</sub>	-41.8	6.33	-48.5
$C_{-}(C)_{2}(H)_{2}$	-23.1	4.52	-27.2
$C - (C)_3(H)$	-10.5	1.24	-10.4
C—(C) <sub>4</sub>	-3.2	-2.69	1.9
(C-C) <sub>1-4</sub>	2.6	0.26	2.0
$C-(C)(H)_2(O)$	-34.9	3.64	-38.2
$C - (C)_2(H)(O)$	-31.1	-0.69	-29.4
$C-(C)_{3}(O)$	-25.0	-2.43	-20.6

<sup>a</sup> Group contributions for methoxybenzoic acids was taken from Ref. [7]. Increments for alkyl chains and ethers were taken from our previous study [37].

*para*-isomers. Analysis of the pairwise interactions of alkoxy substituents on the benzene ring with the carboxyl (see Table 5) have revealed that values for interaction of methoxy or iso-butoxy group with the carboxyl in their *ortho*, *meta*- and *para*-position were very similar. This similarity has allowed to propagate more reliable experimental pairwise interactions derived from the methoxybenzoic acids for estimation thermochemical properties of another parent alkoxybenzoic acids.

In Table 6 we collected group-additivity values required for calculation of  $\Delta_f H_m^o$  (g, 298.15 K),  $\Delta_I^g H_m^o$  (298.15 K), and  $\Delta_f H_m^o$  (liq, 298.15 K) of alkoxycarboxylic acids of different structures. As an example let us consider GA estimation of thermochemical properties of 4-ethoxybenzoic acid, e.g. for vaporization enthalpy we need to sum

 $\Delta_1^g H_m^o$  (298.15 K, 4-ethoxybenzoic acid) =  $\Delta_1^g H_m^o$  (298.15 K, benzene) +  $\Delta H(H \rightarrow OCH_3) + \Delta H(H \rightarrow COOH) + (para CH_3O-COOH) + C-(C)(H)_2(O)$ 

The latter increment C– $(C)(H)_2(O)$  takes into account extending of the methoxy group. More sophisticated example with estimations for 4-octyloxybenzoic acid is given in Table S8.

Comparison of the experimental and GA calculated enthalpies of formation  $\Delta_f H_m^0(g, 298.15 \text{ K})$  for alkoxybenzoic acids is given in Table 4, column 5. As can be seen from this table, independent on the structure and branching estimated values agree with the experiment within the boundaries of experimental uncertainties of 2–3 kJ mol<sup>-1</sup>.

The agreement of the calculated and experimental vaporization enthalpies,  $\Delta_1^g H_m^o(298.15 \text{ K})$  was generally acceptable within the experimental errors of 1-3 kJ mol<sup>-1</sup> (see Table 7 column 4). However it should be mentioned that comparison of the experimental and additive values for the 4-butoxybenzoic acid in Table 7 was performed with the vaporization enthalpy derived from the experimental  $\Delta_{cr}^{g} H_{m}^{o}$  which was re-measured in this work (see Tables 1–3). It has turned out that the value  $\Delta_1^{g} H_m^o(298.15 \text{ K}) = 113.4 \pm 2.6 \text{ kJ mol}^{-1}$  derived from the experimental value  $\Delta_{cr}^{g} H_{m}^{o}(298.15 \text{ K}) = 127.8 \pm 1.0 \text{ kJ mol}^{-1}$  reported in Ref. [9] (see Table 3, footnote j), has shown the deviation from the additivity of 9.1 kJ mol<sup>-1</sup>. We were not able to suggest any reasonable explanation for that and decided to measure 4-butoxybenzoic acid with the transpiration method. In spite of agreement shown for the absolute vapor pressures (see Fig. S2), our new values  $\Delta_{cr}^{g} H_{m}^{o}(298.15 \text{ K}) = 123.2 \pm 1.0 \text{ kJ mol}^{-1}$  and  $\Delta_{l}^{g} H_{m}^{o}(298.15 \text{ K}) =$  $108.8 \pm 2.6$  kJ mol<sup>-1</sup> fit significantly better to the consistency tests performed with the quantum-chemical method (Table 4) and GA procedure (Table 7).

Compounds 1	$\Delta_1^{\mathrm{g}} H_m^{o \ \mathrm{a}} \exp 2$	$\Delta_1^g H_m^o$ add 3	${\Delta^{b} \over 4}$	$\Delta_{f}H_{m}^{o}\left(1 ight)^{\mathrm{a}}\exp rac{5}{5}$	$\Delta_{f}H_{m}^{o}\left( l ight)  ext{ add }$	Δ <sup>c</sup> 7
2-Iso-butoxybenzoic acid	$95.6\pm0.6$	96.5	-0.9	$-614.3 \pm 2.2$	-614.1	-0.2
3-Iso-butoxybenzoic acid	$99.2\pm0.9$	101.3	-2.1	$-629.5 \pm 3.2$	-631.3	1.8
4-Iso-butoxybenzoic acid	$104.1 \pm 2.1$	102.5	1.6	$-641.7\pm3.0$	-636.1	-5.6
4-Etoxybenzoic acid	$95.5\pm2.8$	95.3	0.2	$-579.2 \pm 3.2$	-578.4	-0.8
4-Butoxybenzoic acid	$108.8 \pm 2.6$	104.7	4.1	$-632.7 \pm 3.5$	-630.8	-1.9
4-Octyloxybenzoic acid	$126.7\pm3.8$	124.0	2.7	$-745.0\pm4.8$	-731.6	-13.4

Comparison of the experimental and GA calculated data for alkoxybenzoic acids at T = 298.15 K (in kJ mol<sup>-1</sup>).

<sup>a</sup> From Table 1.

<sup>b</sup> Difference between column 2 and column 3 in this table.

<sup>c</sup> Difference between column 5 and column 6 in this table.

Agreement for the liquid phase enthalpies of formation  $\Delta_f H_m^o$  (liq, 298.15 K) was less sufficient (see Table 7, column 7), especially for the 4-octyloxybenzoic acid. However, the disagreement for the latter compound is rather due to the numerous solid state transitions collected in to the  $\Delta_{298}^{T_{fris}}H_m^o$ -term and used to derive  $\Delta_f H_m^o$  (liq, 298.15 K) (see Table 3), than in the deficiencies of the GA procedure.

## 5. Conclusions

We have applied different experimental thermochemical methods to measure highly pure samples of the 2-,3-, and 4iso-butoxybenzoic acids. Experimental data on  $\Delta_{cr}^g H_m^0$  (298.15 K),  $\Delta_{cr}^1 H_m^0$  (298.15 K), and  $\Delta_1^g H_m^0$  (298.15 K) were derived and together with enthalpies of formation  $\Delta_f H_m^0$  (liq or cr, 298.15 K) were used to obtain the gas-phase enthalpies of formation  $\Delta_f H_m^0$  (g, 298.15 K) for all three isomers. Mutual validation of the experimental and theoretical gas phase enthalpies of formation was performed with the G3MP2 quantum-chemical method. Simple group-additivity procedures have been developed for prediction of enthalpies of formation and enthalpies of vaporization of alkoxybenzoic acids of different structures.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tca.2015.07.011

#### References

- [1] P.S. Pereira Silva, R.A.E. Castro, E. Melro, M.R. Silva, T.M.R. Maria, J. Canotilho, M.E. S. Eusébio, J. Therm. Anal. Calorim., in press, doi: 10.1007/s10973-014-4289-y.
- [2] R. Arnold, D. Beer, G. Bhalay, U. Baettig, S.P. Collingwood, S. Craig, N. Devereux, A. Dunstan, A. Glen, S. Gomez, S. Haberthuer, T. Howe, S. Jelfs, H. Moser, R. Naef, P. Nicklin, D. Sandham, R. Stringer, K. Turner, S. Watson, M. Zurinib, 8-Aryl xanthines potent inhibitors of phosphodiesterase 5, Bioorg. Med. Chem. Lett. 12 (2002) 2587–2590.
- [3] M.S. Gruzdev, O.B. Akopova, T.V. Frolova, Synthesis and study of vitrescent materials based on the alkoxybenzoic acids derivatives and triethanolamine, Russ. J. Gen. Chem. 83 (2013) 652–658.
- [4] H. Lu, J. Wang, X. Song, Supramolecular liquid crystals induced by intermolecular hydrogen bonding, Mol. Cryst. Liq. Cryst. 537 (2011) 93–102.
- [5] T. Iwata, R. Miyata, A. Matsumoto, Columnar and smectic mesophases observed for mixed liquid crystal systems using 4-substituted benzoic acids, Chem. Lett. 42 (2013) 849–851.
- [6] M. Parvez, Structure of o-anisic acid, Acta Cryst., C 43 (1987) 2243-2245.
- [7] S.P. Verevkin, Dz.H. Zaitsau, V.N. Emel'yanenko, E.N. Stepurko, K.V. Zherikova, Benzoic acid derivatives: evaluation of thermochemical properties with complementary experimental and computational methods, Thermochim. Acta (2015), http://dx.doi.org/10.1016/j.tca.2015.03.026

- [8] M.A.V. Ribeiro da Silva, A.I.M.C.L. Ferreira, F.M. Maciel, Experimental standard molar enthalpies of formation of some 4-alkoxybenzoic acids, J. Chem. Thermodyn. 42 (2010) 220–224.
- [9] J.M.S. Fonseca, L.M.N.B.F. Santos, M.J.S. Monte, Thermodynamic study of 4-n-alkyloxybenzoic acids, J. Chem. Eng. Data 55 (2010) 2238–2245.
- [10] J.P. Schroeder, D.W. Bristol, Liquid crystals. IV. Effects of terminal substituents on the nematic mesomorphism of *p*-phenylene dibenzoates, J. Org. Chem. 38 (1973) 3160–3161.
- [11] A.A. Morton, A.E. Brachman, Condensations by sodium. XXXVI. The alkylation of anisole and of o-cresol methyl ether and the composition of a reacting aggregate, J. Am. Chem. Soc. 76 (1954) 2980–2983.
- [12] V.N. Emel'yanenko, S.P. Verevkin, A. Heintz, The gaseous enthalpy of formation of the ionic liquid 1-butyl-3-methylimidazolium dicyanamide from combustion calorimetry, vapor pressure measurements, and ab initio calculations, J. Am. Chem. Soc. 129 (2007) 3930–3937.
- [13] W.N. Hubbard, D.W. Scott, G. Waddington, in: F.D. Rossini (Ed.), Experimental Thermochemistry, Interscience Publishers, New York, NY, 1956, pp. 75–127.
- [14] S.P. Verevkin, V.N. Emel'yanenko, Transpiration method: vapour pressures and enthalpies of vapourization of some low-boiling esters, Fluid Phase Equilib. 226 (2008) 64–75.
- [15] S.P. Verevkin, A.Yu. Sazonova, V.N. Emel'yanenko, Dz.H. Zaitsau, M.A. Varfolomeev, B.N. Solomonov, K.V. Zherikova, Thermochemistry of halogen-substituted methylbenzenes, J. Chem. Eng. Data 60 (2015) 89–103.
- [16] C.G. de Kruif, J.G. Blok, The vapour pressure of benzoic acid, J. Chem. Thermodyn. 14 (1982) 201–206.
- [17] M. Colomina, P. Jimenez, M.V. Roux, C. Turrion, Thermochemical properties of benzoic acid derivatives. VII. Enthalpies of combustion and formation of the o-, m-, and p-methoxybenzoic acids, J. Chem. Thermodyn. 10 (1978) 661–665.
- [18] D. Kulikov, S.P. Verevkin, A. Heintz, Enthalpies of vaporization of a series of aliphatic alcohols: experimental results and values predicted by the ERAS-model, Fluid Phase Equilib. 192 (2001) 187–207.
- [19] C. Gobble, J. Chickos, S.P. Verevkin, Vapour pressures and vaporisation enthalpies of a series of dialkyl phthalates by correlation gas chromatography, J. Chem. Eng. Data 59 (2014) 1353–1365.
- [20] M.J. Frisch, G.W. Trucks, H.B. Schlegel, et al., Gaussian 09, Revision C. 01, Gaussian, Inc, Wallingford, CT, 2010.
- [21] L.A. Curtiss, P.C. Redfern, K. Raghavachari, V. Rassolov, J.A. Pople, Gaussian-3 theory using reduced Mo/ller-Plesset order, J. Chem. Phys. 110 (1999) 4703–4709.
- [22] S.P. Verevkin, V.N. Emel'yanenko, R. Notario, M.V. Roux, J.S. Chickos, J.F. Liebman, Rediscovering the wheel. Thermochemical analysis of energetics of the aromatic diazines, J. Phys. Chem. Lett. 3 (2012) 3454–3459.
- [23] D.A. McQuarrie, Statistical Mechanics, Harper & Row, New York, NY, 1976.
- [24] M.E. Wieser, N. Holden, T.B. Coplen, J.K. Bohlke, M. Berglund, W.A. Brand, P. De Bievre, M. Groning, R.D. Loss, J. Meija, T. Hirata, T. Prohaska, R. Schoenberg, G. O'Connor, T. Walczyk, S. Yoneda, X.K. Zhu, Atomic weights of the elements 2011 (IUPAC technical report), Pure Appl. Chem. 85 (2013) 1047–1078.
- [25] J.D. Cox, D.D. Wagman, V.A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere Pub. Corp, New York, NY, 1989.
- [26] G. Olofsson, in: S. Sunner, M. Mansson (Eds.), Combustion Calorimetry, Pergamon, New York, NY, 1979 (chap. 6).
- [27] J.S. Chickos, W.E. Acree, Enthalpies of sublimation of organic and organometallic compounds, 1910–2001, J. Phys. Chem. Ref. Data 31 (2002) 537–698.
- [28] J.S. Chickos, S. Hosseini, D.G. Hesse, J.F. Liebman, Heat capacity corrections to a standard state: a comparison of new and some literature methods for organic liquids and solids, Struct. Chem. 4 (1993) 271–277.
- [29] V.N. Emel'yanenko, S.P. Verevkin, Benchmark thermodynamic properties of 1,3-propanediol: comprehensive experimental and theoretical study, J. Chem. Thermodyn. 85 (2015) 111–119.
- [30] E.S. Domalski, E.D. Hearing, Heat capacities and entropies of organic compounds in the condensed phase. Volume II, J. Phys. Chem. Ref. Data 19 (1990) 881–1047.
- [31] J.S. Chickos, W.E. Acree, Total phase change entropies and enthalpies: an update on their estimation and applications to the estimations of amphiphillic fluorocarbon-hydrocarbon molecules, Thermochim. Acta 395 (2003) 59-113.
- [32] E.M. Goncalves, F. Agapito, T.S. Almeida, J.A. Martinho Simões, J. Chem. Thermodyn. 73 (2014) 90–96.

Table 7

- [33] V.N. Emel'yanenko, K.V. Zaitseva, F. Agapito, J.A.M. Simões, S.P. Verevkin, Benchmark thermodynamic properties of methylanisoles: experimental and theoretical study, J. Chem. Thermodyn. 85 (2015) 155–162.
- [34] S.P. Verevkin, S.V. Melkhanova, V.N. Emel'yanenko, Dz.H. Zaitsau, M.A. Varfolomeev, B.N. Solomonov, K.V. Zherikova, Thermochemistry of di-halogen-substituted benzenes: data evaluation using experimental and quantum chemical methods, J. Phys. Chem., B 118 (2014) 14479–14492.
- [35] S.W. Benson, Thermochemical Kinetics, second ed., John Wiley & Sons, New York, London, Sydney, Toronto, 1976.
- [36] S.P. Verevkin, V.N. Emel'yanenko, V. Diky, C.D. Muzny, R.D. Chirico, M. Frenkel, New group contribution approach to thermochemical properties of organic compounds: hydrocarbons and oxygen containing compounds, J. Phys. Chem. Ref. Data 42 (2013) 1–33 (033102-1-033102-33).
- [37] G.N. Roganov, P.N. Pisarev, V.N. Emel'yanenko, S.P. Verevkin, Measurement and prediction of thermochemical properties. Improved Benson-type increments for the estimation of enthalpies of vaporization and standard enthalpies of formation of aliphatic alcohols, J. Chem. Eng. Data 50 (2005) 1114–1124.
- [38] A. Salmon, D. Dalmazzone, Prediction of enthalpy of formation in the solid state (at 298.15 K) using second-order group contributions. Part 1. Carbon-hydrogen and carbon-hydrogen-oxygen compounds, J. Phys. Chem. Ref. Data 35 (2006) 1443–1457.
- [39] M.V. Roux, M. Temprado, J.S. Chickos, Y. Nagano, Critically evaluated thermochemical properties of polycyclic aromatic hydrocarbons, J. Phys. Chem. Ref. Data 37 (2008) 1855–1996.