Substituent Effects on the Benzene Ring. Determination of the Intramolecular Interactions of Substituents in *tert*-Alkyl-Substituted Catechols from Thermochemical Measurements

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Chemical equilibria of reactions of transalkylation among *tert*-butylphenols and *tert*-butylcatechols in the liquid phase were investigated in the temperature range 373−483 K. The molar enthalpies of fusion $\Delta_{cr}^{l}H_m^\circ$ of the catechol, 4-*tert*-butylcatechol, and 3,5-di-*tert*-butylcatechol were measured by DSC. The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation $\Delta_f H_m^\circ$ (cr) at the temperature $T = 298.15$ K were measured by means of combustion calorimetry for 4-*tert*-butylcatechol and 3,5-di-*tert*-butylcatechol. The standard molar enthalpies of sublimation of these compounds, and also the enthalpy of vaporization of 3-*tert*-butylcatechol, were obtained from the temperature dependence of the vapor pressure measured by the transpiration method. The measured reaction enthalpies were utilized for reconciliation of calorimetrically derived standard molar enthalpies of formation of *tert*-butyl-substituted phenols and catechols, as a stringent test of thermodynamic consistency of results derived from the diverse techniques employed in this work. Resulting values of $\Delta_f H_m^\circ$(g) of *tert*-butylcatechols were obtained at the temperature $T =$ 298.15 K and used to derive their strain enthalpies. The intramolecular interactions of the substituents were discussed in terms of deviations of $\Delta_f H_m^\circ$(g) from the group additivity rules. No peculiarities in the interaction energy among alkyl groups and the hydroxyl groups in the ortho-, para-, and meta-positions of alkylcatechols in comparison with those of alkyl-substituted phenols were detected. Thus, no new parameters are needed for the prediction of the $\Delta_f H_m^\circ$(g) values of alkylcatechols by using the group-additive procedure.

Introduction

Quantitative analysis of the substituent effects on the benzene ring with emphasis on the alkyl-substituted phenols remains in the center of our research activities. We use a combination of combustion calorimetry and DSC with the transpiration method in order to obtain standard molar enthalpies of formation $\Delta_f H_m^\circ$(g) for compounds of interest and to derive the effects of the intramolecular interactions of substituents. In recent works[1−3] we have additionally involved the results from chemical equilibrium studies of mutual interconversions of alkylphenols in order to establish the consistency of the experimental method used. The remarkable agreement between the enthalpies of formation $\Delta_f H_m^\circ$(l) of alkylphenols obtained from combustion calorimetry and DSC with those derived from the equilibrium study in the liquid phase has encouraged us to extend such comparisons to *tert*-butyl-substituted catechols. A set of chemical reactions (see Figure 1) have been reported[4,5] some years ago. Over the intervening years the thermochemical results on the individual reactions participants became available from the literature: for phenol and *tert*-butylphenols[1,2] and for catechol and *tert*-butylcatechols.[6] The reported values by Steele et al.[7] by DSC of the enthalpy of fusion of 4-*tert*-butylcatechol provided the necessary value for reconciliation of the thermochemical results for *tert*-butylphenols and *tert*-butylcatechols. Disappointingly, the enthalpies of reactions 1−4 derived from equilibrium studies[4,5] and those calculated from the enthalpies of formation (obtained from combustion calorimetry and DSC) of the reaction participants differ by (15−50) kJ·mol^{-1}. This disagreement requires explanation. The explanation could be due to structural peculiarities of alkylcatechols (or alkyl-1,2-dihydroxybenzenes) in comparison to alkylphenols (or alkylmonohydroxybenzenes), but these one does not expect, because no peculiarities were detected for the parent compounds—alkylhydroquinones (or alkyl-1,4-dihydroxybenzenes)—in comparison to alkylphenols.[3] The observed disagreement of the data sets also could be caused by systematic error. The best way to solve such a problem is by additional experimental work.

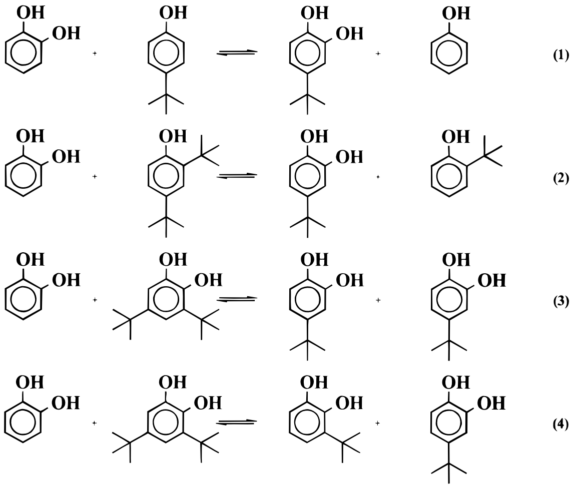

Figure 1. Equilibrium reactions of transalkylation of *tert*-butylcatechols and *tert*-butylphenols in the liquid phase.

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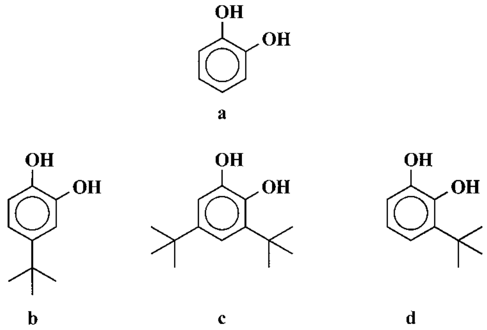

Figure 2. Structures of investigated compounds: catechol (a), 4-*tert*-butylcatechol (b), 3,5-di-*tert*-butylcatechol (c), and 3-*tert*-butylcatechol (d).

This work has five major goals. The first is extended investigation of the chemical equilibria of reactions (see Figure 1) of transalkylation among *tert*-butylphenols and *tert*-butylcatechols in the liquid phase. Our second goal addresses the measurements of the enthalpies of fusion of catechols (see Figure 2) involved in the reactions 1−4. The third is redetermination of the molar enthalpies of formation $\Delta_f H^\circ_m$(cr) of 4-*tert*-butylcatechol and 3,5-di-*tert*-butylcatechol by means of combustion calorimetry. The fourth goal is reconciliation of enthalpies of formation of catechols derived from chemical equilibrium study with those obtained by combination of the results from combustion calorimetry and DSC. From such a comparison we hope to obtain a stringent test of thermodynamic consistency of results derived from the diverse techniques employed in this work. Finally, our aim is to obtain the intramolecular interactions of the substituents on the benzene nucleus in terms of deviations of $\Delta_f H^\circ_m$(g) from the group additivity rules. The interaction energies between the *tert*-butyl group and the hydroxy groups in the ortho-, meta-, and para-positions of *tert*-butylcatechols have been obtained from standard molar enthalpies of formation of catechols (Figure 2) in the gaseous phase. These interactions could be used to predict values of $\Delta_f H^\circ_m$(g) for as yet unmeasured compounds with similar structure.

Experimental Procedure

Materials. All compounds, excluding 3-*tert*-butylcatechol, were purchased from Aldrich or Acros Ltd. 3-*tert*-Butylcatechol was synthesized via isomerization of the appropriate 4-*tert*-butylcatechol with a catalytic amount of sulfonic ion-exchange resin Amberlyst at 333 K and was purified by repeated distillations using a spinning-band column at reduced pressure. The solid catechols were purified by repeated crystallization from ethanol and then finally sublimed under reduced pressure to remove any traces of solvent. The samples did not appear to be hygroscopic, but the sublimed samples were subjected to pellet-drying to remove traces of occluded water and were kept in a desiccator under P_2O_5. Examination of the samples using GLC showed no discernible amounts of impurities. The products were analyzed with a Hewlett-Packard gas chromatograph 5890 Series II equipped with a flame ionization detector and a Hewlett-Packard 3390A integrator: carrier gas (nitrogen) flow 12.1 $cm^3 \cdot s^{-1}$; capillary column HP-5 (stationary phase cross-linked 5% PH ME silicone); column length, inside diameter, and film thickness 30 m × 0.32 mm × 0.25 μm. The standard temperature program of the GLC was $T = 373$ K followed by a heating rate of 0.167 $K \cdot s^{-1}$ to $T = 523$ K.

Table 1. Experimental Results for Reactions 1−4 Obtained from the Glass Vial Technique (temperature *T* and Number of Determinations *n* of Composition within the Time of Equilibrium Study), and Mean Values of the Equilibrium Constants K_N in the Liquid Phase, Calculated from Mole Fractions of the Reaction Participants

reaction	*T*/K	*n*	K_N[a]	reaction	*T*/K	*n*	K_N[a]
1	373	17	2.5 ± 0.2	2	373	12	3.8 ± 0.4
	403	35	2.6 ± 0.1		403	24	3.6 ± 0.1
	413	16	2.4 ± 0.3		413	14	3.4 ± 0.3
	423	15	2.2 ± 0.1		423	10	3.5 ± 0.2
	443	12	2.6 ± 0.2		443	8	3.4 ± 0.4
	453	10	2.6 ± 0.1		453	11	3.6 ± 0.2
	483	11	2.5 ± 0.2		483	7	3.5 ± 0.5
3	373	7	407 ± 104	4	373	12	3.1 ± 1.6
	403	3	218 ± 34		403	5	3.6 ± 1.3
	413	13	206 ± 14		413	15	3.6 ± 0.8
	423	11	185 ± 12		423	7	3.7 ± 0.3
	443	12	143 ± 13		443	16	4.1 ± 0.4
	483	5	103 ± 14		483	13	4.3 ± 0.6

[a] Uncertainty is the standard deviation.

Glass Vial Technique for the Determination of Reaction Enthalpies. The liquid-phase equilibrium study of the reactions (see Figure 1) of mutual transalkylation of *tert*-butylphenols and *tert*-butylcatechols was performed using mixtures of the various isomers with themselves, as well as with catechol, phenol, and *p*-*tert*-butylphenol. Screwed glass vials were filled at least two-thirds of the volume with the initial liquid mixture *tert*-butylcatechols and *tert*-butyl-phenols. Cation-exchange resin Amberlist 15 (Aldrich) in H^+ form was added as a solid catalyst. The quantity of catalyst was approximately 10% of the mass of the mixture. The vial was thermostated at ($T_i \pm 0.1$) K and periodically shaken. After definite time intervals the vial was cooled rapidly in ice and opened. A sample for the GLC analysis was taken from the liquid phase using a syringe. The thermostating of the vial then proceeded at the same temperature. The samples were taken successively until no further change of the composition was observed, indicating that the chemical equilibrium was established. Response factors of all reagents by GLC analysis were determined by using calibration mixtures of the corresponding components prepared gravimetrically. The measured equilibrium constants K_N, calculated from the mole fractions of reaction participants, are presented in Table 1.

DSC Measurements. The thermal behavior of catechols including melting temperatures and enthalpies of fusion was determined with a computer-controlled Perkin-Elmer DSC-2. For all measurements an empty pan run was subtracted and specific heat capacity was calculated. The fusion temperatures and enthalpies were determined as the peak onset temperature and by using a straight baseline for integration, respectively. The temperature and heat flow rate scale of the differential scanning calorimeter was calibrated by measuring high-purity indium ($T_0 =$ 429.8 K and $\Delta H_{ref} = 28.5$ $J \cdot g^{-1}$). The uncertainty for temperature is ±0.5 K, and that for enthalpy of fusion is ±1 $J \cdot g^{-1}$.

Combustion Calorimetry. An isoperibol rotating-bomb macrocalorimeter and platinum-lined bomb were used without rotation for the measurement of energies of combustion of 4-*tert*-butylcatechol and 3,5-di-*tert*-butylcatechol. Six experiments were carried out for each compound. The detailed procedure has been described previously.[1] The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but none was detected. The energy equivalents of the calorimeters ϵ_{calor} were determined with a standard reference sample of benzoic

Table 2. Results from Measurements of the Vapor Pressure p by the Transpiration Method

T^a/K	m^b/mg	$V(N_2)^c/dm^3$	p^d/Pa	T^a/K	m^b/mg	$V(N_2)^c/dm^3$	p^d/Pa
4-*tert*-Butylcatechol; $\ln(p/\mathrm{Pa}) = (36.84 \pm 0.33) - (11873 \pm 103)(T/\mathrm{K})^{-1}$							
303.5	1.06	153.2	0.1029	318.1	1.53	36.84	0.6201
308.2	1.37	111.9	0.1826	320.3	1.63	30.64	0.7918
311.2	2.18	123.9	0.2621	321.7	1.66	25.85	0.9549
314.3	1.66	63.19	0.3906	323.3	1.23	16.73	1.095
316.2	1.85	57.91	0.4752				
$\Delta_{cr}^{g}H_m^\circ(313.4\ \mathrm{K}) = (98.72 \pm 0.86)\ \mathrm{kJ{\cdot}mol^{-1}}$; $\Delta_{cr}^{g}H_m^\circ(298.15\ \mathrm{K}) = (99.21 \pm 0.86)\ \mathrm{kJ{\cdot}mol^{-1}}$							
3-*tert*-Butylcatechol; $\ln(p/\mathrm{Pa}) = (26.11 \pm 0.26) - (8436 \pm 95)(T/\mathrm{K})^{-1}$							
333.7	0.0502	4.470	2.293	357.3	0.0391	0.688	12.16
336.3	0.0511	3.860	2.788	360.2	0.0400	0.579	14.77
339.2	0.0494	2.970	3.453	363.4	0.0314	0.397	18.10
342.2	0.0477	2.410	4.281	366.3	0.0323	0.308	21.75
345.2	0.0468	1.990	5.312	371.2	0.0348	0.234	29.44
348.2	0.0485	1.590	6.581	376.2	0.0357	0.180	39.87
351.2	0.0451	1.250	8.092	381.2	0.0340	0.145	53.51
354.3	0.0425	0.940	9.942	384.3	0.0331	0.109	63.96
$\Delta_{l}^{g}H_m^\circ(359.0\ \mathrm{K}) = (70.14 \pm 0.79)\ \mathrm{kJ{\cdot}mol^{-1}}$; $\Delta_{l}^{g}H_m^\circ(298.15\ \mathrm{K}) = (73.45 \pm 0.79)\ \mathrm{kJ{\cdot}mol^{-1}}$							
3,5-di-*tert*-Butylcatechol; $\ln(p/\mathrm{Pa}) = (37.21 \pm 0.18) - (12472 \pm 59)(T/\mathrm{K})^{-1}$							
313.2	0.717	109.1	0.07316	334.3	1.41	17.38	0.9053
318.3	0.595	48.08	0.1379	337.1	1.38	12.45	1.239
323.2	1.29	60.00	0.2402	340.2	1.25	8.02	1.736
326.1	1.07	34.13	0.3509	343.1	1.36	6.41	2.360
329.0	1.22	27.43	0.4958	346.2	1.04	3.65	3.170
332.2	1.38	22.32	0.6913				
$\Delta_{cr}^{g}H_m^\circ(329.7\ \mathrm{K}) = (103.7 \pm 0.49)\ \mathrm{kJ{\cdot}mol^{-1}}$; $\Delta_{cr}^{g}H_m^\circ(298.15\ \mathrm{K}) = (104.71 \pm 0.49)\ \mathrm{kJ{\cdot}mol^{-1}}$							

[a] Temperature of saturation, N_2 gas flow (0.26 to 0.52) $\mathrm{cm^3{\cdot}s^{-1}}$. [b] Mass of transferred sample condensed at $T = 243$ K. [c] Volume of nitrogen used to transfer sample. [d] Vapor pressure at temperature T of experiment; corrections were made for residual vapor pressure at $T = 243$ K.

acid (sample SRM 39i, N.I.S.T.). From seven experiments, ϵ_{calor} was measured to be $(25066.70 \pm 0.88)\ \mathrm{J{\cdot}K^{-1}}$. Nitrogen oxides were not formed in the calibration experiments due to the high purity of the oxygen used and preliminary bomb flushing. For converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states, the conventional procedure[8] was applied. The sample masses were reduced to vacuum, taking into consideration the density values $\rho(293\ \mathrm{K}) = 1.06\ \mathrm{g{\cdot}cm^{-3}}$ for 4-*tert*-butylcatechol and $\rho(293\ \mathrm{K}) = 0.917\ \mathrm{g{\cdot}cm^{-3}}$ for 3,5-di-*tert*-butylcatechol, which were determined in a calibrated 10 $\mathrm{cm^3}$ pycnometer. The energy of combustion of cotton thread $\Delta_c u^\circ(CH_{1.774}O_{0.887}) = -(16945.2 \pm 4.2)\ \mathrm{J{\cdot}g^{-1}}$ was measured earlier. The molar masses of catechols were evaluated from the relative atomic masses of elements.[9] Converting the energy of the actual bomb process to that of the isothermal process and reducing to standard state were performed as assigned by Hubbard et al.[8]

Transpiration Method. The enthalpies of sublimation of catechols were determined using the method of transpiration[1] in a saturated N_2 stream and applying the Clausius−Clapeyron equation. About 0.5 g of the sample was mixed with glass beads and placed in a thermostated U-tube of length 20 cm and diameter 0.5 cm. At constant temperature (±0.1 K), a nitrogen stream was passed through the U-tube and the transported amount of material was collected in a cold trap. The flow (0.28 to 0.56) $\mathrm{cm^3{\cdot}s^{-1}}$ of the nitrogen stream was optimized in order to reach the saturation equilibrium of the transporting gas at each temperature of the investigation. The amount of condensed substance was determined by GLC analysis using an internal standard (hydrocarbon n-$C_{14}H_{30}$). The vapor pressure p at each saturation temperature was calculated from the amount of product collected within a definite time period, and the small value of the residual vapor pressure at the temperature of condensation was added. The latter was calculated from a linear correlation between $\ln(p)$ and T^{-1} obtained by iteration. With the assumption that Dalton's law of partial pressures applied to the saturated nitrogen stream, values of p from the ideal gas law were calculated:

$$p = mRT_a/V(N_2)M$$

where $R = 8.314\,51\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, m is the mass of transported compound, $V(N_2)$ is the volume of transporting gas, M is the molar mass of the compound, and T_a is the ambient temperature at which the flow rate and accordingly $V(N_2)$ were measured. The molar enthalpies of sublimation or vaporization were calculated from the slope of the linear Clausius−Clapeyron correlation: $\Delta_{cr}^{g}H_m^\circ = -R(\mathrm{d}\ln p/\mathrm{d}T)$. The observed enthalpies of vaporization $\Delta_{l}^{g}H_m^\circ(T)$ or sublimation $\Delta_{cr}^{g}H_m^\circ(T)$ at the temperature T obtained by this procedure are listed in Table 2.

Results and Discussion

Enthalpies of Reaction. The practical advantage of the equilibrium study in comparison with the calorimetric investigation is the direct measurement of the equilibrium constants, which are very important for the prediction of the equilibrium yields. The enthalpies of reactions (Figure 1) of transalkylation of liquid *tert*-butylcatechols and *tert*-butylphenols have been determined in the liquid phase. The equilibrium constants of reactions 1−4 (Table 1), derived from the GLC-measured mole concentrations of the reaction participants, were independent of the composition of the equilibrium mixtures, the quantity of catalyst, and the time of reaction, and can thus be assumed to be equal to the thermodynamic constants. The experimental data were approximated with the equation $\lg K_N = a + b(T/\mathrm{K})^{-1}$, by using the method of least squares. The slope of this line when multiplied by the gas constant affords the enthalpy of reaction $\Delta_r H_m^\circ$ in the liquid phase, and the intercept gives the entropy of reaction $\Delta_r S_m^\circ$. The equilibrium constants of reactions 1−4 measured in this work were in close agreement with our earlier results.[4,5] The

Table 3. Thermodynamic Functions $\Delta_r H^\circ_m$ and $\Delta_r S^\circ_m$ of the Equilibrium Reactions of Mutual Interconversions of *tert*-Butylphenols and Catechols in the Liquid Phase

	$\langle T\rangle^a$	$\lg K_N = a + b(T/K)^{-1}$		$\Delta_r H^\circ_m$	$\Delta_r S^\circ_m$
reaction	K	a	b	$kJ\cdot mol^{-1}$	$J\cdot K^{-1}\cdot mol^{-1}$
1	413.6	0.432 ± 0.011	-16 ± 59	0.3 ± 1.1	8.3 ± 3.0
2	414.6	0.431 ± 0.006	50 ± 31	-1.0 ± 1.2	8.3 ± 2.9
3	415.5	-0.014 ± 0.013	965 ± 68	-18.5 ± 1.3	-0.3 ± 5.6
4	447.5	1.120 ± 0.004	-232 ± 24	4.4 ± 1.2	21.4 ± 6.9

[a] The average temperature of the equilibrium study.

Table 4. Standard Molar Enthalpies of Formation and Enthalpies of Fusion of Phenols and Catechols at T = 298.15 K, Used for Comparison Results of Equilibrium and Calorimetric Studies

	$\Delta_f H^\circ_m(cr)$	$\Delta^l_{cr} H^\circ_m{}^a$	$\Delta_f H^\circ_m(l)$
compound	$kJ\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	$kJ\cdot mol^{-1}$
phenol	-165.1 ± 0.8^b	10.60 ± 0.20^c	-154.5 ± 0.8
2-*tert*-butylphenol			-254.8 ± 1.6^c
4-*tert*-butylphenol	-289.7 ± 1.5^d	15.06 ± 0.20^d	-270.5 ± 1.5
2,4-di-*tert*-butylphenol	-383.4 ± 2.1^d	12.57 ± 0.20^d	-403.0 ± 2.5
catechol	-354.1 ± 1.1^e	18.55 ± 0.20^g	-335.6 ± 1.1
4-*tert*-butylcatechol	-465.2 ± 1.9^f	13.30 ± 0.20^h	-451.9 ± 1.9
3,5-di-*tert*-butylcatechol	-570.3 ± 2.7^f	20.02 ± 0.20^i	-550.3 ± 2.7

[a] Adjusted to the reference temperature (see text). [b] Data from Pedley et al.[19] [c] Data from Verevkin.[12] [d] Data from Verevkin.[1] [e] Data from Ribeiro da Silva et al.[6] [f] This work, from Table 6. [g] This work, $\Delta^l_{cr} H^\circ_m = 22.9 \pm 0.2 kJ\cdot mol^{-1}$ at $T_{fus} = 377.6$ K. [h] This work, $\Delta^l_{cr} H^\circ_m = 15.1 \pm 0.2$ kJ·mol^{-1} at $T_{fus} = 330.4$ K. [i] This work, $\Delta^l_{cr} H^\circ_m = 24.1 \pm 0.2$ kJ·mol^{-1} at $T_{fus} = 372.8$ K.

equilibrium constants were treated together, and numerical results are presented in Table 3. The errors in the thermodynamic functions from the equilibrium study are given by the standard deviations. They were defined in accordance with the requirements of the IUPAC Commission and include the errors in the equilibrium constants K_N as well as deviations of K_N from the linear dependence: $\lg K_N = a + b(T/K)^{-1}$.

Enthalpies of Fusion. We used the enthalpies of fusion of catechols in order to calculate their enthalpies of formation in the liquid phase. The temperatures and enthalpies of fusion were determined by DSC from the first heating of the crystals as received from purification in the temperature interval (300−400) K at a heating rate of 10 K·min^{-1}. The values obtained for the molar enthalpies of fusion at the melting temperatures are reported in Table 4. The DSC measurements on each sample of catechols were repeated twice, and values agreed within the experimental uncertainties ±0.2 kJ·mol^{-1} for the enthalpy of fusion and ±0.5 K for the melting temperature. The thermal behavior of each specimen was investigated during the first and second heating after cooling the sample from the melt at a cooling rate of 10 K·min^{-1}.

The melting process was observed for the catechol with $\Delta^l_{cr} H^\circ_m = (22.87 \pm 0.20)$ kJ·mol^{-1} at 377.6 K on first and second heating. The thermal behavior of the *tert*-butylcatechols was more complicated. The shape of the melting peak of 4-*tert*-butylcatechol in the first run, see inset of Figure 3a, shows a shoulder, indicating polymorphism. After cooling the sample to 200 K in the differential scanning calorimeter, a glass transition at 255 K and no crystallization can be observed during the second heating. The sample remained liquid, and no melting peak was observed at all. Usually the sharp shape of the melting peak indicates the high purity of a sample according to Hemminger and Camenga.[10] We tested the termal stability of 4-*tert*-butylcatechol by heating of the sample at its melting temperature. However, no impurities were detected (using GLC) in the sample after heating. Following, the sample of 4-*tert*-butylcatechol is stable at the temperature of melting, and such a broad peak with a shoulder rather may account for polymorphism. Similar behavior of the pure sample of 4-*tert*-butylcatechol was observed by Steele et al.[7] Their sample was purified by distillation and remained liquid for several weeks after purification before becoming an opaque solid. They measured a very small enthalpy of fusion $\Delta^l_{cr} H^\circ_m = (4.5 \pm 0.2)$ kJ·mol^{-1} at 327 K in comparison with our value (see Table 4). This fact indicates that in their investigation the solid phase at ambient temperature was only partially crystalline. In contrast, our sample of 4-*tert*-butylcatechol was purified by fractional sublimation and white fine needles were obtained by such a procedure. The enthalpy of fusion of these crystals $\Delta^l_{cr} H^\circ_m = (15.1 \pm 0.2)$ kJ·mol^{-1} at 330.4 K should be more reliable for the quantitative characterization of the melting process.

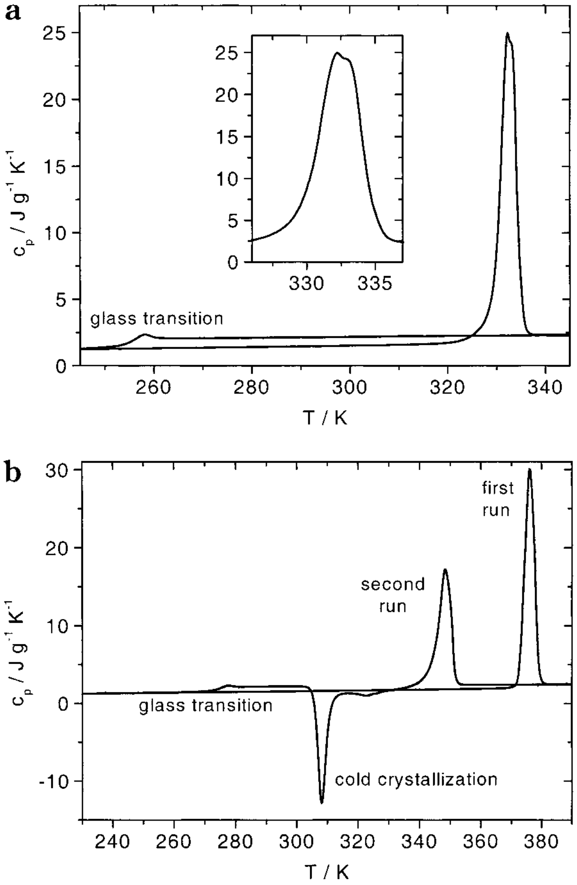

Figure 3. (a) First and second heating of 4-*tert*-butylcatechol. Heating rate 10 K·min^{-1}. The inset shows a magnified part of the melting peak. (b) First and second heating of 3,5-di-*tert*-butylcatechol. Heating rate 10 K·min^{-1}.

The sample of 3,5-di-*tert*-butylcatechol showed a sharp melting peak in the first heating run at 372.5 K, but no peaks were observed during its cooling with the rate 10 K·min^{-1} to 220 K; following, the liquid sample remains undercooled and shows a glass transition at 274 K. However, this undercooled state of the sample is time-limited, and the sample became crystalline during heating or annealing for several hours at room temperature; see Figure 3b. By the second and the third run with the same sample, an exothermal effect, cold crystallization, was observed with a first sharp maximum at 308 K and a smaller one at 323 K (see Figure 3b). The crystalline

Table 5. Results for Typical Combustion Experiments at $T = 298.15$ K ($p^\circ = 0.1$ MPa)[a]

	4-*tert*-butylcatechol	3,5-di-*tert*-butylcatechol
m (substance)/g[b]	0.447 990	0.330 301
m' (cotton)/g[b]	0.001 269	0.000 921
ΔT_c/K[c]	0.588 63	0.479 24
$(\epsilon_{calor})(-\Delta T_c)$/J	−14 755.02	−12 012.96
$(\epsilon_{cont})(-\Delta T_c)$/J	−7.80	−6.29
ΔU_{corr}/J[d]	6.58	4.57
$-m'\Delta_c u'$/J[d]	21.50	15.60
$\Delta_c u^\circ$ (sub)/(J·g^{-1})	−32 870.1	−36 304.2

[a] For the definition of the symbols, see ref 8. Calorimeter: $T_h = 298.15$ K; p^i(gas) = 3.04 MPa; $m^i(H_2O) = 0.78$ g; ΔU(ign) = 1.46 J; m(Pt) = 8.61 g. [b] Masses obtained from apparent masses. [c] $\Delta T_c = T^f - T^i + \Delta T_{corr}$; $(\epsilon_{cont})(-\Delta T_c) = (\epsilon^i_{cont})(T^i - 298.15\ \text{K}) + (\epsilon^f_{cont})(298.15\ \text{K} - T^f + \Delta T_{corr})$. [d] ΔU_{corr}, the correction to standard states, is the sum of items 81 to 85, 87 to 90, 93, and 94 in ref 8.

modification established on heating melts at 343.3 K, which is 29 K lower than the original value. Such behavior may be explained due to delayed reorganization of the crystalline structure of the specimen and polymorphism.

The enthalpies of fusion $\Delta^l_{cr}H^\circ_m$ of the solid catechols measured by DSC refer to the temperatures of fusion. Because of the deviations from $T = 298.15$ K, the observed values of the enthalpies of fusion (see Table 4) had to be corrected to this reference temperature. The corrections were estimated with the help of the correction

$$\{\Delta^l_{cr}H^\circ_m(\langle T_{fus}\rangle) - \Delta^l_{cr}H^\circ_m(298.15\ \text{K})\}/(\text{kJ·mol}^{-1}) = (5.44 \times 10^{-2})\{(\langle T_{fus}\rangle/\text{K}) - 298.15\}$$

following the recommendation of Chickos et al.[11] With these corrections, and the measured values of $\Delta^l_{cr}H^\circ_m(T_m)$ from Table 4, the standard molar enthalpies of fusion at $T = 298.15$ K were calculated (Table 4). In the same manner the enthalpies of fusion of phenol[12] ($\Delta^l_{cr}H^\circ_m = 11.55$ kJ·mol^{-1}) at 315.5 K, 4-*tert*-butylphenol[1] ($\Delta^l_{cr}H^\circ_m = 19.12$ kJ·mol^{-1}) at 372.7 K, and 2,4-di-*tert*-butylphenol[1] ($\Delta^l_{cr}H^\circ_m = 14.39$ kJ·mol^{-1}) at 331.6 K have been adjusted to the reference temperature 298.15 K (see Table 4).

Enthalpies of Formation. Results of typical combustion experiments for 4-*tert*-butylcatechol and 3,5-di-*tert*-butylcatechol are summarized in Table 5. The mean values of the standard specific energies of combustion $\Delta_c u^\circ$, together with its standard deviation, are given in Table 6. To derive $\Delta_f H^\circ_m$(cr) from $\Delta_c H^\circ_m$, molar enthalpies of formation of H_2O(l) [−(285.830 ± 0.042) kJ·mol^{-1}] and CO_2(g) [−(393.51 ± 0.13) kJ·mol^{-1}] were taken, as assigned by *CODATA*.[13] Table 6 lists the derived standard molar enthalpies of combustion and standard molar enthalpies of formation of the dihydroxybenzenes in the condensed and gaseous states. The total uncertainty was calculated according to the guidelines presented by Olofsson.[14] The uncertainty assigned to $\Delta_f H^\circ_m$ is twice the overall standard deviation and includes the uncertainties from calibration, the uncertainties from the combustion energies of the auxiliary materials, and the uncertainties of the enthalpies of formation of the reaction products H_2O and CO_2.

Previous determinations of the standard molar enthalpies of formation $\Delta_f H^\circ_m$(cr) of a number of alkylcatechols were made by Ribeiro da Silva et al.[6] by combustion calorimetry. Their value [−(570.6 ± 2.6) kJ·mol^{-1}] for 3,5-di-*tert*-butylcatechol is in close agreement with our value (Table 6). The present result of −(465.2 ± 1.9) kJ·mol^{-1} for 4-*tert*-butylcatechol is noticeably less negative than their value −(474.0 ± 1.6) kJ·mol^{-1}. The difference is not within the boundaries of the experimental uncertainties. We do not have a reasonable explanation for such a discordance, but we shall use the data from the equilibrium study and DSC measurements in order to obtain $\Delta_f H^\circ_m$(cr) of 4-*tert*-butylcatechol independently and to compare it with the experimental results from combustion calorimetry.

Enthalpies of Sublimation. The experimental enthalpies of sublimation $\Delta^g_{cr}H^\circ_m$ or vaporization $\Delta^g_l H^\circ_m$ at $T = 298.15$ K of *tert*-butylcatechols and the equations for the temperature dependence $\ln(p/\text{Pa}) = a - b(T/\text{K})^{-1}$ are recorded in Table 2. Because of the deviations from $T = 298.15$ K of the average temperatures during measurement by the transpiration method, the observed values of the enthalpies of sublimation (or vaporization) of *tert*-alkylcatechols (see Table 2) had to be corrected to this reference temperature. The corrections were estimated with the help of the modified "Sidgwick correction":

$$\{\Delta^g_{cr}H^\circ_m(\langle T\rangle) - \Delta^g_{cr}H^\circ_m(298.15\ \text{K})\}/(\text{kJ·mol}^{-1}) = (-3.20 \times 10^{-2})\{(\langle T\rangle/\text{K}) - 298.15\}$$

$$\{\Delta^g_{cr}H^\circ_m(\langle T\rangle) - \Delta^g_l H^\circ_m(298.15\ \text{K})\}/(\text{kJ·mol}^{-1}) = (-5.44 \times 10^{-2})\{(\langle T\rangle/\text{K}) - 298.15\}$$

following the recommendation of Chickos et al.[11] With these corrections, and the measured values of $\Delta^g_{cr}H^\circ_m(T)$ or $\Delta^g_l H^\circ_m(T)$ from Table 2, the standard molar enthalpies of sublimation/vaporization at $T = 298.15$ K were calculated (Tables 2 and 6).

The previous determination of the enthalpy of sublimation $\Delta^g_{cr}H^\circ_m$ of 4-*tert*-butylcatechol was made by Ribeiro da Silva et al.[6] using a drop-microcalorimetric method. Their value [(99.3 ± 1.4) kJ·mol^{-1}] is in excellent agreement with ours [(99.21 ± 0.86) kJ·mol^{-1}]. At the same time, the value of $\Delta^g_{cr}H^\circ_m = (100.1 \pm 0.6)$ kJ·mol^{-1} for 3,5-di-*tert*-butylcatechol measured by the same method and in the same laboratory[6] disagrees with our value (see Table 6) substantially. This may be due to the decomposition of the specimen in the drop-microcalorimetric method. Note that our determination of $\Delta^g_{cr}H^\circ_m$ with the transpiration method, where nitrogen is the carrier gas, would appear more reliable, because of the additional protection of the thermolabile specimen by inert gas during the measurement.

The enthalpy of vaporization of 4-*tert*-butylcatechol $\Delta^g_l H^\circ_m = (85.91 \pm 0.89)$ kJ·mol^{-1} at 298.15 K calculated from our results for sublimation and fusion enthalpies is in disagreement with those of Steele et al.:[7] (96.5 ± 2.8) kJ·mol^{-1}, measured using an ebulliometer in the temperature range (438.5 to 516.3) K and extrapolated to the reference temperature. The difference could be attributed to the sample decomposition noted during the ebulliometric measurement.

Consistency Test of the Experimental Results. The thermochemical properties of *tert*-alkylcatechols in the condensed state measured in this work by combustion and differential scanning calorimetry together with the $\Delta_r H^\circ_m$ from the equilibrium study (Tables 1 and 3) of trans-alkylations of *tert*-butylcatechols and *tert*-butylphenols in the liquid state provide a unique possibility to establish the consistency of the results derived from various experimental techniques. The validity of the results measured for 4-*tert*-butylcatechol by combustion calorimetry can be verified by comparison with the results obtained from the equilibrium study of reactions 1 and 2. The enthalpy of

Table 6. Thermochemical Results at $T = 298.15$ K ($p° = 0.1$ MPa)

	state	$-\Delta_c u°$(cr) J·g^{-1}	$-\Delta_c H°_m$(cr) kJ·mol^{-1}	$\Delta_f H°_m$(l or cr) kJ·mol^{-1}	$\Delta^g_{cr} H°_m$ kJ·mol^{-1}	$\Delta_f H°_m$(g) kJ·mol^{-1}
catechol	cr			−354.1 ± 1.1[a]	86.6 ± 1.6[a]	−267.5 ± 1.9
4-*tert*-butylcatechol	cr	32 874.7 ± 3.9	5470.7 ± 1.4	−465.2 ± 1.9	99.21 ± 0.86	−366.0 ± 2.1
3-*tert*-butylcatechol	l			−429.6 ± 3.7[b]	73.45 ± 0.79	−356.1 ± 3.8
3,5-di-*tert*-butylcatechol	cr	36 305.4 ± 4.0	8082.9 ± 1.9	−570.3 ± 2.7	104.71 ± 0.49	−465.6 ± 2.7

[a] Data from Ribeiro da Silva et al.[6] [b] Derived from the enthalpy of reaction 4 (Table 1).

Table 7. Non-Nearest-Neighbor Interactions $\Delta\Delta H_m$(strain) of Alkyl Groups with the Hydroxyl Group at $T = 298.15$ K

	$\Delta_f H°_m$(g)(exp.) kJ·mol^{-1}	$\Delta_f H°_m$(g)(calc)[a] kJ·mol^{-1}	ΔH_m(strain)(alkylcatechol)[b] kJ·mol^{-1}	ΔH_m(strain)(alkylbenzene)[c] kJ·mol^{-1}	$\Delta\Delta H_m$(strain)[d] kJ·mol^{-1}
catechol	−267.5 ± 1.9[e]	−275.1	7.6		
3-methylcatechol	−299.3 ± 1.6[e]	−307.4	8.1	0.0	0.5
4-methylcatechol	−298.4 ± 1.6[e]	−307.4	9.0	0.0	1.4
3-isopropylcatechol	−350.0 ± 2.3[e]	−358.4	8.4	5.0	−4.2
3-isopropyl-6-methylcatechol	−379.1 ± 1.8[e]	−390.7	11.6	5.5	−1.5
3-*tert*-butylcatechol	−356.1 ± 3.8	−392.7	36.6	10.9	18.1
4-*tert*-butylcatechol	−366.0 ± 2.1	−392.7	26.7	10.9	8.2
3,5-di-*tert*-butylcatechol	−465.6 ± 2.7	−510.4	44.8	23.8	13.4

[a] Calculated as the sum of strain-free increments (see text). [b] Strain enthalpy of alkylcatechols defined as $\Delta H_m(\text{strain}) = \Delta_f H°_m(\text{g})(\text{exp}) - \Delta_f(\text{g})(\text{calc})$. [c] Strain enthalpy of alkylbenzene ΔH_m(strain) taken from earlier works (see text). [d] The sum of resulting interactions of alkyl substituents and the OH group in alkylcatechols: $\Delta\Delta H_m(\text{strain}) = \Delta H_m(\text{strain})(\text{alkylcatechol}) - \Delta H_m(\text{strain})(\text{alkylbenzene}) - \Delta H_m(\text{strain})(\text{catechol})$ (see text). [e] Data from Ribeiro da Silva et al.[6]

reaction 1 is defined through the enthalpies of formation of the reaction participants:

$$\Delta_r H°_m(\text{l})_{(1)} = \Delta_f H°_m(\text{l})_{(4-tert-\text{butylcatechol})} + \Delta_f H°_m(\text{l})_{(\text{phenol})} - \Delta_f H°_m(\text{l})_{(\text{catechol})} - \Delta_f H°_m(\text{l})_{(4-tert-\text{butylphenol})}$$

Assuming that the enthalpy of reaction hardly changes on passing from the average temperature of the experimental range to $T = 298.15$ K and using the experimental value $\Delta_r H°_m(\text{l})_{(1)} = (0.3 \pm 1.1)$ kJ·mol^{-1} from Table 3 and enthalpies of formation of phenol and catechol from Table 4, the enthalpy of formation of 4-*tert*-butylcatechol $\Delta_f H°_m(\text{l}) = -(455.4 \pm 2.3)$ kJ·mol^{-1} was calculated. The enthalpy of formation of 4-*tert*-butylcatechol $\Delta_f H°_m(\text{l}) = -(452.6 \pm 3.2)$ kJ·mol^{-1} was also calculated using the enthalpy of reaction 2 from Table 3. Both values are in very close agreement to our result of $\Delta_f H°_m(\text{l}) = -(451.9 \pm 1.9)$ kJ·mol^{-1} derived from a combination of combustion calorimetry and DSC. Using the experimental value of the enthalpy of reaction 3 $\Delta_r H°_m(\text{l})_{(1)} = -(18.5 \pm 1.3)$ kJ·mol^{-1} from Table 3 and enthalpies of formation of catechol and 4-*tert*-butylcatechol from Table 4, the enthalpy of formation of 3,5-di-*tert*-butylcatechol $\Delta_f H°_m(\text{l}) = -(549.7 \pm 3.2)$ kJ·mol^{-1} was calculated. Again this value, derived from the equilibrium study, is in very close agreement with $\Delta_f H°_m(\text{l}) = -(550.3 \pm 2.7)$ kJ·mol^{-1} derived from a combination of combustion calorimetry and DSC.

The discussion in this section shows clearly that satisfying thermodynamic consistency can be obtained when the standard molar enthalpies of formation obtained by the two independent methods are compared in the liquid phase. This remarkable result supports essentially the validity of the whole experimental procedure concerning all experimental techniques presented in this paper.

Strain Enthalpies of Catechols. The concept of strain[15] and strain energy provides a basis that helps us to correlate the structures, stabilities, and reactivities of molecules. Strain enthalpy reflects a nonadditive component of the enthalpy of a molecule. The nature of such deviations from additivity appears unique for each molecule. We define the strain of a molecule as the difference between the experimental standard molar enthalpy of formation $\Delta_f H°_m(\text{g})$ and the calculated sum of strain-free increments[16] of the Benson type[17] for the molecule. The system of strain-free increments is based on the standard enthalpies of formation $\Delta_f H°_m(\text{g})$ of simple homologous ("strainless") molecules. Strain-free group additivity increments for hydrocarbons[16] and arenes[18] are well defined. Their advantage with respect to the classic Benson increments is the possibility to determine strain enthalpies. All the increments necessary in this work are as follows: $\Gamma(\text{CH}_3\text{-[C]}) = -42.05$ kJ·mol^{-1}; $\Gamma(\text{CH}_2[2\text{C}]) = -21.46$ kJ·mol^{-1}; $\Gamma(\text{CH}[3\text{C}]) = -9.04$ kJ·mol^{-1}; $\Gamma(\text{C}[4\text{C}]) = -1.26$ kJ·mol^{-1}; $\Gamma(\text{C}_B\text{H}[2\text{C}_B]) = 13.72$ kJ·mol^{-1} (C_B represents the aromatic C atoms); $\Gamma(\text{C}_B[\text{C},2\text{C}_B]) = 23.51$ kJ·mol^{-1}; $\Gamma(\text{C}_B[\text{OH},2\text{C}_B]) = 23.51$ kJ·mol^{-1}; $\Gamma(\text{OH}[\text{C}_B]) = -188.5$ kJ·mol^{-1} {calculated from $\Delta_f H°_m(\text{g}) = -(96.4 \pm 0.9)$ kJ·mol^{-1} of phenol[19] and the sum of the aforementioned increments for the benzene ring}. By using these group-additivity parameters and the values of $\Delta_f H°_m(\text{g})$ of catechols (Table 6) derived in this research, the values of strain enthalpies $\Delta H_m(\text{strain}) = \{\Delta_f H°_m(\text{g}) - \sum \text{increments}\}$ of alkyl-substituted catechols have been estimated. These resulting non-nearest-neighbor interactions of alkyl substituents with the OH groups in the gaseous state are listed in Table 7. All alkylcatechols are strained by about (8 to 45) kJ·mol^{-1} (Table 7). Elucidation of the nature of strain in alkylcatechols is aided by comparison with the strain of the similar shaped alkylbenzenes. Standard molar enthalpies of formation $\Delta_f H°_m(\text{g})$ and strain enthalpies ΔH_m(strain) of toluene[19] [(50.4 ± 0.6 and 0.0) kJ·mol^{-1}; isopropylbenzene[19] (4.0 ± 1.0 and 5.0) kJ·mol^{-1}; 1-methyl-4-isopropylbenzene[12] (−27.8 ± 1.1 and 5.5) kJ·mol^{-1}; *tert*-butylbenzene[20] (−24.42 ± 0.8 and 10.9) kJ·mol^{-1}; and 1,3-di-*tert*-butylbenzene[20] (−129.15 ± 0.7 and 23.8) kJ·mol^{-1}] were taken from the literature. These alkylbenzenes are a relevant structural model of strain in the mono- and dialkyl-substituted catechols studied. Their strain enthalpies describe the intrinsic strain of the secondary alkylbenzenes and the *tert*-alkylbenzenes due to steric repulsions of alkyl groups and the benzene ring attached to the tertiary and quaternary carbon atoms. Each of the molecules in Table 7 possesses the embedded intrinsic strain Γ^{ortho}(hydroxyl) = 7.6 kJ·mol^{-1} of catechol itself {calculated from $\Delta_f H^\circ_m$(g) of catechol and the sum of the aforementioned increments for the benzene ring}. Comparison of the strains of alkylbenzenes and catechol allowed the derivation of the effects of non-nearest-neighbor interactions of alkyl substituents on the benzene ring with the OH group directly. We calculated the differences $\Delta\Delta H_m$(strain) between individual strains for each alkylcatechol and the sum of strain of the appropriate alkyl-substituted benzene plus the intrinsic strain of catechol (Table 7). These values $\Delta\Delta H_m$(strain) were interpreted as the sum of excess interactions of alkyl substituents on the benzene ring with the OH group.

The values for the pairwise interactions of a para- or meta-methyl substituent with the hydroxyl group in methylcatechols indicate (Table 7) a very weak destabilization (about 0.5 kJ·mol^{-1} to 1.5 kJ·mol^{-1}) in accordance with the results for the methyl- and ethyl-substituted phenols.[19] The same trends were observed for the para- and meta-pairwise interactions of isopropyl and *tert*-butyl substituents with the hydroxyl group in alkyl-substituted catechols (Table 7). The similar weak destabilization of (1.7 kJ·mol^{-1} to 3.9 kJ·mol^{-1}) was also detected in para- and meta-alkylphenols with secondary[12] and tertiary[1] alkyl substituents. Taking into account the average experimental uncertainties of the values of enthalpies of formation of ±2.0 kJ·mol^{-1}, no correction terms were necessary for the application of the group-contribution correlation for $\Delta_f H^\circ_m$(g) of the para- and meta-alkyl-substituted catechols.

The ortho interactions of the methyl or isopropyl group with the hydroxyl group in the alkylcatechols seem to be negligible (Table 7) within the boundaries of experimental uncertainties of ±2 kJ·mol^{-1}. This conclusion agrees with the absence of ortho interactions of primary and secondary alkyl substituents with the hydroxyl group in alkylphenols.

The para and meta interactions of the *tert*-butyl group with the hydroxyls derived from 4-*tert*-butylcatechol led to a destabilization of 8 kJ·mol^{-1} (Table 7). The similar weak destabilization of (2 kJ·mol^{-1} to 3 kJ·mol^{-1}) was also detected in para and meta tertiary alkylphenols.[1]

The ortho interactions of the *tert*-butyl group with the hydroxyl derived from 3-*tert*-butylcatechol and 3,5-di-*tert*-butylcatechol led to a meaningful destabilization of (13 to 18) kJ·mol^{-1} (Table 7) due to steric repulsion of the hydrogen by the alkyl substituent. This destabilization is about the same as that of the ortho interaction of the *tert*-alkyl group with the OH group Γ^{ortho}(*t*-alkyl) = 12.5 kJ·mol^{-1} (mean value from mono-ortho-substituted phenols[1]). The "buttress" interaction[2] energy among the *tert*-butyl and the hydroxy groups in their adjacent OH−OH−*tert*-butyl position on the benzene ring is not distinguishable within the boundaries of the experimental uncertainties.

Quantitative analysis of the pairwise interactions of substituents on the benzene ring in alkylcatechols demonstrated that there are no peculiarities in the interaction energy among the alkyl and hydroxyl groups in the ortho-, para-, and meta-positions of alkylcatechols in comparison with the case of alkyl-substituted phenols.[1,2] Thus, no new parameters are needed for the prediction of the $\Delta_f H^\circ_m$(g) of similar shaped alkylcatechols by using the group-additive procedure (exception for the intrinsic strain Γ^{ortho}(hydroxyl) = 7.6 kJ·mol^{-1} of catechol itself).

Literature Cited

(1) Verevkin, S. P. Thermochemistry of Phenols. Quantification of the Ortho-, Para-, and Meta-interactions in Tert-alkyl Substituted Phenols. *J. Chem. Thermodyn.* **1999**, *31*, 559−585.
(2) Verevkin, S. P. Thermochemistry of phenols: buttress effects in steric hindered phenols. *J. Chem. Thermodyn.* **1999**, *31*, 1397−1416.
(3) Verevkin, S. P. Substituent effects on the benzene ring. Prediction of the thermochemical properties of alkyl substituted hydroquinones. *Phys. Chem. Chem. Phys.* **1999**, *1*, 127−133.
(4) Verevkin, S. P. Ph.D. Thesis, Minsk State University, Minsk, 1984.
(5) Nesterova, T. N.; Verevkin, S. P.; Rempel, R. D.; Merdzanov, V. R.; Roshupkina, I. Yu. Thermodynamic princyples of the transalkylation of sterically hindered phenols. *Zh. Prikl. Khim. (Leningrad)* **1990**, *63*, 1771−1775; CA 113:230728.
(6) Ribeiro da Silva, M. D. M. C.; Ribeiro Da Silva, M. A. V. Enthalpies of combustion of 1,2-dihydroxybenzene and of six alkyl substituted 1,2-dihydroxybenzenes, *J. Chem. Thermodyn.* **1984**, *16*, 1149−1155.
(7) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A. Vapor Pressure, Heat Capacity, and Density along the Saturation Line, Measurements for Dimethyl Isophthalate, Dimethyl Carbonate, 1,3,5-Triethylbenzene, Pentafluorphenol, 4-Tert-Butylcatechol, α-Methylstyrene, and N,N′-Bis(2-hydroxyethyl)ethylenediamine. *J. Chem. Eng. Data* **1997**, *42*, 1021−1036.
(8) Hubbard, W. N.; Scott, D. W.; Waddington, G. *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; pp 75−127.
(9) Atomic weights of the elements. *Pure Appl. Chem.* **1994**, *66*, 2423−2444.
(10) Hemminger, W. F.; Cammenga, H. K. *Methoden der Thermischen Analyse;* Springer: Berlin, 1989.
(11) Chickos, J. S.; Hosseini, S.; Hesse, D. G.; Liebman, J. F. Heat Capacity Corrections to a Standard State: A Comparison of New and Some Literature Methods for Organic Liquids and Solids. *Struct. Chem.* **1993**, *4*, 271−278.
(12) Verevkin, S. P. Determination of the *ortho*-, *para*-, and *meta*-interactions in *secondary*-alkylphenols from thermochemical measurements. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 1467−1474.
(13) *CODATA Key Values for Thermodynamics*; Cox, J. D., Wagman, D. D., Medvedev, V. A., Eds.; Hemisphere: New York, 1989.
(14) Olofsson, G. *Combustion calorimetry*; Sunner, S., Mansson, M., Eds.; Pergamon: New York, 1979; Chapter 6.
(15) Liebman, J. F.; Greenberg, A. *Strained Organic Molecules*; Organic Chemistry Series 38; Academic Press: New York, 1978.
(16) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. B. The evaluation of strain in hydrocarbons. The strain in adamantane and its origin. *J. Am. Chem. Soc.* **1970**, *92*, 2377−2386.
(17) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976; p 274.
(18) Beckhaus, H.-D. Force Field for the Calculation of Structure and Enthalpy of Formation of Alkylbenzenes. *Chem. Ber.* **1983**, *116*, 86−96.
(19) Pedley, J. P.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.
(20) Verevkin, S. P. Thermochemical Properties of Branched Alkyl substituted Benzenes. *J. Chem. Thermodyn.* **1998**, *30*, 1029−1040.

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