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Strain Effects in Phenyl-Substituted Methanes. Geminal Interaction between Phenyl and the Electron-Releasing Substituent in Benzylamines and Benzyl Alcohols

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The standard ($p° = 0.1$ MPa) molar enthalpies of formation $\Delta_f H°_m(l)$ at $T = 298.15$ K of *N*,*N*-dimethylbenzylamine, α-methylbenzylamine, and α,α-dimethylbenzylamine were determined by means of combustion calorimetry. The standard molar enthalpies of vaporization of these compounds and also of benzylamine, benzyl alcohol, and α,α-dimethylbenzyl alcohol were obtained from the temperature dependence of the vapor pressure measured in a flow system. Resulting values of $\Delta_f H°_m(g)$ were obtained at $T = 298.15$ K and used to derive strain enthalpies of benzyl derivatives. The intramolecular interactions of the substituents were discussed in terms of deviations of $\Delta_f H°_m(g)$ from the group additivity rules. These values provide a further improvement on the group-contribution methodology for estimation of the thermodynamic properties of organic compounds.

Introduction

Benzyl radicals, produced by the thermal decomposition of divers benzyl derivatives, are widely used as initiators of radical polymerization (Van-Chin-Syan, 1984). It has also recently been suggested that benzyl radicals may play an important role in stimulating spontaneous ignition, in both diesel and petrol engines (Davis et al., 1998). Knowledge of the thermochemical properties of benzyl derivatives is necessary to determine the radical stabilization energies and strength of a C−C bond in these compounds (Beckhaus et al., 1990). In recent years considerable activity has taken place with respect to the determination of the enthalpies of formation of amines (Ribeiro da Silva, 1996, 1997; Steele et al., 1996, Verevkin 1997a,b; 1998a; Verevkin et al., 1998) but with limited emphasis on benzyl-substituted species. Thus, a systematical study of the thermochemistry of benzyl derivatives seems to be important for practical and theoretical reasons.

Strain enthalpies are apparent in organic compounds when the observed standard molar enthalpies of formation in the gaseous state are compared with values for strain-free structure calculated using the group-additivity methodology. Investigations of strain in benzyl derivatives have been made recently (Verevkin, 1999a,b). The resulting interactions of phenyl and electron-withdrawing substituents (CN and CO_2R) exhibit the moderate geminal destabilization of 5−10 kJ·mol^{-1}, which arises mainly from repulsive forces by dipolar interactions. Repulsions of phenyl with the electron-releasing geminal substituent NH_2 in benzylamines and OH in benzyl alcohols (Figure 1) were of interest in this work. What is the interaction energy between phenyl and amino or hydroxy substituents adjacent to the geminal C atom? To answer this question, the standard molar enthalpies of formation in the gas phase $\Delta_f H°_m(g)$ at $T = 298.15$ K of *N*,*N*-dimethylbenzylamine, α-methylbenzylamine, and α,α-dimethylbenzylamine (see Figure 1) were obtained from calorimetrically measured energies of combustion and molar enthalpies of vaporization determined by a transpiration method. Reliable data for $\Delta_f H°_m(l)$ of benzylamine (Carson et al., 1977) and benzyl alcohol (Papina et al., 1995), and $\Delta_f H°_m(cr)$ of α,α-dimethylbenzyl alcohol (Van-Chin-Syan, 1984) were already available from the literature. The enthalpies of vaporization of benzylamine reported by Carson et al. (1977) and Majer and Svoboda (1985) differ by 7 kJ·mol^{-1}. The enthalpy of vaporization of benzyl alcohol was measured almost seventy years ago by Mathews (1926). The enthalpy of vaporization and enthalpy of sublimation of α,α-dimethylbenzyl alcohol reported by Van-Chin-Syan (1984) were measured by means of the effusion method on a sample containing 0.32 mol % impurities. These facts encouraged a redetermination of enthalpies of vaporization and sublimation for the aforementioned compounds.

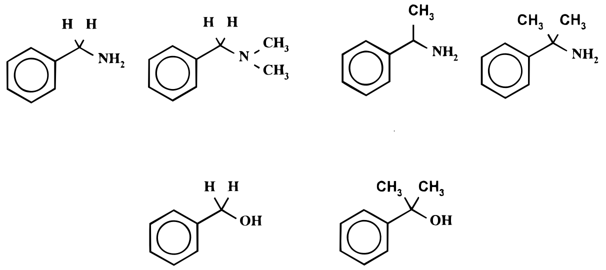

Figure 1. Structures of investigated compounds: benzylamine, *N*,*N*-dimethylbenzylamine, α-methylbenzylamine, α,α-dimethylbenzylamine, benzyl alcohol, and α,α-dimethylbenzyl alcohol.

Experimental Procedure

Materials. Commercially available samples of benzyl derivatives (Figure 1) were purified by repeated distillation in vacuo. To avoid traces of water in samples used for combustion experiments, the purified liquid samples were dried over molecular sieves and distilled once more before the combustions. Such a procedure provided colorless material, and the absence of water was shown by Karl Fischer titration. The determination of purity was carried

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Table 1. Physical Properties of the Materials Used for Combustion Experiments in the Present Study

	formula	purity/%	$\rho_{(293\ \mathrm{K})}$/g·cm^{-3}	$c_{\mathrm{p}(298.15\ \mathrm{K})}{}^{b}$/J·K^{-1}·g^{-1}	$10^{-6}(\delta V/\delta T)_{\mathrm{p}}{}^{c}$/dm^3·K^{-1}
N,*N*-dimethylbenzylamine	$C_9H_{13}N$	99.99	0.900[a]	2.0	1.0
α-methylbenzylamine	$C_8H_{11}N$	99.96	0.940[a]	1.46	1.0
α,α-dimethylbenzylamine	$C_9H_{13}N$	99.99	0.913[a]	1.63	1.0
cotton[d]	$CH_{1.77}O_{0.89}$		1.500	1.67	0.1
polyethene[e]	$CH_{1.930}$		0.920	2.53	0.1

[a] Measured with a pycnometer. [b] From DSC measurements. [c] Estimated. [d] $\Delta_c u°_{(\mathrm{cotton})} = -(16945.2 \pm 4.2)$ J·g^{-1}. [e] $\Delta_c u°_{(\mathrm{polyethene})} = -(46361.0 \pm 3.1)$ J·g^{-1}.

out by GC (see Table 1). In the sample of α-methylbenzylamine used for the combustion experiments about 0.05 mass % unidentified impurities (very close to the main peak) was detected (no corrections were applied in the calculation of the molar enthalpies of combustion).

All compounds were handled under an inert atmosphere (N_2) using carefully dried solvents. We used the following equipment: GC, Carlo Erba Fraktometer Vega Series GC 6000, Hewlett Packard Integrator 3390A, N_2-flow 0.333 cm^3·s^{-1}, SE-30 capillary column of length 25 m. The standard temperature program of the GC was $T = 313$ K for 60 s, followed by a heating rate of 0.167 K·s^{-1} to $T = 523$ K. Specific heat capacities were determined with a Perkin-Elmer DSC-2C.

Transpiration Method. The enthalpies of vaporization and of sublimation of the benzyl derivatives were determined using the method of transference in a saturated N_2 stream (Beckhaus et al., 1980; Chickos et al., 1995). 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. A nitrogen stream was passed through the U-tube at constant temperature (±0.1 K), and the transported amount of material was condensed in a cooled trap. The amount of condensed product was determined by GC analysis using an internal standard (hydrocarbons n-$C_{11}H_{24}$ or n-$C_{13}H_{28}$). The purities of the samples for the transpiration were better than 0.999 mole fraction, but this is not of concern, since capillary gas chromatography allowed us to separate even the minor contaminations from the major peak. 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. To derive the standard molar enthalpy of vaporization at the mean temperature $\langle T\rangle$ of the experimental temperature range, $\Delta_l^g H°_m(T)$, the integrated form of the linear Clausius–Clapeyron equation

$$\ln(p/\mathrm{Pa}) = a - b\cdot(T/\mathrm{K})^{-1} \tag{1}$$

where $b = \Delta_l^g H°_m(T)\cdot R^{-1}$, was used. The observed enthalpies of vaporization $\Delta_l^g H°_m(T)$ and of sublimation $\Delta_{cr}^g H°_m(T)$ at the temperature T obtained by this procedure are listed in Table 2. The experimental data were approximated with the linear equation $\ln(p) = f(T^{-1})$ (see Table 2) using the method of least squares. The error in the enthalpy of vaporization was defined as the deviation of the experimental ln(p) from this linear correlation.

Combustion Calorimetry. For the measurement of the enthalpy of combustion of benzylamines, an isoperibol calorimeter with a stirred water bath was used. The detailed procedure has been described previously (Beckhaus et al., 1980; Verevkin et al., 1992). The combustion products were examined for carbon monoxide (Dräger tube) and unburnt carbon, but neither was detected. The energy equivalent of the calorimeter $\epsilon_{\mathrm{calor}}$ (Table 3) was determined with a standard reference sample of benzoic acid (sample SRM 39i, NIST). For reduction of the data to standard conditions, conventional procedures (Hubbard et al., 1956) were used. The atomic weights used were those recommended by the IUPAC Commission (Atomic weights of the elements. *Pure Appl. Chem.* **1994**). A summary of auxiliary quantities for the combustion experiments and information necessary for reducing apparent mass to mass in vacuo is given in Table 1.

Results and Discussion

Combustion Calorimetry. Results for typical combustion experiments on benzyl derivatives are given in Table 3. The individual values of the standard specific energy of combustion $\Delta_c u°$ are given in Table 4. Enthalpies of combustion (the given standard deviations of the mean include the uncertainties from calibration and the uncertainties from the combustion energies of the auxiliary materials) and enthalpies of formation of the compounds studied are given in Table 5. To derive $\Delta_f H°_m$(l) from $\Delta_c H°_m$, the following molar enthalpies of formation were used (CODATA, 1989): for H_2O(l), −(285.83 ± 0.04) kJ·mol^{-1}; for CO_2(g), −(393.51 ± 0.13) kJ·mol^{-1}. Table 5 lists the derived standard molar enthalpies of formation in the liquid, crystalline, and gaseous states.

Previous determination of the standard molar enthalpy of formation $\Delta_f H°_m$(l) of *N*,*N*-dimethylbenzylamine was made by Miroshnichenko et al. (1996) by means of combustion calorimetry. Their value $\Delta_f H°_m(\mathrm{l}) = (28.90 + 0.42)$ kJ·mol^{-1} is in close agreement with ours (Table 5). Measurements of the thermochemical properties of α-methylbenzylamine and α,α-dimethylbenzylamine are reported for the first time.

Enthalpies of Vaporization. The resulting enthalpies of vaporization $\Delta_l^g H°_m$ at $T = 298.15$ K are recorded in Table 2. Because of the deviations from $T = 298.15$ K, the observed values of the enthalpies of vaporization or sublimation of benzyl derivatives measured by transpiration had to be adjusted to the reference temperature. The corrections were estimated with the help of the correlation

$$\{\Delta_l^g H°_m(\langle T\rangle) - \Delta_l^g H°_m(298.15\ \mathrm{K})\}/(\mathrm{kJ\cdot mol^{-1}}) = -6.0 \times 10^{-2}\cdot\{(\langle T\rangle/\mathrm{K}) - 298.15\}$$

following the recommendation of Chickos et al. (1992). With these corrections and the measured values the standard molar enthalpies of vaporization or sublimation at $T = 298.15$ K were calculated (Tables 2 and 5).

Previous determinations of the standard molar enthalpy of vaporization $\Delta_l^g H°_m$ of *N*,*N*-dimethylbenzylamine were made by Miroshnichenko et al. (1996) by means of a Calvet calorimeter. Their value $\Delta_l^g H°_m = (50.08 \pm 0.90)$ kJ·mol^{-1} is in very close agreement with ours (Table 5).

Carson et al. (1977) determined the enthalpy of vaporization of benzylamine $\Delta_l^g H°_m = (53.6 \pm 2.1)$ kJ·mol^{-1}

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
benzylamine; $\ln(p/\text{Pa}) = (25.50 \pm 0.23) - (6257 \pm 69)\cdot(T/\text{K})^{-1}$							
283.4	5.55	4.25	30.96	299.2	4.70	1.15	95.20
285.3	8.83	6.02	34.69	300.3	5.99	1.28	108.9
288.3	6.57	3.38	45.74	301.3	5.11	1.08	110.1
290.3	7.83	3.49	52.66	304.2	5.11	0.882	134.6
291.3	7.45	3.06	57.07	307.2	5.70	0.784	168.6
294.3	4.96	1.69	68.64	310.3	6.93	0.751	213.9
297.5	5.31	1.38	89.77	313.3	6.19	0.555	258.6
$\Delta_l^g H°_m(298.2\ \text{K}) = (52.02 \pm 0.57)\ \text{kJ}\cdot\text{mol}^{-1}$; $\Delta_l^g H°_m(298.15\ \text{K}) = (52.02 \pm 0.57)\ \text{kJ}\cdot\text{mol}^{-1}$							
N,*N*-dimethylbenzylamine; $\ln(p/\text{Pa}) = (20.33 \pm 0.15) - (5884 \pm 45)\cdot(T/\text{K})^{-1}$							
288.2	6.79	1.43	89.20	313.3	9.96	0.387	474.3
293.2	6.92	1.02	126.1	318.2	11.0	0.326	621.9
298.2	7.39	0.759	180.6	323.2	12.0	0.264	833.2
303.3	8.09	0.590	253.4	328.2	9.83	0.171	1057.0
308.3	8.75	0.465	347.2				
$\Delta_l^g H°_m(308.2\ \text{K}) = (48.93 \pm 0.37)\ \text{kJ}\cdot\text{mol}^{-1}$; $\Delta_l^g H°_m(298.15\ \text{K}) = (49.53 \pm 0.37)\ \text{kJ}\cdot\text{mol}^{-1}$							
α-methylbenzylamine; $\ln(p/\text{Pa}) = (22.28 \pm 0.11) - (6584 \pm 34)\cdot(T/\text{K})^{-1}$							
283.4	6.96	3.90	38.25	303.6	11.9	1.37	179.9
288.5	8.79	3.17	58.45	308.4	8.25	0.680	249.6
293.6	8.37	2.01	86.92	313.3	5.29	0.311	349.4
298.4	11.4	1.92	123.4	318.3	4.04	0.165	501.9
$\Delta_l^g H°_m(300.8\ \text{K}) = (54.74 \pm 0.28)\ \text{kJ}\cdot\text{mol}^{-1}$; $\Delta_l^g H°_m(298.15\ \text{K}) = (54.90 \pm 0.28)\ \text{kJ}\cdot\text{mol}^{-1}$							
α,α-dimethylbenzylamine; $\ln(p/\text{Pa}) = (22.15 \pm 0.28) - (6783 \pm 84)\cdot(T/\text{K})^{-1}$							
283.5	16.7	18.54	16.80	308.5	13.3	2.04	119.8
293.4	8.09	4.20	35.60	313.5	19.5	2.24	159.6
298.3	14.5	4.72	56.47	318.5	11.0	0.864	233.6
303.3	14.6	3.29	81.74	323.3	6.91	0.401	316.4
$\Delta_l^g H°_m(303.4\ \text{K}) = (56.40 \pm 0.70)\ \text{kJ}\cdot\text{mol}^{-1}$; $\Delta_l^g H°_m(298.15\ \text{K}) = (56.71 \pm 0.70)\ \text{kJ}\cdot\text{mol}^{-1}$							
benzyl alcohol; $\ln(p/\text{Pa}) = (28.71 \pm 0.26) - (7798 \pm 77)\cdot(T/\text{K})^{-1}$							
277.4	2.48	32.11	1.77	298.3	2.20	4.09	12.32
278.4	2.04	24.60	1.90	300.3	1.80	2.49	16.56
283.4	0.562	3.97	3.24	303.3	2.45	2.73	20.56
285.4	2.06	12.14	3.89	06.2	2.46	2.23	25.27
287.3	2.44	10.90	5.13	309.2	2.48	1.83	31.05
290.3	2.22	8.04	6.33	312.2	2.60	1.46	40.80
292.4	2.18	6.11	8.18	315.2	2.91	1.24	53.77
293.4	1.85	5.21	8.14	318.2	3.42	1.21	64.7
296.4	2.54	5.06	11.5				
$\Delta_l^g H°_m(297.8\ \text{K}) = (64.84 \pm 0.64)\ \text{kJ}\cdot\text{mol}^{-1}$; $\Delta_l^g H°_m(298.15\ \text{K}) = (64.82 \pm 0.64)\ \text{kJ}\cdot\text{mol}^{-1}$							
α,α-dimethylbenzyl alcohol; $\ln(p/\text{Pa}) = (36.04 \pm 0.29) - (9960 \pm 83)\cdot(T/\text{K})^{-1}$							
276.4	2.52	45.64	1.014	294.4	4.98	9.96	9.113
279.5	2.61	33.39	1.431	297.3	6.04	8.90	12.35
282.4	3.52	30.20	2.128	298.4	3.29	4.04	14.81
285.4	4.47	25.03	3.258	300.4	5.32	5.61	17.27
288.4	3.64	14.51	4.568	302.4	2.76	2.23	22.52
291.4	4.28	12.31	6.336				
$\Delta_{cr}^g H°_m(289.4\ \text{K}) = (82.81 \pm 0.69)\ \text{kJ}\cdot\text{mol}^{-1}$; $\Delta_{cr}^g H°_m(298.15\ \text{K}) = (82.28 \pm 0.69)\ \text{kJ}\cdot\text{mol}^{-1}$							
α,α-dimethyl-benzyl alcohol; $\ln(p/\text{Pa}) = (28.29 \pm 0.18) - (7622 \pm 59)\cdot(T/\text{K})^{-1}$							
311.2	4.70	1.900	45.07	326.2	6.01	0.788	139.0
314.2	4.64	1.480	57.12	329.2	7.80	0.854	166.4
317.2	4.73	1.220	70.60	332.2	8.06	0.690	212.9
320.2	4.90	0.985	90.68	335.2	6.60	0.459	261.9
323.2	5.90	0.985	109.1	338.2	6.89	0.393	319.5
$\Delta_l^g H°_m(324.7\ \text{K}) = (63.37 \pm 0.49)\ \text{kJ}\cdot\text{mol}^{-1}$; $\Delta_l^g H°_m(298.15\ \text{K}) = (64.96 \pm 0.49)\ \text{kJ}\cdot\text{mol}^{-1}$							

[a] Temperature of saturation at N_2 gas flow 0.26−0.52 cm$^3\cdot$s^{-1}. [b] Mass of transferred sample condensed at $T = 243$ K. [c] Volume of nitrogen used to transfer mass m of sample. [d] Vapor pressure at temperature T, calculated from m and the residual vapor pressure at $T = 243$ K.

using ebulliometry. Majer and Svoboda (1985) reported $\Delta_l^g H°_m = 60.16\ \text{kJ}\cdot\text{mol}^{-1}$ for this compound. Our value $\Delta_l^g H°_m = (52.02 \pm 0.57)\ \text{kJ}\cdot\text{mol}^{-1}$ is in close agreement with those from Carson et al. (1977) within the boundaries of the experimental uncertainties.

The value of the enthalpy of vaporization of benzyl alcohol, measured by ebulliometry, has already been reported in the literature (Matthews, 1926). Pedley et al. (1986) reanalyzed his original value $\Delta_l^g H°_m = (50.50 \pm 0.04)\ \text{kJ}\cdot\text{mol}^{-1}$ to $\Delta_l^g H°_m = (60.29 \pm 0.42)\ \text{kJ}\cdot\text{mol}^{-1}$. Ambrose and Ghiassee (1990) also measured the values of the parameters in the Antoine equation for vapor pressure using ebulliometry in the temperature range 404.1−507.4 K. From this data one can assess the value of $\Delta_l^g H°_m$ at $T = 298.15$ K of benzyl alcohol with the help of the equation (Reid et al., 1977)

$$\Delta_l^g H°_m/(\text{J}\cdot\text{mol}^{-1}) = (2.3R\Delta ZBT^2)\cdot(T + C)^{-2}$$

where $R = 8.314\,51\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, B and C are Antoine equation parameters, and ΔZ is the difference in the compression factors of the vapor and the liquid. The value

Table 3. Results from Typical Combustion Experiments at 298.15 K[a]

	N,*N*-dimethylobenzylamine	α-methylbenzylamine	α,α-dimethylbenzylamine
m(substance)[b]/g	0.338822	0.640719	0.600227
m'(cotton)[b]/g	0.000967	0.001009	0.001054
m''(polyethene)[b]/g	0.558747	0.273444	0.287314
ΔT_c[c]/K	1.57568	1.49961	1.47971
$(\epsilon_{calor})\cdot(-\Delta T_c)$/J	−39533.02	−37659.11	−37159.37
$(\epsilon_{cont})\cdot(-\Delta T_c)$/J	−22.81	−20.78	−20.60
ΔU_{corr}[d]/J	15.75	16.52	15.67
$-m'\cdot\Delta_c u'$/J	16.38	17.09	17.86
$-m''\cdot\Delta_c u''$/J	25904.04	12677.12	13320.16
$\Delta U_{dec}(HNO_3)$/J	30.09	43.59	38.81
$\Delta_c u°$(substance)/J·g^{-1}	−40103.7	−38900.3	−39628.2

[a] For the definition of the symbols, see Hubbard et al. (1956): $T_h = 298.15$ K; V(bomb) = 0.2664 dm^3; p^i(gas) = 3.04 MPa; $m^i(H_2O)$ = 0.78 g; ΔU(ign) = 1.5 J; m(Pt) = 12.18 g. [b] Masses obtained from apparent masses. [c] $\Delta T_c = T^f - T^i + \Delta T_{corr}$; $(\epsilon_{cont})\cdot(-\Delta T_c) = (\epsilon^i_{cont})\cdot(T^i - 298.15\ K) + (\epsilon^f_{cont})\cdot(298.15\ K - T^f + \Delta T_{corr})$. ϵ_{calor} = (25089.5 ± 1.2) J·K^{-1} for *N*,*N*-dimethylbenzylamine; and ϵ_{calor} = (25112.6 ± 1.9) J·K^{-1} for other compounds. [d] ΔU_{corr}, the correction to standard state, is the sum of items 81−85, 87−90, 93, and 94 in Hubbard et al. (1956).

Table 4. Values of Specific Energies of Combustion $\Delta_c u°$ at T = 298.15 K ($p°$ = 0.1 MPa)[a]

N,*N*-dimethylabenzylamine	α-methylbenzylamine	α,α-dimethylbenzylamine
	$-\Delta c_u°$/(J·g^{-1})	
40103.7	38900.3	39628.2
40092.0	38904.4	39628.9
40141.9	38887.8	39625.8
40097.1	38911.0	39625.1
40152.9	38904.9	39628.7
	$\langle\Delta c_u°\rangle$/(J·g^{-1})	
40117.5 ± 12.5	38901.7 ± 3.9	39627.34 ± 0.78

[a] $\langle\Delta c_u°\rangle$ denotes mean value.

Table 5. Experimental Results for Benzyl Derivatives at T = 298.15 K

	$\Delta_c H°_m$[a]/kJ·mol^{-1}	$\Delta_f H°_m$(l)/kJ·mol^{-1}	$\Delta_l^g H°_m$[b]/kJ·mol^{-1}	$\Delta_f H°_m$(g)/kJ·mol^{-1}
benzylamine		34.2 ± 1.7[c]	52.02 ± 0.57	86.2 ± 1.8
N,*N*-dimethylbenzylamine	−5431.1 ± 1.7	31.7 ± 2.1	49.53 ± 0.37	81.2 ± 2.1
α-methylbenzylamine	−4719.83 ± 0.58	−0.3 ± 1.2	54.90 ± 0.28	54.6 ± 1.2
α,α-dimethylbenzylamine	−5364.85 ± 0.44	−34.6 ± 1.3	56.71 ± 0.70	22.1 ± 1.5
benzyl alcohol		−154.9 ± 3.0[d]	64.82 ± 0.64	−90.1 ± 3.1
α,α-dimethylbenzyl alcohol		−250.4 ± 2.3[e]	82.28 ± 0.69[f]	−168.1 ± 2.4

[a] Calculated from the specific enthalpies of combustion in Table 4. [b] From the measurements of vapor pressure at different temperatures from Table 2 using the Clausius−Clapeyron equation. [c] The result was taken from Carson et al. (1977). [d] The result was taken from Papina et al. (1995). [e] The enthalpy of formation for the solid compound $\Delta_f H°_m$(cr) was taken from Van-Chin-Syan et al. (1984). [f] Enthalpy of sublimation $\Delta_{cr}^g H°_m$ (see Table 2).

of $\Delta Z \approx 1$ was calculated using the Haagenmacher equation (Reid et al., 1977) for benzyl alcohol at the reference temperature T = 298.15 K. Hence, the enthalpy of vaporization $\Delta_l^g H°_m$ = 66.9 kJ·mol^{-1} was estimated by the equation above. The present measured value of the enthalpy of vaporization $\Delta_l^g H°_m$ = (64.82 ± 0.64) kJ·mol^{-1} is essentially different from the very earlier result, but it is still in an acceptable agreement with the result from Ambrose and Ghiassee (1990). The determination of the $\Delta_f H°_m$(l) of benzyl alcohol has long been a popular endeavour by using combustion calorimetry. The impressive scatter of the experimental values [−(154.9 ± 3.0) kJ·mol^{-1} (Papina et al., 1995), −(161.0 ± 1.3) kJ·mol^{-1} (Parks et al., 1954), −174.0 kJ·mol^{-1} (Landrieu et al., 1929), and −167.0 kJ·mol^{-1} (Schmidlin, 1906)] could be explained by the hygroscopic nature of this compound. The recent work of Papina et al. (1995) has been done very carefully on a sample of impeccable purity; that is why we have preferred their value. The measured in this work enthalpy of vaporization $\Delta_l^g H°_m$ of benzyl alcohol allowed us to derive $\Delta_f H°_m$(g) = −(90.1 ± 3.1) kJ·mol^{-1} for this compound. However, we were still reticent to discuss this value due to large discrepancies among experimental data for both $\Delta_l^g H°_m$ values mentioned above. Thus, we searched for other sources to get the enthalpy of formation of benzyl alcohol. Fortunately, the desired value could also be derived from the enthalpy of reaction of dehydrogenation of benzyl alcohol:

$$\text{benzyl alcohol} \leftrightarrow \text{benzaldehyde} + H_2$$

$\Delta_r H°_m$(298.15 K) = 53.93 kJ·mol^{-1}, measured by Cubberley and Mueller (1946) in the gas phase using the equilibrium technique. With the help of the $\Delta_f H°_m$(g) = −(36.7 ± 2.9) kJ·mol^{-1} of benzaldehyde (Pedley et al., 1986) we estimated the gaseous enthalpy of formation $\Delta_f H°_m$(g) = −90.6 kJ·mol^{-1} of benzyl alcohol. This value is in excellent agreement with those (Table 5) obtained by combining the selected $\Delta_f H°_m$(l) from combustion calorimetry and the enthalpy of vaporization from transpiration. Concordance of the data obtained from different sources supports the correctness of the value of $\Delta_f H°_m$(g) of benzyl alcohol listed in Table 6.

Previous determination of the standard molar enthalpy of vaporization $\Delta_l^g H°_m$ and the enthalpy of sublimation of the α,α-dimethylbenzyl alcohol was made by Van-Chin-Syan et al. (1984) by means of the effusion method. Their values $\Delta_l^g H°_m$ = (56.4 ± 1.3) kJ·mol^{-1} and $\Delta_{cr}^g H°_m$ = (87.5

Table 6. Non-Nearest-Neighbor Interactions of Phenyl Substituent and Functional Group in Benzyl Derivatives at T = 298.15 K (in kJ·mol^{-1})

	$\Delta_f H°_m$(g)(exp)	$\Delta_f H°_m$(g)(calc)[a]	H_s[b]	H_s[c]	ΔH_s[b]
benzylamine	86.2 ± 1.8	84.6	1.6		1.6 ± 1.8
N,*N*-dimethylbenzylamine	81.2 ± 2.1	84.3	−3.1		−3.1 ± 2.1
α-methylbenzylamine	54.6 ± 1.2	49.5	5.1	5.0	0.1 ± 1.2
α,α-dimethylbenzylamine	22.1 ± 1.5	11.3	10.8	10.9	−0.1 ± 1.5
meso-*N*,*N*′-dimethyl-1,2-dimethyl-1,2-diphenylethylendiamine	169.1 ± 3.1[e]	112.1	57.0	54.0[h]	3.0 ± 3.1
benzyl alcohol	−90.1 ± 3.1	−100.4	10.3		10.3 ± 3.1
α,α-dimethylbenzyl alcohol	−168.1 ± 2.4	−176.8	8.7	10.9	−2.2 ± 2.4
α,α-dimethyl-*p*-isopropylbenzyl alcohol	−242.9 ± 3.3[f]	−260.1	17.2	15.8	1.4 ± 3.3
α,α,α′,α′-tetramethyl-1,4-benzenedimethanol	−406.2 ± 3.2[f]	−435.8	29.6	23.8	5.8 ± 3.2
benzyl fluoride	−126.27 ± 0.73[g]	−140.6			14.3 ± 0.7

[a] Calculated as the sum of strain-free increments (see text). [b] Strain enthalpy of benzyl derivatives $H_s = \Delta_f H°_m(\mathrm{g})(\mathrm{exp}) - \Delta_f H°_m(\mathrm{g})(\mathrm{calc})$. [c] Strain enthalpy of alkylbenzene H_s taken from earlier works (Pedley et al., 1986; Verevkin, 1998). [d] The sum of resulting interactions of the phenyl subtituent and the functional group in benzyl derivatives: $\Delta H_s = H_s(\text{benzyl derivative}) - H_s(\text{alkylbenzene})$ (see text). The uncertainties of the interactions were suggested to be only equal to those of the experimental $\Delta_f H°_m$(g). [e] The result was taken from Wirt (1988): $\Delta_f H°_m(\mathrm{cr}) = (56.8 \pm 2.6)$ kJ·mol^{-1}; $\Delta_{cr}^{g} H°_m = (112.3 \pm 1.7)$ kJ·mol^{-1}; $\Delta_{cr}^{l} H°_m = (36.0 \pm 0.4)$ kJ·mol^{-1}. [f] The result was taken from Van-Chin-Syan et al. (1984). [g] The result was taken from Schaffer et al. (1997). [h] Calculated using the force field MM2 by Wirth (1988).

± 2.6) kJ·mol^{-1} are essentially different from our results (see Table 2), and these discrepancies exceed the assigned uncertainties. Perhaps they are the result of impurities in the sample claimed by Van-Chin-Syan et al. (1984). The enthalpy of sublimation of α,α-dimethylbenzyl alcohol measured in this work was used to derive $\Delta_f H°_m$(g) for this compound (see Tables 5 and 6).

Strain Enthalpy H_s ***of*** *Benzyl Derivatives.* The group additivity scheme of the Benson type (Benson, 1976) is widely used for the calculation of standard molar enthalpies of formation at 298.15 K. The system of strain-free increments (Schleyer et al., 1970) is somewhat similar but generally based on the standard enthalpies of formation $\Delta_f H°_m$(g) of simple homologous ("strainless") molecules. Strain-free group additivity increments for hydrocarbons (Schleyer et al., 1970) and arenes (Beckhaus, 1983) are well defined. Their advantage with respect to the classic Benson increments (Benson, 1976) is the possibility to determine the strain enthalpy of a molecule.

We define the strain H_s of a molecule as the difference between the experimental standard enthalpy of formation $\Delta_f H°_m$(g) and the calculated sum of the strain-free Benson type increments for this molecule. The strain-free increments for the calculation of enthalpies of formation of amines (Verevkin et al., 1998) and alcohols (Verevkin, 1998b) have been derived recently. All the increments necessary in this work are as follows: $CH_3[C] = -42.05$ kJ·mol^{-1}; $CH_2[2C] = -21.46$ kJ·mol^{-1}; $CH[3C] = -9.04$ kJ·mol^{-1}; $C[4C] = -1.26$ kJ·mol^{-1}; $C_BH[2C_B] = 13.72$ kJ·mol^{-1} (C_B represents the aromatic C atoms); and $C_B[C,2C_B] = 23.51$ kJ·mol^{-1}. The strain-free group additivity increments for amino compounds (Verevkin et al., 1998a) are as follows: $N[C,2H] = 19.4$ kJ·mol^{-1}; $N[2C,H] = 64.1$ kJ·mol^{-1}; $N[3C] = 103.2$ kJ·mol^{-1}; $CH_3[N] = -42.05$ kJ·mol^{-1}; $CH_2[N,C] = -26.9$ kJ·mol^{-1}; $CH[N,2C] = -20.0$ kJ·mol^{-1}; $C[N,3C] = -16.1$ kJ·mol^{-1}. The strain-free group additivity increments for hydroxy compounds (Verevkin, 1998c) are as follows: $HO[C] = 159.45$ kJ·mol^{-1}; $CH_3[OH] = -42.05$ kJ·mol^{-1}; $CH_2[OH,C] = -29.3$ kJ·mol^{-1}; $CH[OH,2C] = -28.8$ kJ·mol^{-1}; $C[OH,3C] = -25.3$ kJ·mol^{-1}. By using these group-additivity parameters and the values of $\Delta_f H°_m$(g) of benzyl derivatives (Table 5) determined in this research, the values of the strain enthalpies $H_s = \{\Delta_f H°_m(\mathrm{g}) - \sum \text{increments}\}$ of benzyl derivatives have been estimated. These resulting strain interactions of phenyl with the amino and hydroxy groups in the gaseous state are listed in Table 6.

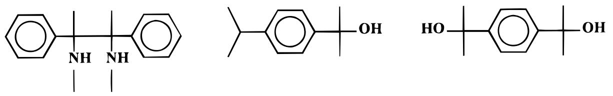

Figure 2. Structures of *meso*-*N*,*N*′-dimethyl-1,2-dimethyl-1,2-diphenylethylenediamine, α,α-dimethyl-*p*-isopropylbenzyl alcohol, and α,α,α′,α′-tetramethyl-1,4-benzenedimethanol.

The understanding of the strain in benzyl derivatives is improved by comparison to that of the strain in similarly shaped alkylbenzenes: ethylbenzene, isopropylbenzene, and *tert*-butylbenzene. The standard molar enthalpies of formation $\Delta_f H°_m$(g) and strain enthalpies H_s of ethylbenzene (29.9 kJ·mol^{-1} and 0.0 kJ·mol^{-1}), isopropylbenzene (4.0 kJ·mol^{-1} and 5.0 kJ·mol^{-1}), and *tert*-butylbenzene (−24.4 kJ·mol^{-1} and 10.9 kJ·mol^{-1}) are already known from the literature. The enthalpies of formation of these compounds were taken from Pedley et al. (1986), except for that of *tert*-butylbenzene (Verevkin, 1998c). These alkylbenzenes are relevant structural patterns of strain in the benzyl derivatives studied. Their strain enthalpies describe the intrinsic strain of the alkylbenzenes due to steric repulsions of alkyl groups and the benzene ring attached to the tertiary or quaternary carbon atom. Comparison with the strain of alkylbenzenes allowed the derivation of the strain effects directly. We calculated the differences ΔH_s between individual strains for each benzyl derivative and the strain of the appropriate alkyl-substituted benzene (Table 6). These values ΔH_s were interpreted as the sum of excess geminal interactions of phenyl and amino or hydroxy substituents on the central C atom. In order to provide a broader basis for comparison, we report the interpretation of some other compounds (see Figure 2), containing the benzyl fragment ajacent to the amino or hydroxy group. The derived strain enthalpies for benzylamines and benzyl alcohols are listed in Table 6 and are compared with the H_s values for the corresponding structures of the alkylbenzenes.

Almost all benzyl derivatives listed in Table 6 are strained. However, in most cases the observed amount of destabilization could no doubt be attributed to the inherent strain in alkylbenzenes. Thus, no additional interactions of phenyl and amino groups could be detected in the benzylamines independent of the type of substitution of the central C atom. A similar trend has also been observed for the substituted benzyl alcohols (Table 6), excepted for benzyl alcohol itself, which exhibits a noticeable interaction

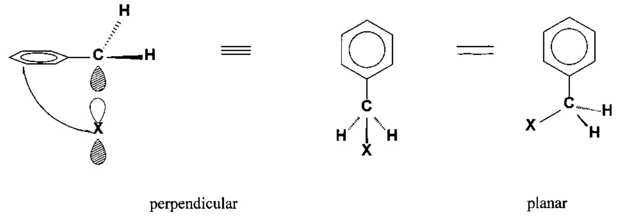

Figure 3. Conformational preferences of benzyl−X compounds.

between phenyl and hydroxy groups of (10.3 ± 3.1) kJ·mol^{-1}. Apparently, the observed geminal destabilization arises mainly from repulsive forces between the phenyl and hydroxy groups by dipolar interactions. A plausible explanation of the observed destabilization of benzyl alcohol is suggested by the work of Penner et al. (1987). By means of spectral analyses and ab initio methods, they determined the conformational preferences of some benzyl−X derivatives with the aim of establishing whether stabilizing interactions enhance the conformational preference for the perpendicular structure (see Figure 3). Except for X = F, the compounds studied (X = Cl, SH, SMe, S(O)Me) adopt mainly the conformation in which the C−H bond is perpendicular to the plane of the benzene ring. The authors proposed therefore the existence of a "benzylic anomeric effect" and that its magnitude, as a function of X, is S(O)-Me > Cl > SH, SMe > F. Recently, we have already reported (Schaffer et al., 1997) that benzyl fluoride exhibits a noticeable destabilization of (14.3 ± 0.7) kJ·mol^{-1}. The exceptional planar conformation of benzyl fluoride (X = F) determined by Penner et al. (1987) and the profound destabilization of this molecule established in our thermochemical study are evidences that a possible "benzylic anomeric effect" is destroyed by a dipole−dipole interaction between the phenyl and fluorine substituents. A similar explanation seems to be acceptable for the sensible destabilization observed in benzyl alcohol as well. At the same time, the dipole−dipole interactions between the phenyl and hydroxy groups in α,α-dimethylbenzyl alcohol, α,α-dimethyl-*p*-isopropylbenzyl alcohol, and α,α,α′,α′-tetramethyl-1,4-benzenedimethanol are hardly larger than the boundaries of the experimental uncertainties of ±3.5 kJ·mol^{-1} (Table 6). Hence, it is reasonable to presume that methyl groups are able to disorder the optimal orientation of dipoles in the suggested planar conformation of α-substituted benzyl alcohols.

Although the corrections for strain H_s determined in this work are moderate, these values provide a further improvement on the group-contribution methodology for estimation of the thermodynamic properties of organic compounds.

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