Benchmark thermochemistry of methylbenzonitriles: Experimental and theoretical study

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ABSTRACT

The gas-phase enthalpies of formation of 2-, 3-, and 4-methylbenzonitrile at T = 298.15 K were studied by combustion calorimetry, and their vaporization enthalpies were determined using the transpiration method. The composite ab initio methods W1-F12 and G4 were used to calculate the gas-phase enthalpies of formation for these three methylbenzonitriles. These theoretical values were found to be in excellent agreement with the corresponding experimental data. The analysis of these data revealed that the interaction between cyano and methyl groups is slightly stabilizing. Using the experimental data a set of group-additivity terms, which allows to estimate thermochemical properties for methyl and cyano substituted benzenes, was proposed. These terms, together with theoretical data, were subsequently used to reassess the thermochemical properties of 2,6-dimethylbenzonitrile and 2,4,6-trimethylbenzonitrile.

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1. Introduction

Several chemical properties of the benzene moiety are dependent on its aromaticity, which varies with the number and nature of its substituents [1]. The cyano group, CN, is a prototypical electron withdrawing substituent. Because of their rich chemistry, cyano substituted benzenes (*i.e.*, benzonitriles) are important intermediates in organic synthesis [1]. While the thermochemical properties of some benzonitriles of interest are known [2–7], those for several other simple CN substituted benzenes have yet to be determined. This hinders our knowledge of these aromatic compounds, and prevents the quantitative study of the chemical reactions in which they take part. Group additivity schemes can provide rough estimates of the thermochemical properties of substituted benzene rings [8]. Nevertheless, a deeper understanding of such species and of their reactivity requires high-accuracy thermochemical data. Furthermore, benchmark quality thermochemical data are crucial for the testing of high-accuracy ab initio methods.

This is particularly relevant since these theoretical gas-phase data, together with experimental phase change values, can now be used in the determination of condensed phase properties [9,10].

The methylbenzonitriles, which feature a cyano group and an electron donating methyl group, are a simple family of benzonitriles for which experimental data is unavailable. In this work we report a new experimental study of the thermochemistry of 2-, 3-, and 4-methylbenzonitriles by combustion calorimetry [11] and the transpiration method [12]. Experimental values for the liquid and gaseous enthalpies of formation were evaluated and recommended as benchmark values. These data were compared with those determined by G4 [13] and W1-F12 [14] quantum chemical calculations. Using this information, group additivity parameters were derived for the estimation of the thermochemical properties of similar compounds.

2. Experimental

2.1. Materials

Samples of 2-, 3-, and 4-methylbenzonitrile of commercial origin were used (see table 1). Liquid samples were additionally purified by fractional distillation in vacuum. The solid sample of

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TABLE 1
Provenance and purity of the materials.

Material	CASRN	Origin	GC purity (mass fraction)
2-Methylbenzonitrile	529-19-1	Acros, 98%	0.9991[a]
3-Methylbenzonitrile	620-22-4	Aldrich, 99%	0.9996[b]
4-Methylbenzonitrile	104-85-8	Acros, 98 + %	0.9994
2,4,6-Trimethylbenzonitrile	2571-72-0	Aldrich	0.9996

[a] The water content of 660.15 ppm in 2-methylbenzonitrile was measured Karl-Fisher titration.
[b] The water content of 2010.0 ppm in 3-methylbenzonitrile was measured Karl-Fisher titration.

4-methylbenzonitrile was purified by fractional sublimation in vacuum. Final purities of the samples (see table 1) were determined using GC. The samples were analyzed with a Hewlett Packard gas chromatograph 5890 Series II equipped with a flame ionization detector and a HP-5 capillary column (column of length, inside diameter, and film thickness of 25 m · 0.32 mm · 0.25 µm). The GC temperature program started at T = 303 K, followed by heating at a rate of 0.167 K · s^{-1} to T = 573 K.

2.2. High-precision combustion calorimetry

An isoperibol bomb calorimeter was used to measure the energy of combustion of the methylbenzonitriles. About 0.3 g of sample was encapsulated in a commercially available polyethylene bulb (NeoLab, Heidelberg) of 1 cm^3 volume, which was used as sample container. The loaded container was subsequently placed in the bomb and burned in oxygen at a pressure of 3.04 MPa. The detailed procedure has been previously described [11]. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon but neither was detected. The energy equivalent of the calorimeter ε_{calor} = (14889.1 ± 0.9) J · K^{-1} was determined with a standard reference sample of benzoic acid (sample SRM 39j, N.I.S.T.). Correction for nitric acid formation was based on titration with 0.1 mol · dm^{-3} NaOH (aq). Auxiliary quantities required for the data treatment of combustion experiments are given in table S1 (electronic supporting information). Conventional procedures were used for the reduction of the data to standard conditions [15]. Results for typical combustion

experiments are presented in table 2. All combustion results are collected in tables S2-S4 (electronic supporting information).

2.3. Vapor pressure measurements using the transpiration method

With the fractional distillation of the samples of 2-methylbenzonitrile and 3-methylbenzonitrile we were not able to remove the residual amount of water. In order to remove traces of water from the sample a careful pre-conditioning of the sample was performed inside of the saturator prior to the transpiration experiments. After filling of the U-shaped saturator with the fresh distilled sample, the carrier gas with the flow rate of 1 dm^3 · h^{-1} was passed through the system at T = 312 K. From our experience, any volatile impurities are easily removed during such a pre-conditioning within few hours. Monitoring of purification is performed by GC analysis of the sample withdrawn from the cooling trap. The flame-ionization detector of the GC is not sensitive for water. In order to prove absence of water traces in the sample, numerous probes were taken consequently in the course of the sample flushing. After the amount of compound collected in the cold trap (determined by GC analysis with an internal standard) within a specific length of time became constant, the sample was considered to be ready for vapor pressure measurements.

Absolute vapor pressures of the liquid methylbenzonitriles were measured using the transpiration method [12]. About 0.5 g of sample was mixed with small glass beads and placed in a U-shaped saturator. A well-defined nitrogen stream was passed through the saturator at a constant temperature (T_i ± 0.1 K) and the transported material was collected in a cold trap. The amount of condensed sample was determined by GC analysis using an external standard (n-C$_8$H$_{18}$). Vapor pressures, p_i, at each temperature, T_i, were calculated from the amount of product collected within a definite period of time, assuming the validity of the ideal gas law as well as the validity of Dalton's law applied to the nitrogen stream saturated with the substance i:

$$p_i = m_i \cdot R \cdot T_a / V \cdot M_i; \qquad V = V_{N2} + V_i; \qquad (V_{N2} \gg V_i), \qquad (1)$$

where R = 8.314462 J · K^{-1} · mol^{-1}, m_i is the mass of the condensed compound, M_i is the molar mass of the compound i, and V_i is its volume contribution to the gaseous phase. V_{N2} is the volume of the carrier gas and T_a is the ambient temperature of the flow meter. The carrier gas flow rate was measured with an HP Agilent soap film

TABLE 2
Results for typical combustion experiments at T = 298.15 K ($p°$ = 0.1 MPa) of the methylbenzonitriles.[a]

	2-Methylbenzonitrile	3-Methylbenzonitrile	4-Methylbenzonitrile
m (substance)/g	0.417726	0.356488	0.283101
m' (cotton)/g	0.001136	0.001019	0.000826
m'' (polyethylene)/g	0.309255	0.345134	0.424687
ΔT_c/K	1.99044	1.95074	2.01652
$(\varepsilon_{calor}) \cdot (-\Delta T_c)$/J	−29635.8	−29044.8	−30024.2
$(\varepsilon_{cont}) \cdot (-\Delta T_c)$/J	−31.91	−31.61	−33.34
ΔU_{decomp} HNO$_3$/J	65.7	69.58	63.91
ΔU_{corr}/Jd	12.21	11.44	12.11
$-m' \cdot \Delta_c u'$/J	19.25	17.27	14
$-m'' \cdot \Delta_c u''$/J	14336.23	15999.48	19687.34
$\Delta_c u°/(J \cdot g^{-1})$	−36469.7	−36406.9	−36312.6

[a] The definition of the symbols assigned according to reference [15] as follows: m (substance), m' (cotton), and m'' (polyethylene) are the mass of compound burnt, the mass of fuse (cotton) and the mass of polyethylene pieces used in each experiment. Masses were corrected for buoyancy using densities listed in table S1. The mass of 2-methylbenzonitrile was corrected with 660.15 ppm of water. The mass of 3-methylbenzonitrile was corrected with 2010.0 ppm of water. V(bomb) = 0.32 dm^3 is the internal volume of the calorimetric bomb; p^i(gas) = 3.04 MPa is the initial oxygen pressure in the bomb; m^i(H$_2$O) = 1.00 g is the mass of water added to the bomb for dissolution of combustion gases; $\Delta T_c = T^f - T^i + \Delta T_{corr}$ is the corrected temperature rise from initial temperature T^i to final temperature T^f, with the correction ΔT_{corr} for heat exchange during the experiment; ε_{cont} are the energy equivalents of the bomb contents in their initial ε^i_{cont} and final states ε^f_{cont}, the contribution for the bomb content is calculated with $(\varepsilon_{cont}) \cdot (-\Delta T_c) = (\varepsilon^i_{cont}) \cdot (T^i - 298.15) + (\varepsilon^f_{cont}) \cdot (298.15 - T^f + \Delta T_{corr.})$. ΔU_{decomp} HNO$_3$ is the energy correction for the nitric acid formation. ΔU_{corr} is the correction to standard states.

TABLE 3

Absolute vapor pressures p, and standard vaporization enthalpies and entropies of methylbenzonitriles obtained by the transpiration method.

T/K^a	m/mg^b	$V(N_2)^c/dm^3$	T_a/K^d	Flow/dm$^3 \cdot$h^{-1}	p/Pa^e	$u(p)/Pa^f$	$\Delta_l^g H_m°$/kJ$\cdot$mol^{-1}	$\Delta_l^g S_m°$/J$\cdot$K$^{-1} \cdot$mol^{-1}
				2-Methylbenzonitrile; $\Delta_l^g H_m°$ $(T = 298.15 K) = (54.8 \pm 0.3)$ kJ $\cdot$ mol^{-1} $\ln(p/p°) = \frac{278.67}{R} - \frac{73540.31}{R \cdot (T \cdot K)} - \frac{62.7}{R} \ln\left(\frac{T/K}{298.15}\right)$			
287.4	1.66	1.702	294.2	2.92	20.64	0.54	55.52	122.6
289.2	1.71	1.518	294.0	2.94	23.89	0.62	55.40	122.2
290.3	1.13	0.926	295.4	3.09	25.82	0.67	55.34	121.9
292.4	1.91	1.334	296.2	2.97	30.43	0.79	55.21	121.5
296.3	2.09	1.078	294.0	2.94	40.75	1.04	54.96	120.6
298.1	1.60	0.736	301.2	2.94	46.70	1.19	54.85	120.3
300.7	2.07	0.791	296.2	2.97	55.31	1.41	54.69	119.5
305.1	1.75	0.482	296.2	1.11	76.84	1.95	54.41	118.7
308.2	1.65	0.367	301.2	1.10	96.10	2.43	54.22	118.2
311.0	2.59	0.467	294.2	1.51	116.24	2.93	54.04	117.6
312.0	3.06	0.510	294.0	1.30	125.67	3.17	53.98	117.5
312.0	1.58	0.266	296.2	1.10	124.81	3.15	53.98	117.4
314.9	3.41	0.477	294.0	1.30	149.37	3.76	53.79	116.7
316.1	3.13	0.403	294.2	1.51	162.45	4.09	53.72	116.6
318.1	4.56	0.515	296.2	1.11	186.50	4.69	53.59	116.2
321.1	3.80	0.367	301.2	1.10	221.63	5.57	53.41	115.5
322.2	4.06	0.352	296.2	1.11	242.52	6.09	53.34	115.5
324.2	3.57	0.276	296.2	1.10	272.86	6.85	53.22	115.1
				3-Methylbenzonitrile: $\Delta_l^g H_m°$ $(T = 298.15 K) = (57.5 \pm 0.4)$ kJ $\cdot$ mol^{-1} $\ln(p/p°) = \frac{284.75}{R} - \frac{76181.01}{R \cdot (T \cdot K)} - \frac{62.7}{R} \ln\left(\frac{T/K}{298.15}\right)$			
279.8	0.93	2.765	294.0	4.48	7.20	0.20	58.64	130.3
281.3	1.30	3.353	295.2	2.01	8.29	0.23	58.54	130.0
283.7	1.31	2.690	294.0	4.48	10.33	0.28	58.39	129.5
285.7	1.03	1.813	295.2	3.40	12.06	0.33	58.27	128.9
288.3	1.00	1.404	295.2	3.37	15.13	0.40	58.10	128.4
290.3	1.26	1.494	297.2	4.48	18.01	0.48	57.98	128.0
292.4	1.34	1.308	294.9	2.01	21.54	0.56	57.85	127.6
294.3	1.36	1.140	294.9	2.01	25.16	0.65	57.73	127.3
297.2	1.34	0.905	294.9	2.01	31.03	0.80	57.55	126.5
300.0	1.23	0.662	297.2	1.89	39.37	1.01	57.37	126.0
302.1	1.60	0.731	294.9	2.01	46.06	1.18	57.24	125.6
304.1	1.28	0.505	293.7	1.89	53.17	1.35	57.11	125.1
307.7	2.14	0.646	293.7	1.89	69.05	1.75	56.89	124.4
309.2	2.16	0.595	293.2	1.88	75.50	1.91	56.80	123.9
310.1	2.00	0.505	293.7	1.89	82.91	2.10	56.74	123.9
312.0	2.20	0.501	293.2	1.88	91.59	2.31	56.62	123.3
313.7	2.68	0.533	293.7	1.88	104.87	2.65	56.52	123.1
				4-Methylbenzonitrile: $\Delta_l^g H_m°$ $(T = 298.15 K) = (55.9 \pm 0.4)$ kJ $\cdot$ mol^{-1} $\ln(p/p°) = \frac{276.30}{R} - \frac{74552.58}{R \cdot (T \cdot K)} - \frac{62.7}{R} \ln\left(\frac{T/K}{298.15}\right)$			
302.1	1.25	0.826	292.7	1.18	31.54	0.81	55.61	117.1
303.2	2.12	1.323	295.0	1.89	33.77	0.87	55.55	116.8
305.3	1.20	0.634	295.7	1.19	40.02	1.03	55.41	116.5
309.1	2.01	0.835	295.7	1.89	50.79	1.29	55.17	115.4
311.0	1.98	0.693	295.7	1.19	60.08	1.53	55.05	115.4
313.1	2.82	0.879	295.7	1.51	67.47	1.71	54.92	114.7
315.0	2.26	0.600	295.2	2.00	79.22	2.01	54.80	114.6
319.1	2.98	0.628	295.7	1.51	99.93	2.52	54.55	113.5
320.9	2.39	0.433	295.7	1.18	115.89	2.92	54.43	113.4
322.9	2.23	0.359	295.7	1.44	130.26	3.28	54.31	113.0
325.0	2.80	0.402	295.7	1.51	146.31	3.68	54.18	112.4
325.0	2.79	0.402	295.7	1.51	145.77	3.67	54.17	112.4
329.0	3.92	0.443	295.7	1.44	185.62	4.67	53.93	111.6
331.0	2.62	0.257	292.7	1.02	211.83	5.32	53.80	111.4
332.8	4.15	0.368	295.7	1.47	237.36	5.96	53.69	111.1
334.9	4.71	0.377	295.7	1.51	262.87	6.60	53.55	110.5

[a] Saturation temperature ($u(T) = 0.1$ K).
[b] Mass of transferred sample condensed at $T = 243$ K.
[c] Volume of nitrogen ($u(V) = 0.005$ dm^3) used to transfer m ($u(m) = 0.0001$ g) of the sample.
[d] T_a is the temperature of the soap bubble meter used for measurement of the gas flow.
[e] Vapor pressure at temperature T, calculated from m and the residual vapor pressure at $T = 243$ K estimated by iteration.
[f] Uncertainties of experimental vapor pressures were calculated according to the following equation: $u(p/Pa) = 0.025 + 0.025(p/Pa)$.

flow meter (model 0101-0113). The volume of the carrier gas V_{N2} was determined from the flow rate and the time measurement. Experimental results are given in table 3.

2.4. DSC study of melting temperature and enthalpy of fusion

The thermal behavior of 4-methylbenzonitrile and 2,4,6-trimethylbenzonitrile, including melting temperature and enthalpy of fusion, was studied with a computer-controlled differential scanning calorimeter (Perkin-Elmer Pyris Diamond DSC). No phase transitions prior melting were observed. The sample was hermetically sealed in a 50 µL pan supplied by Perkin Elmer. An empty pan was used as reference for all measurements. The fusion temperature and the enthalpy were determined as the peak onset temperature and by using a straight baseline for integration, respectively. The DSC measurements were repeated in triplicate and values agreed within the experimental uncertainties of $u(\Delta_{cr}^l H_m°) = 0.2$ kJ $\cdot$ mol^{-1} for the enthalpy of fusion and of

$u(T) = 0.5$ K for the melting temperature. Standard molar enthalpies of fusion of $\Delta_{cr}^l H_m^\circ = 16.1 \pm 0.2$ kJ·mol^{-1} at $T_{fus} = 299.3$ K for 4-methylbenzonitrile and of $\Delta_{cr}^l H_m^\circ = 15.5 \pm 0.2$ kJ·mol^{-1} at $T_{fus} = 325.5$ K for 2,4,6-trimethylbenzonitrile were derived.

2.5. Computational details

The enthalpies of the compounds under study were determined using both the G4 [13] and the W1-F12 [14] composite procedures. In the case of the latter the structures of all molecules were optimized with B3LYP-D3 dispersion corrected [16] hybrid density functional [17,18] using the cc-pVTZ basis set [19]. Vibrational frequencies calculated with the same method were scaled by 0.985 [14]. The enthalpy values at $T = 298.15$ K for both G4 and W1-F12 were evaluated according to standard thermodynamic procedures [20].

Atomic point charges for the methylbenzonitriles were determined by fitting the B3LYP-D3/cc-pVTZ quantum mechanical electrostatic potential (ESP), using the CHELPG method [21] (grid spacing = 0.01 nm). Nucleus independent chemical shifts (NICS) [22,23] for each benzonitrile were obtained from NMR shielding tensor calculations at the GIAO MP2/aug-cc-pVTZ level [24–27], using the B3LYP-D3/cc-pVTZ optimized structures.

The optimized geometries and frequencies used in W1-F12 calculations and the ESP atomic point charges were determined with NWChem 6.2 [28]. CFOUR [29] was used to obtain the diagonal Born–Oppenheimer corrections [30–32] required by the W1-F12 procedure. G4 and NMR shielding tensor calculations were performed using Gaussian 09 [33]. All other calculations were performed with Molpro 2012.1 [34].

3. Results and discussion

3.1. Enthalpies of formation of methylbenzonitriles from combustion calorimetry

The mean values of the standard specific energies of combustion $\Delta_c u^\circ$ and the molar combustion enthalpies $\Delta_c H_m^\circ$ for all three methylbenzonitriles are given in table 4. The molar standard enthalpies of formation $\Delta_f H_m^\circ$ (liq or cr) were calculated based on the reaction:

$$C_8H_7N + 9.75O_2 = 8CO_2 + 3.5H_2O + 0.5N_2 \qquad (2)$$
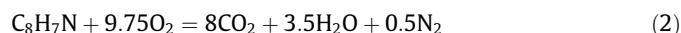
according to the Hess law using the molar enthalpies of formation of H_2O (liq) and CO_2 (g) assigned by CODATA [35]. Total uncertainties were calculated according to the guidelines presented by Olofsson [36]. The uncertainties assigned to $\Delta_f H_m^\circ$ (liq or cr) are twice the overall standard deviations and include the uncertainties from calibration, combustion energies of the auxiliary materials,

and the uncertainties of the enthalpies of formation of the reaction products H_2O and CO_2. The residual water concentration in the liquid sample was determined by Karl Fischer titration before starting experiments and appropriate corrections have been made for combustion results. The enthalpies of formation of the methylbenzonitriles were measured for the first time.

3.2. Vapor pressures of methylbenzonitriles by the transpiration method

Vapor pressures p_i measured at different temperatures were fitted with the following equation [12]:

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

where a and b are adjustable parameters and T_0 is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K). $\Delta_l^g C_{p,m}^\circ$ is the difference of the molar heat capacities of the gaseous and the liquid phases respectively. For the liquid methylbenzonitriles studied by transpiration a value of $\Delta_l^g C_{p,m}^\circ = -62.7$ J·mol^{-1}·K^{-1} was calculated according the procedure developed by Chickos and Acree [37]. The latter was based on the value $C_{p,m}^\circ$ (liq, $T = 298.15$ K) $= 200.4$ J·mol^{-1}·K^{-1}, estimated by a group-contribution method [38].

Vapor pressures for 2-methylbenzonitrile and 4-methylbenzonitrile were reported 120 years ago [39]. The primary data are not available, but the smoothed data were published later in the compilation by Stull [40]. Our new absolute vapor pressures are in acceptable agreement with the ancient results, in spite of the fact that the purity of samples and experimental methods from [39] are not available. All three isomers were also studied at temperatures close to the boiling point by using isoteniscope [41]. Any comparison with our vapor pressures is not possible due to significantly different temperature ranges of investigation.

3.3. Enthalpies of vaporization of methylbenzonitriles by the transpiration method

Vapor pressures of methylbenzonitriles were studied at temperatures around $T = 298.15$ K. Vaporization enthalpies were derived from the temperature dependence of vapor pressures using equation (4):

$$\Delta_l^g H_m^\circ(T) = -b + \Delta_l^g C_{p,m} \cdot T \qquad (4)$$

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

$$\Delta_l^g S_m^\circ(T) = \Delta_l^g H_m^\circ / T + R\ln(p_i/p^\circ) \qquad (5)$$

TABLE 4
Thermochemical data at $T = 298.15$ K ($p^\circ = 0.1$ MPa) for benzonitriles (kJ·mol^{-1}).[a]

Compounds	State	$-\Delta_c u^{\circ b}$ J·g^{-1}	$-\Delta_c H_m^\circ$ kJ·mol^{-1}	$\Delta_f H_m^\circ$	$\Delta_l^g H_m^\circ$	$\Delta_f H_m^\circ$ (g)
2-Methylbenzonitrile	liq	36468.2 ± 2.3	4275.3 ± 1.1	126.8 ± 1.5	54.8 ± 0.3	181.6 ± 1.5
3-Methylbenzonitrile	liq	36422.1 ± 3.8	4269.9 ± 1.4	121.4 ± 1.8	57.5 ± 0.4	178.9 ± 1.8
4-Methylbenzonitrile	cr	36323.8 ± 2.8	4258.4 ± 1.2	109.9 ± 1.6	55.9 ± 0.4[c]	181.8 ± 1.6
Benzonitrile	liq			164.6 ± 0.7 [43]	51.1 ± 0.1 [43]	215.7 ± 0.7
2,6-Dimethylbenzonitrile	cr			62.3 ± 1.5 [6]	83.9 ± 2.8[d] [6]	146.2 ± 3.2
2,4,6-Trimethylbenzonitrile	cr			23.5 ± 1.6 [6]	82.9 ± 1.6[d] [6]	106.4 ± 2.3
				6.5 ± 2.8 [7]	78.0 ± 1.2[d] [7]	84.5 ± 3.0

[a] Uncertainties correspond to expanded uncertainties of the mean (0.95 confidence level).

[b] Uncertainties reported for the specific energy of combustion correspond to the standard deviation of the mean.

[c] Enthalpy of sublimation for 4-methylbenzonitrile $\Delta_{cr}^g H_m^\circ$ ($T = 298.15$ K) $= 55.9 + 16.0 = 71.9 \pm 0.4$ kJ·mol^{-1} was derived using $\Delta_{cr}^l H_m^\circ$ ($T = 298.15$ K) $= 16.0 \pm 0.2$ kJ·mol^{-1} (see table 8).

[d] Enthalpy of sublimation.

Experimental results of the transpiration experiments are summarized in tables 3 and 4. As expected, the experimental vaporization enthalpies for 2-, 3-, and 4-methylbenzonitrile do not differ significantly. Nevertheless, the value for 3-methylbenzonitrile is ca. (1.5 to 2.5) kJ · mol^{-1} higher than those for the *ortho* and *para* isomers (table 4). For the sake of comparison we treated the available smoothed vapor pressures from [40,41] in the same way as own results using equations (3) and (4). Vaporization enthalpies adjusted to the reference temperature 298.15 K from [40] were as follows: 2-methylbenzonitrile 53.7 kJ · mol^{-1} and 4-methylbenzonitrile 54.4 kJ · mol^{-1}. Enthalpies of vaporization adjusted to T = 298.15 K from [41] were as follows: 2-methylbenzonitrile 57.0 kJ · mol^{-1}, 3-methylbenzonitrile 56.8 kJ · mol^{-1}, and 4-methylbenzonitrile 57.3 kJ · mol^{-1}. It was not possible to assigned uncertainties of vaporization enthalpies derived from the smoothed data of unknown quality, but from our experiences an overall uncertainties including uncertainties due to temperature adjustments could assessed within (1.5 to 2.5) kJ · mol^{-1}. Thus, within the combined experimental uncertainties the old and new data can be considered as in acceptable agreement. It is now also interesting to compare our new results for vaporization enthalpies of methylbenzonitrile with those for structurally similar compounds, *e.g.* with dimethylbenzenes, since the second CH$_3$-group has roughly the same size as the CN-group. In this case the vaporization enthalpies available [2] for 1,2-dimethylbenzene (43.5 ± 0.3) kJ · mol^{-1}, 1,3-dimethylbenzene (42.7 ± 0.3) kJ · mol^{-1}, and 1,4-dimethylbenzene (42.4 ± 0.3) kJ · mol^{-1} are significantly closer, than those for methylbenzonitriles. Apparently, a stronger (dipole–dipole) interaction in methylbenzonitriles is responsible for the more specific structuring of the liquid phase in comparison to dimethylbenzenes.

3.4. Experimental gas phase enthalpies of formation of the methylbenzonitriles at T = 298.15 K

The gas phase molar enthalpies of formation were calculated as the sum of liquid (or crystal) molar enthalpies of formation and molar enthalpies of vaporization (or sublimation) (table 4). These values are essentially close (within 2 to 3 kJ · mol^{-1}) for all three isomers. A similar trend was also observed for the $\Delta_f H_m^\circ$ (g, T = 298.15 K) values for 1,2-dimethylbenzene (19.0 ± 1.1) kJ · mol^{-1}, 1,3-dimethylbenzene (17.2 ± 0.8) kJ · mol^{-1}, and 1,4-dimethylbenzene (17.9 ± 1.0) kJ · mol^{-1} (all data from [3]). This fact could be considered as an evidence of an internal consistency of both data sets. With respect to the very carefully purified and sufficiently attested samples used in this work, our new experimental thermochemical results for methylbenzonitriles (table 4) can be now recommended as benchmark thermochemical properties for validation of theoretical $\Delta_f H_m^\circ$ (g, T = 298.15 K) data from quantum-chemical calculations.

3.5. Comparison of experimental and theoretical enthalpies of formation of methylbenzonitriles

The gaseous enthalpies of formation of methylbenzonitriles were calculated using the composite methods G4 and W1-F12, and the values thus obtained were compared with the experimental data.

Enthalpies, H_{298}, (see table 5) calculated by G4 for the most stable conformations of the methylbenzonitriles (see figure 1) were converted to enthalpies of formation $\Delta_f H_m^\circ$ (g, T = 298.15 K) using the conventional ring-conserving homodesmic reaction:
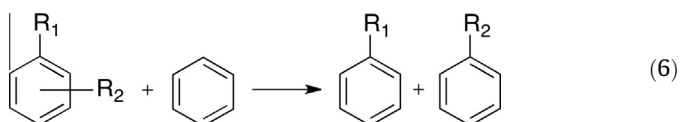
$$ \text{(6)} $$

TABLE 5
G4 and W1-F12 enthalpies at T = 298.15 K (in Hartree) for the molecules studied in this work.

Compounds	H_{298}/Hartree	
	G4	W1-F12[a]
2-Methylbenzonitrile	−363.596483	−363.778268
3-Methylbenzonitrile	−363.595963	−363.776800
4-Methylbenzonitrile	−363.595352	−363.777132
Benzene	−232.088586	−232.197242
Toluene	−271.370151	−271.494689
Benzonitrile	−324.313042	−324.478738
2,6-Dimethylbenzonitrile	−402.879911	−403.077670
2,4,6-Trimethylbenzonitrile	−442.162029	−442.376028
1,2-Dimethylbenzene	−310.651869	−310.792607
1,3-Dimethylbenzene	−310.651617	−310.792126
1,4-Dimethylbenzene	−310.651408	−310.791868

[a] The H_{298} values calculated by W1-F12 for hydrogen, carbon and nitrogen are −(0.497341, 37.851387, 54.609009) Hartree, respectively.
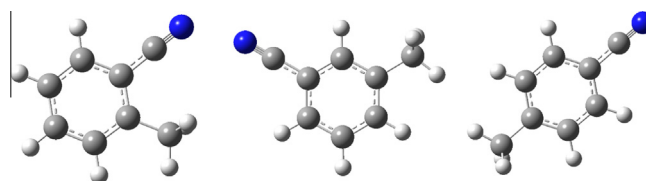

FIGURE 1. Optimized structures of methylbenzonitriles: 2-methylbenzonitrile, 3-methylbenzonitrile, 4-methylbenzonitrile.

where R$_1$ and R$_2$ are methyl and nitrile substituents. Using the enthalpies of reaction (6) (in reverse way) for methylbenzonitriles calculated by G4 (see table 6, column 2) together with the enthalpies of formation, $\Delta_f H_m^\circ$ (g), for benzene and toluene from [2], and benzonitrile (see table 4) theoretical enthalpies of formation of all methylbenzonitrile isomers were calculated (see table 6).

Gas-phase enthalpies of formation of each compound were also calculated from the corresponding atomization reaction, using the W1-F12 H_{298} data in table 5 together with the CODATA recommended values for the enthalpies of formation of the carbon, hydrogen, and nitrogen atoms [35]. Doing so yields theoretical data that are independent from those obtained using the G4 method and from experiment, and thus provides further verification of both.

The theoretical enthalpies of formation of methylbenzonitriles are in very good agreement with the corresponding experimental values. Moreover, the two independent theoretical procedures used lead to essentially the same results. This strongly validates both the experimental and the theoretical results, and is further proof of the benchmark quality of the thermochemical data for substituted benzenes provided herein.

We have previously stated that accurate standard molar enthalpy of formation data in the solid or liquid phase can be obtained by combining high-level quantum chemistry gas-phase enthalpy of formation values with experimentally determined enthalpies of vaporization [9,10]. The validity of that statement is again reinforced by the very good agreement between experimental and high-level ab initio data in table 6.

3.6. Pairwise interactions of substituents on the benzene ring (gas phase, T = 298.15 K)

The enthalpies of the general disproportionation reaction (6), $\Delta_r H_m^\circ$, calculated according to the Hess Law provide a measure of the pairwise interaction of substituents on the benzene ring.

TABLE 6
Pairwise interactions of substituents, $\Delta_r H_m^\circ$, on the benzene ring calculated from the theoretical and experimental data, and comparison of the theoretical and experimental enthalpies of formation $\Delta_f H_m^\circ$ (g) at T = 298.15 K (in kJ · mol^{-1}).

Compounds	$\Delta_r H_m^\circ$ [a]	$\Delta_r H_m^\circ$ [b]	$\Delta_r H_m^\circ$ (g)$_{exp}$ [c]	$\Delta_f H_m^\circ$ (g)[d]	$\Delta_f H_m^\circ$ (g)[e]	$\Delta_f H_m^\circ$ (g)$_{exp}$
2-Methylbenzonitrile	−4.9	−5.5	−1.3	178.0	179.1	181.6 ± 1.5
3-Methylbenzonitrile	−3.5	−1.6	−4.0	179.4	183.0	178.9 ± 1.8
4-Methylbenzonitrile	−1.9	−2.5	−1.1	181.0	182.1	181.8 ± 1.6
2,6-Dimethylbenzonitrile	−9.8	−10.6	−3.2	140.3	141.6	146.2 ± 3.2 [7]
2,4,6-trimethylbenzonitrile	−11.3	−13.0	−10.9	106.0	106.8	106.4 ± 2.3 [7]
1,2-Dimethylbenzene	−0.4	−1.2	1.7	16.9	15.7	19.0 ± 1.1 [2]
1,3-Dimethylbenzene	0.3	0.0	−0.1	17.6	16.9	17.2 ± 0.8 [2]
1,4-Dimethylbenzene	0.8	0.7	0.6	17.5	17.6	17.9 ± 1.0 [2]

[a] Enthalpy of reaction (6) calculated according to the Hess law using the G4 H_{298} values for the reaction participants.
[b] Enthalpy of reaction (6) calculated according to the Hess law using the W1-F12 H_{298} values for the reaction participants.
[c] Calculated using reaction (6) and the experimental enthalpies of formation for all reaction participants.
[d] Calculated according to the Hess law using the G4 theoretical $\Delta_r H_m^\circ$ values and the experimental enthalpies of formation of C_6H_5-R_1, C_6H_5-R_2, and C_6H_6 involved in reaction (6).
[e] Calculated from an atomization reaction, using the W1-F12 H_{298} value for each compound and the CODATA recommended enthalpies of formation for carbon, hydrogen, and nitrogen.
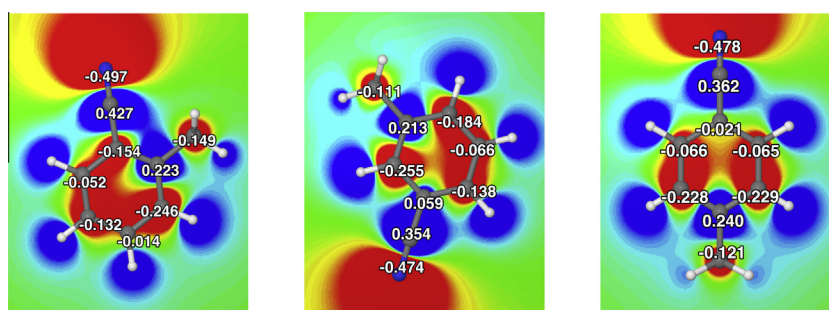

FIGURE 2. Atomic point charges determined for 2-methylbenzonitrile (left), 3-methylbenzonitrile (center), and 4-methylbenzonitrile (right). The corresponding electrostatic potentials are mapped on the molecular plane. In the color spectrum adopted (see the web version of this article) red and blue denote, respectively, the regions of highest and lowest electron density. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Interactions of different substituents in their *ortho-*, *meta-*, and *para-*position on benzene derived according to reaction (6) are fundamental in physical organic chemistry, because they usually indicate the stability or the reactivity of a substituted benzene. Admittedly, the *meta-*, and *para-*interactions of different substituents on the benzene ring in most cases are weak. In contrast, the *ortho-*interactions (especially for bulky substituents) are often strong due to steric repulsions, and they are crucially dependent on the size and the nature of substituent. Methyl and nitrile substituents are small in size, thus only weak pairwise interaction values are expected for the methylbenzonitriles studied in this work.

The $\Delta_r H_m^\circ$ values can be calculated either using the experimental $\Delta_f H_m^\circ$ (g) of the reaction participants or they can be derived directly from enthalpies H_{298} calculated by the theoretical methods. Comparison of experimental and theoretical pairwise interactions is given in table 6. The energetics of *ortho-*, *meta-*, and *para-*pairwise interactions of two methyl substituents were also calculated using the available thermochemical data on dimethylbenzenes [2] (see table 6). The agreement between experimental and theoretical $\Delta_r H_m^\circ$ values for both series is good (on the level of experimental uncertainties of 1 to 2 kJ · mol^{-1}). Interestingly, not only are 3- and 4-methylbenzonitile noticeably stabilized, but the same is also true even for 2-methylbenzonitrile. This is contrary to the reasonable expectation of destabilization due to close proximity of an electron donating (CH$_3$) and electron withdrawing group (CN). We have previously observed the same phenomena when CH$_3$O and CH$_3$ substituents are in 1,2-position on the benzene ring [9]. One could posit that this weak stabilization could be due to very weak intramolecular hydrogen bonding. However, given that noticeable stabilization has been also

observed for *meta-* and *para-*methylbenzonitriles, this should instead be due to the interplay of stereoelectronic effects between substituents.

In order to study these effects, atomic point charges were determined for each of the methylbenzonitriles. Analysis of these charges (figure 2) reveals that the higher enthalpies of formation obtained experimentally for 2- and 4-methylbenzonitrile correspond to a higher polarization of the C—N bond and to a higher accumulation of negative charge in the methyl group. This suggests that the slightly higher stability of 3-methylbenzonitrile stems from a higher degree of electron delocalization, which should lead to an also slightly lower aromaticity of its benzene ring. This is in keeping with the NICS(1)$_{zz}$ [22,23] values of −(28.2, 27.9, and 28.3) determined for, respectively, 2-, 3-, and 4-methylbenzonitrile. Moreover, these NICS(1)$_{zz}$ values are strongly correlated with the experimental gas-phase enthalpies of formation determined in the present work (R^2 = 0.99101; see figure 3).

3.7. Prediction of thermochemical properties of benzene derivatives by group-additivity

A very simple procedure to predict gas-phase enthalpies of formation of substituted benzenes was suggested in 1970 by Cox and Pilcher [8]. Starting with a benzene molecule and exchanging one of its H atoms by a given substituent R, a contribution, $\Delta H(H \rightarrow R)$, specific for that particular R is obtained. For the sake of simplicity, the original procedure considered pairwise interactions as negligible within ±10 kJ · mol^{-1} [8]. This procedure was very practical for the quick and rough appraisal of the $\Delta_f H_m^\circ$ (g, T = 298.15 K) of substituted benzenes. Several precise
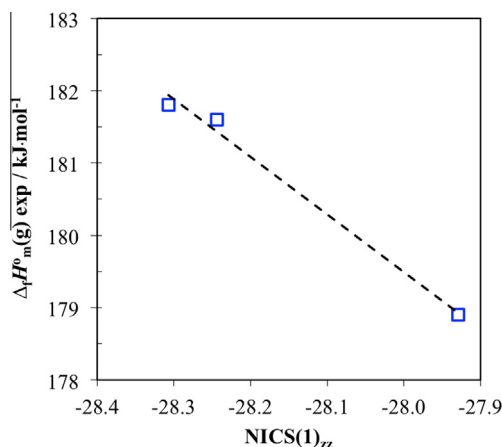
FIGURE 3. Correlation between the NICS(1)$_{zz}$ values and the experimental gas-phase enthalpies of formation determined for the methylbenzonitriles.

TABLE 7
Parameters for the calculation of enthalpies of vaporization, $\Delta_l^g H_m^\circ$, and enthalpies of formation in the gas phase, $\Delta_f H_m^\circ$ (g), and in the liquid phase, $\Delta_f H_m^\circ$ (liq), of substituted benzonitriles at $T = 298.15$ K (in kJ · mol^{-1}).

Groups	$\Delta_f H_m^\circ$ (g)	$\Delta_l^g H_m^\circ$	$\Delta_f H_m^\circ$ (liq)
Benzene	82.9	33.9	49.0
$\Delta H(H \rightarrow CH_3)$	−32.8	4.2	−37.0
$\Delta H(H \rightarrow CN)$	132.8	17.2	114.2
ortho(CH$_3$–CN)	−1.3	−0.5	0.6
meta(CH$_3$–CN)	−4.0	2.2	−4.8
para(CH$_3$–CN)	−1.1	0.6	−0.3
ortho(CH$_3$–CH$_3$)	1.7	1.2	0.5
meta(CH$_3$–CH$_3$)	−0.1	0.4	−0.5
para(CH$_3$–CH$_3$)	0.6	0.1	0.5

measurements on the di-, tri-, and poly-substituted benzenes published since 1970 have allowed the development of a more detailed procedure, which accounts for contributions from the pairwise interactions on the benzene ring.

Using the $\Delta_f H_m^\circ$ (g, $T = 298.15$ K) for benzene [2], toluene [2], and benzonitrile [43], the contributions for the exchange of an hydrogen with a methyl, $\Delta H(H \rightarrow CH_3)$, and a cyano group, $\Delta H(H \rightarrow CN)$, on the benzene ring have been derived (see table 7). The contributions listed in table 7 can be used to accurately predict the $\Delta_f H_m^\circ$ (g, $T = 298.15$ K) of di-substituted benzenes using the basic procedure proposed by Cox and Pilcher [8], extended with the numeric contributions for pairwise interactions derived in this work (see table 7). The same procedure can be applied for the prediction of vaporization enthalpies of di-substituted benzenes using the $\Delta_l^g H_m^\circ$ ($T = 298.15$ K) for benzene [2], toluene [2], and benzonitrile [43], and the appropriate contributions to the vaporization enthalpy for exchange of hydrogen with the CH$_3$ and CN substituents (see table 8). In order to derive the latter pairwise

contributions the enthalpies of vaporization of methylbenzonitriles measured in this work were used.

Enthalpies of formation in the liquid phase, $\Delta_f H_m^\circ$ (liq, $T = 298.15$ K), for 2- and 3-methylbenzonitrile were derived in this work by using combustion calorimetry (see table 5). For 4-methylbenzonitrile the experimental enthalpy of formation in the crystalline state and the experimental enthalpy of fusion (see table 8) were combined. These values are often required in chemical engineering calculations. Using the set of the liquid phase enthalpies of formation established for the methylbenzonitriles, it is also possible to derive pairwise interactions of CH$_3$ and CN substituents on the benzene ring in the liquid phase. These terms can be used for prediction of $\Delta_f H_m^\circ$ (liq, $T = 298.15$ K) of methyl and cyano substituted benzenes. Using the $\Delta_f H_m^\circ$ (liq, $T = 298.15$ K) for benzene [2], toluene [2], and benzonitriles [43], the appropriate $\Delta H(H \rightarrow CH_3)$ and $\Delta H(H \rightarrow CN)$ contributions as well as pairwise substituent interactions in the liquid phase were derived (see table 7).

Having derived benchmark quality thermochemical data for the three simplest methylbenzonitriles, we now turn our attention to more complex compounds of the same family. The case of 2,4,6-trimethylbenzonitrile is of particular interest, given that two significantly different sets of thermochemical data have been reported for this compound (table 4) [6,7]. These data can be analyzed and compared with that for 2,6-dimethylbenzontrile [6]. In contrast with the mono-methylbenzonitriles studied in this work, both 2,6-dimethylbenzontrile and 2,4,6-trimethylbenzontrile possess an additional non-additive contribution due to the presence of the sequence CH$_3$–CN–CH$_3$ on the benzene ring. For such molecules a buttress effect could be expected [42]. This effect can be derived using the pairwise interactions listed in table 8, provided that the thermochemical data for 2,6-dimethylbenzontrile and 2,4,6-trimethylbenzontrile are consistent. However, even a simple consistency test indicates the presence of an incongruence in these data. Indeed, the difference between the gas-phase enthalpies of formation of 2,6-dimethylbenzontrile and 2,4,6-trimethylbenzontrile is expected to be approximately equal to the contribution $\Delta H(H \rightarrow CH_3) = -32.8$ kJ · mol^{-1} (table 7). However, using the experimental data in table 4 leads to a difference of (106.4 to 146.2) = −39.8 kJ · mol^{-1}. This difference is also larger in magnitude than (106.0 to 140.3) = −34.3 kJ · mol^{-1} and (106.8 to 141.6) = −34.8 kJ · mol^{-1} which are obtained from, respectively, the G4 and W1-F12 data (table 6). Therefore, the experimental gas-phase enthalpy of formation of 2,6-dimethylbenzontrile seems to be in error, and the theoretical results should consequently be preferred.

Using the group additivity terms derived in the present work leads to a gas-phase enthalpy of formation of 147.4 kJ · mol^{-1} for 2,6-dimethylbenzontrile, and a value of 114.8 kJ · mol^{-1} for that of 2,4,6-trimethylbenzontrile. Comparison of these values with the theoretical $\Delta_f H_m^\circ$ (g) data in table 6 reveals that the magnitude of the buttress effect in both these compounds is of ca. (6 to 7) kJ · mol^{-1}.

TABLE 8
Compilation of the phase transition experimental enthalpy data for benzonitriles derivatives (in kJ · mol^{-1}).

Compounds	T_{fus}, K	$\Delta_{cr}^l H_m^\circ$ at T_{fus}	$\Delta_{cr}^l H_m^{\circ\,a}$	$\Delta_f H_m^\circ$ (liq)[b]	$\Delta_l^g H_m^\circ$
			at $T = 298.15$ K		
4-Methylbenzonitrile	299.3	16.1 ± 0.2	16.0 ± 0.2	125.9 ± 1.6	55.9 ± 0.4
2,6-Dimethylbenzonitrile	364.0	19.7 ± 1.0[c]	17.1 ± 1.5	79.4 ± 2.1	66.8 ± 3.2[d]
2,4,6-Trimethylbenzonitrile	325.5	15.5 ± 0.2	14.3 ± 0.4	37.8 ± 1.7	68.6 ± 1.7[d]

[a] The experimental enthalpies of fusion $\Delta_{cr}^l H_m^\circ$ measured at T_{fus} and adjusted [37] to $T = 298.15$ K.
[b] Values taken from table 4.
[c] Calculated according to the Walden rule: $\Delta_{cr}^l H_m^\circ$ (at T_{fus}) = 0.054 · T_{fus}.
[d] Calculated as the difference $\Delta_{cr}^g H_m^\circ - \Delta_{cr}^l H_m^\circ$.

4. Conclusion

The thermochemical properties for 2-, 3-, and 4-methylbenzonitrile were measured using high-precision combustion calorimetry and the transpiration method. From these results reliable gas- and liquid-phase data were recommended. The benchmark-quality data provided for methylbenzonitriles renders these compounds valuable for the validation quantum chemical methods.

The internal consistency of the new experimental data was confirmed by G4 and W1-F12 calculations. The excellent agreement between theoretical and experimental values provided further proof that, when accurate experimental data for the gas-phase is unavailable these data can be obtained with high-accuracy theoretical methods. Moreover, these gas-phase data can be combined with experimental phase-change values, leading to the thermochemical properties in the liquid or crystal state.

Using the experimental data presented in the present work a set of parameters for the calculation of enthalpies of vaporization, $\Delta_l^g H_m^\circ$, as well of enthalpies of formation in the gas $\Delta_f H_m^\circ$ (g) and in the liquid phase, $\Delta_f H_m^\circ$ (liq), of substituted benzonitriles at T = 298.15 K was proposed. These parameters were used to study the thermochemistry of 2,6-dimethylbenzontrile and of 2,4,6-trimethylbenzonitrile. Comparison with theoretical calculations and the available experimental data revealed an inconsistency for the gas-phase enthalpy of formation of 2,6-dimethylbenzontrile. Analysis of the gas-phase enthalpies of formation calculated using group-additivity terms and quantum chemistry methods allowed to quantify the buttress effect in these benzonitriles.

The pairwise interaction between methyl and cyano groups was found to be slightly stabilizing for the three methylbenzonitriles. Analysis of atomic point charges and NICS(1)$_{zz}$ values calculated for these compounds allowed to rationalize their stability trend in terms of the magnitude of charge delocalization.

Acknowledgment

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.jct.2015.07.025.

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