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Vapor Pressures and Phase Transitions of a Series of the Aminonaphthalenes

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Vapor pressures of 1-aminonaphthalene, 1,8-diaminonaphthalene, 1,5-diaminonaphthalene, *N*,*N*-dimethyl-1-aminonaphthalene, 1,8-*N*,*N*,*N*′,*N*′-tetramethyldiaminonaphthalene, and 1,5-*N*,*N*,*N*′,*N*′-tetramethyldiaminonaphthalene have been determined by the transpiration method. The molar enthalpies of sublimation and the molar enthalpies of vaporization have been determined from the temperature dependence of the vapor pressure. Experimental vaporization and sublimation enthalpies were checked for internal consistency with help of available data on fusion enthalpies.

Introduction

Certain aromatic diamines, such as 1,8-diaminonaphthalene or 1,8-*N*,*N*,*N*′,*N*′-tetramethyldiaminonaphthalene (see Figure 1), are found to have exceptionally high basicity constants: this is due to spatial interaction of the basic centers, which are in close proximity. Such compounds have been called the proton sponges.[1] The two factors that are most important in causing this effect are, on the one hand, the extreme steric strain in these systems and the destabilizing effect of the overlap of the nitrogen lone pairs of the neutral diamines and, on the other hand, the strong N···H···N hydrogen bonds that are formed on mono protonation and that lead to a considerable relaxation of the steric strain.[1] The unusual properties of the proton sponges provide examples of the fact that cooperative steric interactions of reactive structural elements can lead to properties that cannot be derived from an isolated consideration of the various functional groups. Such "proximity effects" are certainly of general importance in chemistry and biochemistry. Thermochemical methods provide quantitative data for interactions of substituents on the naphthalene ring. In this work, we focus on measuring of the vapor pressures, enthalpies of sublimation, and enthalpies of vaporization of the naphthalene derivatives related to the proton sponges shown in Figure 1.

Experimental Section

Samples of 1-aminonaphthalene, 1,8-diaminonaphthalene, 1,5-diaminonaphthalene, *N*,*N*-dimethyl-1-aminonaphthalene, and 1,8-*N*,*N*,*N*′,*N*′-tetramethyldiaminonaphthalene were of commercial origin (Aldrich, Fluka). The sample of 1,5-*N*,*N*,*N*′,*N*′-tetramethyldiaminonaphthalene was prepared by methylation of 1,5-diaminonaphthalene according to procedures elaborated by Sorokin et al.:[2] a mixture of 23.9 mL of Me_2SO_4 (0.253 mol), 25 mL MeOH, and 72.3 g of $Na_2CO_3 \cdot 10H_2O$ (0.253 mol) was added to 5.0 g of 1,5-diaminonaphthalene (0.032 mol). The reaction mixture was stirred well (CO_2 was evolved) for 5 h. After that time, the reaction mixture was basified with solution of NaOH in water to a strongly basic solution with pH of 12 to 13, and the methylation product was extracted with benzene. The benzene was evaporated, and the residue was crystallized after 2 to 3 h. Yield was 6.41 g (94.7 %), melting point was at 361 K. The compound was purified by repeated re-crystallization from ethanol. The structure of the 1,5-*N*,*N*,*N*′,*N*′-tetramethyldiaminonaphthalene was confirmed by NMR spectroscopy.

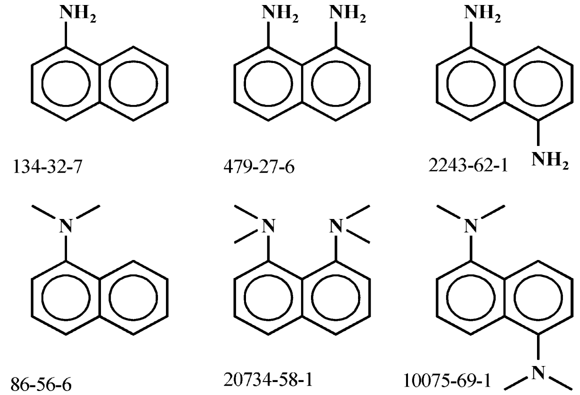

Figure 1. Structures of aminonaphthalene derivatives and their Chemical Abstracts Registry Numbers (CASRN): 1-aminonaphthalene (134-32-7); 1,8-diaminonaphthalene (479-7-6); 1,5-diaminonaphthalene (2243-62-1); *N*,*N*-dimethyl-1-aminonaphthalene (86-56-6); 1,8-*N*,*N*,*N*′,*N*′-tetramethyldiaminonaphthalene (20734-58-1); 1,5-*N*,*N*,*N*′,*N*′-tetramethyldiaminonaphthalene (10075-69-1).

The degree of purity of all naphthalene derivatives studied was determined using a Hewlett-Packard gas chromatograph 5890 series II equipped with a flame ionization detector and a Hewlett-Packard 3390A integrator. The carrier gas (nitrogen) flow was 12.1 $cm^3 \cdot s^{-1}$. A capillary column HP-5 (stationary phase crosslinked 5 % phenyl methyl silicone) was used with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 mm. The standard temperature program of the GC was $T = 363$ K for 180 s followed by a heating rate of 0.167 $K \cdot s^{-1}$ to $T = 523$ K. No impurities (greater than mass fraction 0.002) could be detected in the samples used for the vapor pressure measurements. Melting temperature and enthalpy of fusion of 1,8-diaminonaphthalene were determined with a Perkin-Elmer DSC-2C.

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Vapor pressures were determined using the method of transpiration in a saturated nitrogen stream,[3,4] and enthalpies of naphthalene derivatives were obtained applying the Clausius−Clapeyron equation. About 0.5 g of the sample was mixed with glass beads and placed in a thermostatted U-shaped tube having a length of 20 cm and a diameter of 0.5 cm. Glass beads with diameter of 1 mm provide surface, which was sufficient for the vapor−liquid equilibration. At constant temperature (± 0.1 K), a nitrogen stream was passed through the U-tube, and the transported amount of gaseous material was collected in a cooling trap. The flow rate of the nitrogen stream was measured using a soap bubble flowmeter and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. On the one hand, flow rate of nitrogen stream in the saturation tube should be not too slow in order to avoid the transport of material from U-tube due to diffusion. On the other hand the flow rate should be not too fast in order to reach the saturation of the nitrogen stream with a compound. We tested our apparatus at different flow rates of the carrier gas in order to check the lower boundary of the flow below which the contribution of the vapor condensed in the trap by diffusion becomes comparable to the transpired one. In our apparatus, the contribution due to diffusion was negligible at a flow rate up to 0.11 $\text{cm}^3\cdot\text{s}^{-1}$. The upper limit for our apparatus where the speed of nitrogen could already disturb the equilibration was at a flow rate of 1.5 $\text{cm}^3\cdot\text{s}^{-1}$. Thus, we carried out the experiments in the flow rate interval of (0.28 to 0.52) $\text{cm}^3\cdot\text{s}^{-1}$, which has ensured that transporting gas was in saturated equilibrium with the coexisting liquid phase in the saturation tube. The mass of compound collected within a certain time interval was determined by dissolving it in a suitable solvent with a known amount of external standard (hydrocarbon). This solution was analyzed using a gas chromatograph equipped with autosampler. Uncertainty of the sample amount determined by GC analysis was assessed to be within (1 to 3) %. The peak area of the compound related to the peak of the external standard (hydrocarbon n-C_nH_{2n+2}) is a direct measure of the mass of the compound condensed into the cooling trap provided a calibration run has been made. From this information the vapor pressure of the compound under study can be determined (i.e., the ideal gas law can be applied provided that the vapor pressure of the substance is low enough). Real gas corrections arising from interactions of the vapor with the carrier gas were negligible. The saturation vapor pressure p_i^{sat} at each temperature T_i was calculated from the amount of product collected within a known period of time, 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 $\ln(p_i^{\text{sat}})$ and T^{-1} obtained by iteration. Assuming that Dalton's law of partial pressures applied to the nitrogen stream saturated with the substance i of interest is valid, values of p_i^{sat} were calculated:

$$p_i^{\text{sat}} = m_iRT_{\text{a}}/VM_{\text{i}}; \quad V = V_{\text{N2}} + V_i; \quad (V_{\text{N2}} \gg V_i) \tag{1}$$

where $R = 8.314472\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, m_i is the mass of transported compound, M_i is the molar mass of the compound, and V_i is its volume contribution to the gaseous phase. V_{N2} is the volume of transporting gas, and T_{a} is the temperature of the soap bubble meter. The volume of transporting gas V_{N2} was determined from the flow rate and time measurements. The flow rate was maintained constant with help of the high precision needle valve (Hoke, C1335G6BMM-ITA). The accuracy of the volume V_{N2} measurements from flow rate was established to be (± 0.001 dm^3) with help of series of experiments, where volume the nitrogen was measured with gas-clock or by water withdrawing from calibrated gasometer. Data of p_i^{sat} have been obtained as a function of temperature and were fitted using following equation:[3]

$$R \ln p_i^{\text{sat}} = a + \frac{b}{T} + \Delta_{\text{cr}}^{\text{g}}C_p \ln\left(\frac{T}{T_0}\right) \tag{2}$$

This equation was fitted to the experimental p, T data using a and b as adjustable parameters. The T_0 appearing in eq 2 is an arbitrarily chosen reference temperature, which has been chosen to be 298.15 K. Consequently from eq 2, the expression for the sublimation enthalpy at temperature T is derived:

$$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}(T) = -b + \Delta_{\text{cr}}^{\text{g}}C_{\text{p}}T \tag{3}$$

Experimental results with parameters a and b are listed in Table 1. Values of $\Delta_{\text{cr}}^{\text{g}}C_p$ have been derived according to a procedure developed by Chickos et al.[5] When the vapor pressures were measured over liquid samples of aminonaphthalene derivatives, eq 2 gives the expression for the vaporization enthalpy $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}$ at temperature T. Values of $\Delta_{\text{l}}^{\text{g}}C_p$ required for the data treatment in this case have been derived according to a procedure developed by Chickos and Acree.[6] We have checked experimental and calculation procedure with measurements of vapor pressures of n-alcohols[3] and substituted naphthalenes.[7] It turned out that vapor pressures derived from the transpiration method were reliable within (1 to 3) % and that their accuracy was governed by reproducibility of the GC analysis. Contributions to the experimental error due to fluctuations of the nitrogen stream or temperature were negligible in comparison to the aforementioned error bars of the GC analysis. In order to assess the uncertainty of the vaporization enthalpy, the experimental data were approximated with the linear equation $\ln(p_i^{\text{sat}}) = f(T^{-1})$ using the method of least squares. The uncertainty in the enthalpy of vaporization was assumed to be identical with the as average deviation of experimental $\ln(p_i^{\text{sat}})$ values from this linear correlation.

Results and Discussion

Vapor pressure measurements on 1,8-diaminonaphthalene, 1,5-diaminonaphthalene, *N*,*N*-dimethyl-1-aminonaphthalene, 1,8-*N*,*N*,*N*′,*N*′-tetramethyldiaminonaphthalene, and 1,5-*N*,*N*,*N*′,*N*′-tetramethyldiaminonaphthalene have been performed for the first time. Critical evaluation of the available thermochemical properties for 1- and 2-aminonaphthalene was reported by Das et al.,[8] but the phase transitions data on these species is apparently in disarray. Indeed, Das et al.[8] recommended the value $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}} = (65.0 \pm 4.0)\ \text{kJ}\cdot\text{mol}^{-1}$ for 1-aminonaphthalene. This enthalpy of sublimation was assessed from the selected value $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}} = (74.1 \pm 4.0)\ \text{kJ}\cdot\text{mol}^{-1}$ measured by Karyakin et al.[9] (using an effusion method) and the difference between enthalpies of fusion of 1- and 2-aminonaphthalene 9.1 $\text{kJ}\cdot\text{mol}^{-1}$ reported by Khetarpal et al.[10] (see Table 2). Thus, the estimate by Das et al.[8] of $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}} = (65.0 \pm 4.0)\ \text{kJ}\cdot\text{mol}^{-1}$ and our result $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}} = (88.1 \pm 0.4)\ \text{kJ}\cdot\text{mol}^{-1}$ from Table 1 are different over 20 $\text{kJ}\cdot\text{mol}^{-1}$. The value $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}} = (90.0 \pm 4.2)\ \text{kJ}\cdot\text{mol}^{-1}$ cited in the NIST WebBook[11] as the experimental result from Balson[12] should support our result, but unfortunately this reference does not contain any data on 1-aminonaphthalene. The comprehensive compilation by Stull[13] contains vapor pressure data for 1- and 2-aminonaphthalene over a wide range of temperature from 377 K to their boiling point. It should be mentioned, that the origin of the data presented there is unclear,

Table 1. Vapor Pressures p, Sublimation Enthalpy $\Delta_{cr}^{g}H_m$, and Vaporization Enthalpy $\Delta_{l}^{g}H_m$ Obtained by the Transpiration Method

T	m	$V(N_2)$	N_2 flow	p	$(p_{exp} - p_{calc})$	$\Delta_{cr}^{g}H_m$ or $\Delta_{l}^{g}H_m$	T	m	$V(N_2)$	N_2 flow	p	$(p_{exp} - p_{calc})$	$\Delta_{cr}^{g}H_m$ or $\Delta_{l}^{g}H_m$
K[a]	mg[b]	dm^3[c]	cm^3·s^{-1}	Pa[d]	Pa	kJ·mol^{-1}	K[a]	mg[b]	dm^3[c]	cm^3·s^{-1}	Pa[d]	Pa	kJ·mol^{-1}
1-Aminonaphthalene(cr), $\Delta_{cr}^{g}H_m(298.15\ \mathrm{K}) = (88.11 \pm 0.40)\ \mathrm{kJ{\cdot}mol^{-1}}$													
$\ln(p/\mathrm{Pa}) = \frac{307.1}{R} - \frac{95978.9}{R(T/\mathrm{K})} - \frac{26.4}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
290.3	0.56	153.5	7.03	0.06	0.00	88.32	311.5	0.67	15.11	6.74	0.76	0.00	87.76
293.3	0.57	104.6	7.23	0.09	0.00	88.24	314.2	0.79	13.22	6.84	1.03	0.01	87.69
298.3	1.06	107.3	6.84	0.17	0.00	88.11	316.2	1.07	14.88	6.84	1.24	−0.03	87.63
303.3	0.44	25.19	7.13	0.30	−0.01	87.97	318.2	1.02	11.23	6.84	1.55	−0.01	87.58
308.3	0.59	18.54	6.74	0.55	0.01	87.84	320.2	0.84	7.58	6.84	1.91	−0.01	87.53
1-Aminonaphthalene(l), $\Delta_{l}^{g}H_m(298.15\ \mathrm{K}) = (73.29 \pm 0.43)\ \mathrm{kJ{\cdot}mol^{-1}}$													
$\ln(p/\mathrm{Pa}) = \frac{313.2}{R} - \frac{96542.6}{R(T/\mathrm{K})} - \frac{78.0}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
323.2	0.87	5.46	7.28	2.71	0.04	71.34	341.1	1.12	1.82	7.28	10.53	−0.08	69.94
326.2	0.96	4.73	7.28	3.44	0.03	71.10	344.1	1.04	1.33	7.28	13.27	0.12	69.71
329.2	1.04	4.12	7.28	4.29	−0.04	70.87	347.1	1.17	1.21	7.28	16.44	0.20	69.47
332.3	1.48	4.73	7.28	5.33	−0.18	70.63	350.1	1.13	0.971	7.28	19.91	−0.04	69.24
335.3	1.22	3.03	7.28	6.83	−0.09	70.39	353.1	0.86	0.607	7.28	24.28	−0.13	69.00
338.1	1.16	2.31	7.28	8.59	0.07	70.17							
1,8-Diaminonaphthalene(cr), $\Delta_{cr}^{g}H_m(298.15\ \mathrm{K}) = (94.08 \pm 0.37)\ \mathrm{kJ{\cdot}mol^{-1}}$													
$\ln(p/\mathrm{Pa}) = \frac{303.5}{R} - \frac{102520.6}{R(T/\mathrm{K})} - \frac{28.3}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
304.4	0.19	174.6	4.94	0.017	0.000	93.91	327.2	0.20	14.04	4.94	0.223	0.001	93.26
307.3	0.15	96.2	4.94	0.024	0.000	93.83	329.1	0.21	12.00	4.88	0.273	0.002	93.21
310.3	0.19	87.52	4.94	0.034	0.000	93.74	330.2	0.27	14.08	4.94	0.302	−0.001	93.18
313.6	0.23	71.29	4.88	0.051	0.001	93.65	331.2	0.27	12.44	4.88	0.339	0.003	93.15
315.2	0.26	67.91	4.88	0.061	0.001	93.60	331.8	0.15	6.67	4.94	0.348	−0.010	93.13
318.2	0.40	71.63	4.94	0.086	0.002	93.52	332.2	0.22	9.39	4.94	0.372	0.000	93.12
320.3	0.19	29.39	4.94	0.101	−0.005	93.46	333.2	0.18	6.91	4.88	0.414	0.002	93.09
322.2	0.22	27.01	4.94	0.130	−0.001	93.40	333.7	0.14	5.19	4.94	0.422	−0.011	93.08
323.5	0.15	15.01	4.88	0.152	0.002	93.37	335.2	0.23	6.71	4.94	0.526	0.022	93.04
324.2	0.17	15.97	4.94	0.162	0.000	93.35	335.7	0.19	5.52	4.94	0.535	0.005	93.02
326.5	0.18	13.18	4.88	0.210	0.004	93.28							
1,8-Diaminonaphthalene(l), $\Delta_{l}^{g}H_m(298.15\ \mathrm{K}) = (79.57 \pm 0.25)\ \mathrm{kJ{\cdot}mol^{-1}}$													
$\ln(p/\mathrm{Pa}) = \frac{322.9}{R} - \frac{106943.6}{R(T/\mathrm{K})} - \frac{91.8}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
339.5	0.22	5.44	4.98	0.62	0.01	75.78	361.4	0.44	2.32	4.98	2.95	−0.11	73.77
341.5	0.20	4.32	4.98	0.72	0.00	75.60	364.5	0.37	1.54	4.98	3.73	−0.04	73.49
344.6	0.28	4.86	4.98	0.91	0.00	75.31	367.6	0.49	1.66	4.98	4.59	−0.04	73.20
346.1	0.20	2.99	4.98	1.03	0.01	75.18	370.6	0.44	1.20	4.98	5.67	0.06	72.93
349.3	0.22	2.70	4.98	1.28	−0.01	74.88	373.2	0.41	0.955	4.98	6.63	0.02	72.69
352.4	0.26	2.49	4.98	1.62	−0.01	74.60	376.2	0.39	0.747	4.98	8.04	0.07	72.41
355.3	0.33	2.49	4.98	2.03	0.02	74.33	379.3	0.36	0.581	4.98	9.66	0.03	72.13
358.5	0.31	1.91	4.98	2.50	0.00	74.04							
1,5-Diaminonaphthalene(cr), $\Delta_{cr}^{g}H_m(298.15\ \mathrm{K}) = (120.16 \pm 0.65)\ \mathrm{kJ{\cdot}mol^{-1}}$													
$\ln(p/\mathrm{Pa}) = \frac{340.9}{R} - \frac{128595.7}{R(T/\mathrm{K})} - \frac{28.3}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
345.3	0.10	113.1	4.81	0.0139	0.0003	118.83	359.3	0.13	31.47	4.81	0.0656	−0.0026	118.43
347.3	0.12	104.6	4.81	0.0175	0.0002	118.77	360.4	0.43	90.59	4.81	0.0741	−0.0028	118.40
349.3	0.13	89.07	4.81	0.0221	0.0002	118.71	361.3	0.14	26.21	4.81	0.0856	0.0007	118.37
350.3	0.14	89.55	4.81	0.0242	−0.0004	118.68	363.4	0.16	23.97	4.81	0.1051	−0.0015	118.31
351.3	0.15	83.77	4.81	0.0272	−0.0004	118.66	366.4	0.23	24.69	4.81	0.1455	−0.0014	118.23
353.3	0.17	73.83	4.81	0.0350	0.0002	118.60	368.4	0.23	20.12	4.81	0.1808	−0.0005	118.17
354.3	0.21	84.74	4.81	0.0383	−0.0006	118.57	369.3	0.29	22.05	4.81	0.2045	0.0053	118.15
355.3	0.17	60.45	4.81	0.0442	0.0006	118.54	371.3	0.32	20.04	4.81	0.2502	0.0051	118.09
357.3	0.25	71.59	4.81	0.0540	−0.0006	118.49							
N,*N*-Dimethyl-1-aminonaphthalene(l), $\Delta_{l}^{g}H_m(298.15\ \mathrm{K}) = (66.92 \pm 0.16)\ \mathrm{kJ{\cdot}mol^{-1}}$													
$\ln(p/\mathrm{Pa}) = \frac{311.6}{R} - \frac{92676.0}{R(T/\mathrm{K})} - \frac{86.4}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$													
283.2	0.67	37.68	4.69	0.26	0.00	68.16	313.3	0.81	3.01	4.69	3.89	−0.07	65.62
285.2	0.99	45.10	4.69	0.32	0.00	68.00	316.3	0.81	2.34	4.69	4.97	−0.05	65.37
287.7	1.30	45.45	4.69	0.41	0.01	67.78	319.4	0.91	2.03	4.69	6.42	0.03	65.11
291.3	1.21	30.17	4.69	0.58	0.01	67.48	322.2	0.85	1.56	4.69	7.85	−0.05	64.87
295.3	0.45	7.92	4.75	0.83	−0.01	67.14	325.3	0.91	1.33	4.69	9.89	−0.07	64.61
298.2	0.55	7.56	4.75	1.05	−0.04	66.90	328.2	1.07	1.25	4.69	12.34	0.05	64.37
304.2	0.43	3.36	4.69	1.84	−0.01	66.39	331.2	1.26	1.17	4.69	15.45	0.24	64.11
307.3	1.34	7.90	4.91	2.45	0.04	66.13	334.3	1.15	0.860	4.69	19.29	0.42	63.85
310.3	0.65	3.07	4.91	3.05	−0.05	65.88							

Table 1 (Continued)

1,8-*N*,*N*,*N*′,*N*′-Tetramethyldiaminonaphthalene(cr), $\Delta_{cr}^{g}H_m$(298.15 K) = (94.73 ± 0.80) kJ·mol^{-1}

$$\ln(p/\mathrm{Pa}) = \frac{353.5}{R} - \frac{110587.2}{R(T/\mathrm{K})} - \frac{53.2}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$$

T K^a	m mg^b	$V(N_2)$ dm$^{3\,c}$	N_2 flow cm^3·s^{-1}	p Pa^d	$(p_{exp} - p_{calc})$ Pa	$\Delta_{cr}^{g}H_m$ or $\Delta_{l}^{g}H_m$ kJ·mol^{-1}	T K^a	m mg^b	$V(N_2)$ dm$^{3\,c}$	N_2 flow cm^3·s^{-1}	p Pa^d	$(p_{exp} - p_{calc})$ Pa	$\Delta_{cr}^{g}H_m$ or $\Delta_{l}^{g}H_m$ kJ·mol^{-1}
290.7	0.50	125.5	5.92	0.045	−0.001	95.12	304.3	0.71	29.98	5.88	0.270	0.005	94.40
293.2	0.49	83.82	5.95	0.065	0.001	94.99	306.7	0.59	19.25	5.80	0.343	−0.011	94.27
296.1	0.73	88.69	5.92	0.094	0.000	94.84	308.4	0.66	17.50	5.90	0.433	−0.002	94.18
298.3	0.27	24.88	5.90	0.124	−0.001	94.72	308.5	0.90	22.34	5.80	0.454	0.015	94.18
298.7	0.47	42.09	5.75	0.126	−0.005	94.70	310.9	0.76	14.99	5.88	0.576	−0.008	94.05
301.4	0.46	26.95	5.95	0.192	0.007	94.56	313.7	0.62	8.70	5.80	0.802	−0.006	93.90

1,8-*N*,*N*,*N*′,*N*′-Tetramethyldiaminonaphthalene(l), $\Delta_{l}^{g}H_m$(298.15 K) = (76.72 ± 0.35) kJ·mol^{-1}

$$\ln(p/\mathrm{Pa}) = \frac{351.8}{R} - \frac{109097.1}{R(T/\mathrm{K})} - \frac{108.9}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$$

T K^a	m mg^b	$V(N_2)$ dm$^{3\,c}$	N_2 flow cm^3·s^{-1}	p Pa^d	$(p_{exp} - p_{calc})$ Pa	$\Delta_{cr}^{g}H_m$ or $\Delta_{l}^{g}H_m$ kJ·mol^{-1}	T K^a	m mg^b	$V(N_2)$ dm$^{3\,c}$	N_2 flow cm^3·s^{-1}	p Pa^d	$(p_{exp} - p_{calc})$ Pa	$\Delta_{cr}^{g}H_m$ or $\Delta_{l}^{g}H_m$ kJ·mol^{-1}
323.7	1.37	7.65	3.45	2.04	0.03	73.95	343.4	1.47	1.77	3.37	9.46	−0.05	71.81
326.2	1.48	6.61	3.45	2.54	0.06	73.68	346.3	1.63	1.61	3.45	11.52	−0.21	71.49
329.2	1.51	5.35	3.45	3.20	0.02	73.35	349.2	1.56	1.26	3.45	13.97	−0.44	71.18
332.1	1.61	4.48	3.45	4.08	0.07	73.04	352.3	1.60	1.03	3.45	17.56	−0.32	70.84
333.3	0.86	2.18	3.08	4.47	0.06	72.91	355.2	2.16	1.09	3.45	22.50	0.72	70.53
334.5	1.11	2.61	3.37	4.84	−0.01	72.78	358.4	2.46	1.01	3.45	27.75	0.81	70.18
337.5	1.16	2.19	3.37	5.99	−0.12	72.45	361.2	2.59	0.891	3.45	32.98	0.66	69.88
340.3	1.23	1.91	3.37	7.33	−0.23	72.15	364.3	3.01	0.863	3.45	39.66	0.28	69.54

1,5-*N*,*N*,*N*′,*N*′-Tetramethyldiaminonaphthalene(cr), $\Delta_{cr}^{g}H_m$(298.15 K) = (98.55 ± 0.40) kJ·mol^{-1}

$$\ln(p/\mathrm{Pa}) = \frac{348.0}{R} - \frac{114416.0}{R(T/\mathrm{K})} - \frac{53.2}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$$

T K^a	m mg^b	$V(N_2)$ dm$^{3\,c}$	N_2 flow cm^3·s^{-1}	p Pa^d	$(p_{exp} - p_{calc})$ Pa	$\Delta_{cr}^{g}H_m$ or $\Delta_{l}^{g}H_m$ kJ·mol^{-1}	T K^a	m mg^b	$V(N_2)$ dm$^{3\,c}$	N_2 flow cm^3·s^{-1}	p Pa^d	$(p_{exp} - p_{calc})$ Pa	$\Delta_{cr}^{g}H_m$ or $\Delta_{l}^{g}H_m$ kJ·mol^{-1}
318.2	0.53	37.59	3.13	0.165	0.002	97.49	338.2	0.41	3.33	2.66	1.440	0.015	96.43
322.2	0.61	27.32	5.46	0.262	0.004	97.28	339.2	0.62	4.74	5.69	1.532	−0.045	96.37
325.2	0.69	22.42	5.61	0.360	0.001	97.12	340.7	0.60	4.09	5.46	1.739	−0.093	96.29
326.7	0.51	13.76	5.58	0.432	0.008	97.04	341.3	0.61	3.63	5.18	1.952	−0.002	96.26
328.1	0.58	13.78	5.51	0.493	−0.002	96.96	343.2	0.69	3.45	4.60	2.351	0.004	96.16
328.2	0.61	14.64	5.49	0.491	−0.009	96.96	344.4	0.55	2.49	5.53	2.574	−0.066	96.10
329.6	0.60	11.94	5.51	0.591	0.010	96.88	345.7	0.69	2.71	5.42	3.001	0.007	96.03
330.6	0.58	10.91	5.46	0.625	−0.025	96.83	348.2	0.63	1.90	4.57	3.918	0.113	95.89
331.2	0.59	9.33	5.60	0.733	0.044	96.80	349.5	0.60	1.67	2.86	4.230	−0.075	95.83
331.9	0.62	9.67	5.52	0.751	0.009	96.76	350.7	0.58	1.42	2.83	4.832	0.013	95.76
332.7	0.47	6.82	4.54	0.809	0.002	96.72	351.5	0.59	1.34	2.86	5.213	0.020	95.72
333.5	0.64	8.27	5.22	0.899	0.021	96.68	353.2	0.62	1.18	2.83	6.210	0.131	95.63
335.7	0.60	6.35	5.44	1.104	0.000	96.56	354.5	0.57	0.955	2.86	6.941	0.091	95.56
338.1	0.63	5.21	5.21	1.407	−0.003	96.43	355.7	0.63	0.934	2.80	7.956	0.314	95.50

[a] Temperature of saturation. [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.

Table 2. Comparison of Enthalpies of Fusion Measured by DSC with Those Calculated as the Difference $\Delta_{cr}^{l}H_m = \Delta_{cr}^{g}H_m - \Delta_{l}^{g}H_m$ at $T = 298$ K from Transpiration[a]

compound	$\Delta_{cr}^{g}H_m$ [b] at 298.15 K kJ·mol^{-1}	$\Delta_{l}^{g}H_m$ [b] at 298 K kJ·mol^{-1}	$\Delta_{cr}^{l}H_m$ [c] at T_{fus} kJ·mol^{-1}	$\Delta_{cr}^{l}H_m$ [d] at 298 K kJ·mol^{-1}	$\Delta_{cr}^{l}H_m$ [e] at 298 K kJ·mol^{-1}	Δ[f] kJ·mol^{-1}
1	2	3	4	5	6	7
1-aminonaphthalene (I)	88.11 ± 0.40	73.29 ± 0.43	14.49/323.2 K[10]	12.5		
		73.6[13]	15.33/323.2 K[8]	13.4		
			16.18/323 K[14]	14.2	14.9	−0.7
2-aminonaphthalene	93.7[g]	74.6[13]	23.61/386.2[10]	19.1		
	74.1 ± 1.7[9,11]					
II	94.08 ± 0.37	79.57 ± 0.25	16.15[h]/339.8	13.5	14.5	−1.0
III	120.16 ± 0.65		25.5[i]/469.5 K	14.6		
IV		66.92 ± 0.16				
V	94.73 ± 0.80	76.72 ± 0.35	17.6[i]/324 K	16.2	18.0	−1.8
VI	98.55 ± 0.40		19.6[i]/361 K	16.2		

[a] 1-Aminonaphthalene (I); 1,8-diaminonaphthalene (II); 1,5-diaminonaphthalene (III); *N*,*N*-dimethyl-1-aminonaphthalene (IV); 1,8-*N*,*N*,*N*′,*N*′-tetramethyldiaminonaphthalene (V); 1,5-*N*,*N*,*N*′,*N*′-tetramethyldiaminonaphthalene (VI). [b] Results from this work (see Table 1). [c] The enthalpy of fusion $\Delta_{cr}^{l}H_m$ measured by DSC. [d] The enthalpy of fusion $\Delta_{cr}^{l}H_m$ measured by DSC and extrapolated to 298.15 K (see text). [e] The enthalpy of fusion $\Delta_{cr}^{l}H_m$, calculated as the difference $\Delta_{cr}^{g}H_m - \Delta_{l}^{g}H_m$ from Table 1. [f] The difference between columns 5 and 6. [g] Calculated as the sum of columns 3 and 4. [h] The enthalpy of fusion measured in this work using DSC-2, Perkin-Elmer (calibrated with indium). [i] Calculated using the modified[15] Walden's rule: $\Delta_{cr}^{l}H_m(T_{fus}) = 54.4$ (J·K^{-1}mol^{-1})·T_{fus} (K).

methods of measurements are unknown, as well as are errors of measurements and purities of compounds. In spite of this fact, we treated the results from Stull[13] using eqs 2 and 3 and calculated enthalpies of vaporization for the sake of comparison with our results: $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\ \mathrm{K}) = 73.6\ \mathrm{kJ \cdot mol^{-1}}$ for 1-aminonaphthalene and $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\ \mathrm{K}) = 74.6\ \mathrm{kJ \cdot mol^{-1}}$ for 2-aminonaphthalene. These results look quite reasonable, because according our previous findings for 1- and 2 substituted naphthalenes, their enthalpies of vaporization usually differ by only (1 to 2) $\mathrm{kJ \cdot mol^{-1}}$. Direct comparison of vapor pressures reported by Stull[13] with those in this work (Table 1) is not possible because of completely different temperature ranges, but the agreement of vaporization enthalpies $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\ \mathrm{K})$ derived from vapor pressures in both studies is very close (see Table 2). In addition, results from this work together with the vapor pressures reported by Stull[13] led us to claim $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}} = (74.1 \pm 4.0)\ \mathrm{kJ \cdot mol^{-1}}$ for 2-aminonaphthalene measured by Karyakakin et al.[9] as unreliable and instead to suggest the more arguable value $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\ \mathrm{K}) = 93.7\ \mathrm{kJ \cdot mol^{-1}}$ calculated from $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\ \mathrm{K}) = 74.6\ \mathrm{kJ \cdot mol^{-1}}$ for 2-aminonaphthalene derived in this work from results by Stull[13] and the fusion enthalpy for this compound reported by Khetarpal et al.[10] and adjusted to the reference temperature 298.15 K (see Table 2).

A valuable test of consistency of the experimental data on sublimation and vaporization enthalpies measured in this work provides a comparison with a set of experimental values of enthalpies of fusion of the solid aminonaphthalenes (see Table 2). Indeed, in this work, most of the solid aminonaphthalenes were investigated by the method of transference in both ranges, above and below the temperature of fusion and the values $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\ \mathrm{K})$ and $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\ \mathrm{K})$ were derived (see Tables 1 and 2). For each compound studied, comparison (see Table 2) of the enthalpy of fusion, $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}$, calculated as the difference $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}} - \Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (both values referred to $T = 298.15$ K) from Table 1, and the enthalpy of fusion $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}$ measured at T_{fus} (and adjusted to $T = 298.15$ K, see below) demonstrate discrepancies only on the level of (1 to 2) $\mathrm{kJ \cdot mol^{-1}}$ and are acceptable within the boundaries of the experimental uncertainties of the methods used. Hence, the set of vaporization and sublimation enthalpies of aminonaphthalenes given in the Table 1 possess the internal consistency.

The experimental enthalpies of fusion $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}$ are referred to the melting temperature and are recorded in Table 2. Because of the deviations from $T = 298.15$ these observed values of the enthalpies of fusion of aminonaphthalenes had to be corrected to this reference temperature. The corrections were estimated with help of the equation:[5,6]

$$\begin{aligned}\{\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}(T_{\mathrm{fus}}/\mathrm{K}) - \Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}(298.15\ \mathrm{K})\}/(\mathrm{J \cdot mol^{-1}}) = \\ \{(0.75 + 0.15C_p^{\mathrm{cr}})[(T_{\mathrm{fus}}/\mathrm{K}) - 298.15]\} - \\ \{(10.58 + 0.26C_p^{\mathrm{l}})[(T_{\mathrm{fus}}/\mathrm{K}) - 298.15]\} \quad (4)\end{aligned}$$

With these corrections and the measured values of $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}(T_{\mathrm{fus}})$, the standard molar enthalpies of fusion at $T = 298.15$ K, $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}(298.15\ \mathrm{K})$, were calculated (Table 2).

The experimental vapor pressures, enthalpies of sublimation, enthalpies of vaporization, and enthalpies of fusion of aminonaphthalenes fill a gap in our knowledge of the thermochemical data for “proton sponges”. Values of enthalpies of vaporization $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ or sublimation $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$ at the reference temperature 298.15 K are required to obtain gaseous enthalpies of formation $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{g})$ of organic compounds, provided that their enthalpies of formation in condensed phase $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{l\ or\ cr})$ are known. Experimental values for $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{l\ or\ cr})$ of the same series of aminonaphthalenes from combustion calorimetry will be a subject of our forthcoming paper.

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