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Thermochemical Properties of Formamide Revisited: New Experiment and Quantum Mechanical Calculations

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Supporting Information

ABSTRACT: Formamide is one of the key compounds in organic chemistry. Surprisingly, the experimental thermochemical data for this compound are scarce. In this work, the standard molar enthalpy of formation in the gaseous state of formamide $\Delta_f H_m°$(g, 298.15 K) = (−188.6 ± 0.4) kJ·mol^{-1} has been derived from enthalpy of formation $\Delta_f H_m°$(l, 298.15 K) = (−571.4 ± 0.3) kJ·mol^{-1} (measured calorimetrically) and the molar enthalpy of vaporization $\Delta_l^g H_m$ = (62.2 ± 0.3) kJ·mol^{-1} obtained from the vapor pressure measurements. To verify the experimental data, first-principles calculations have been performed using density functional theory (DFT), MPn, W1U, CBS-n, and Gn methods.

1. INTRODUCTION

Formamide is a widespread polar solvent. It is used primarily for manufacturing sulfa drugs and vitamins synthesis and as a softener for paper and fiber.[1] It dissolves many ionic compounds that are insoluble in water. One may expect a sufficient amount of thermodynamic data on such an important compound. Surprisingly, there is a real lack of reliable thermochemical quantities for formamide in the open literature. Indeed, the most popular and gratis NIST database[2] provides only one reference, where enthalpy of formation $\Delta_f H_m°(l) = -251.0$ kJ·mol^{-1} and enthalpy of vaporization $\Delta_l^g H_m = 65.0$ kJ·mol^{-1} of formamide at 298.15 K are cited as the primary data source from Bauder and Gunthard.[3] As a matter of fact, these data were taken from Dow Chemical Co. files which are not readily available. Thus, the origin of the data presented is unclear, and methods of the measurements as well as the errors of measurements and purity of samples are unknown. No experimental determination of the enthalpy of formation of formamide has been found in the open literature (up to August 2011). For this reason, a series of combustion experiments have been performed on a carefully purified sample of formamide, and a new experimental value for enthalpy of formation $\Delta_f H_m°$(l) has been derived from these measurements. These data together with the enthalpy of vaporization $\Delta_l^g H_m$ measured from the transpiration method have been used to calculate the enthalpy of formation of formamide in the gaseous state $\Delta_f H_m°(g) = \Delta_f H_m°(l) + \Delta_l^g H_m$. To verify this value of $\Delta_f H_m°$(g), ab initio calculations using different methods have been performed.

2. EXPERIMENTAL SECTION

2.1. Materials. The liquid samples of formamide (purchased from Acros) having a mass-fraction purity of about 0.995 were purified by repeated distillation in vacuum. Examination of the samples using GC showed no discernible amounts of impurities. The sample was analyzed with a Hewlett-Packard gas chromatograph 5890 Series II equipped with a flame ionization detector and Hewlett-Packard 3390A integrator using carrier gas (nitrogen) flow of 12.1 cm^3·s^{-1} and a capillary column HP-5 (stationary phase cross-linked 5 % PH ME silicone); column length, inside diameter, and film thickness 25 m × 0.32 mm × 0.25 μm. The temperature program of the GC started at T = 298 K, followed by a heating rate of 0.167 K·s^{-1} to T = 523 K.

2.2. Combustion Calorimetry. An isoperibol bomb calorimeter[4] was used for the measurement of the energy of combustion of formamide. From a practical point of view, careful encapsulation of the sample is important in combustion calorimetry of liquids. In the present study, we used commercially available polyethylene bulbs (NeoLab, Heidelberg) of 1 cm^3 volume as the sample container for liquids to reduce the capillary effect and make encapsulation easier. The liquid specimen was transferred to polyethylene bulbs with a syringe. The narrow neck of the container was compressed with special tweezers and was sealed outside the glovebox by heating with hot air. Then, the loaded container was placed in the bomb and burned in oxygen at a pressure of 3.04 MPa. The detailed procedure has been described previously.[5] The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but none was detected. The energy equivalent of the calorimeter ε_{calor} was determined with a standard reference sample of benzoic acid (sample SRM 39j, N.I.S.T.). From nine experiments, ε_{calor} was measured to be (14807.1 ± 0.9) J·K^{-1}.

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Table 1. Results of Combustion Experiments at T = 298.15 K ($p°$ = 0.1 MPa) of Formamide[a]

m(substance)/g[b]	0.574291	0.689951	0.631301	0.58596	0.57101
m'(cotton)/g[b]	0.003408	0.003776	0.003286	0.003691	0.003242
m''(ampule)/g[b]	0.283077	0.33766	0.477202	0.414893	0.389683
ΔT_c/K[c]	1.38594	1.6575	2.04355	1.80944	1.71768
$(\varepsilon_{calor})\cdot(-\Delta T_c)$/J	−20521.68	−24542.82	−30258.98	−26792.62	−25433.93
$(\varepsilon_{cont})\cdot(-\Delta T_c)$/J	−25.93	−32.01	−40.45	−35.07	−33
ΔU_{decomp} HNO_3/J	68.39	80.63	92.58	80.03	78.84
ΔU_{corr}/J[d]	8.12	10	11.84	10.39	9.8
$-m'\cdot\Delta_c u'$/J	57.75	63.98	55.68	62.54	54.94
$-m''\cdot\Delta_c u''$/J	13123.73	15654.26	22123.56	19234.85	18066.09
$\Delta_c u°$(liq)/ (J·g^{-1})	−12693.3	−12705.2	−12697.2	−12696.9	−12709.5

[a] For the definition of the symbols, see ref 5: T_h = 298.15 K; V(bomb) = 0.32 dm^3; p^i(gas) = 3.04 MPa; $m^i(H_2O)$ = 1.00 g. [b] Masses obtained from apparent masses; correction for the water content 448 ppm (Karl Fischer titration) has been applied. [c] $\Delta T_c = T^f - T^i + \Delta T_{corr}$; $(\varepsilon_{cont})\cdot(-\Delta T_c) = (\varepsilon^i_{cont})\cdot(T^i - 298.15\ K) + (\varepsilon^f_{cont})\cdot(298.15\ K - T^f + \Delta T_{corr})$. [d] ΔU_{corr}, the correction to standard states, is the sum of items 81 to 85, 87 to 90, 93, and 94 in ref 5.

Correction for nitric acid formation was based on the titration with 0.1 mol·dm^{-3} NaOH(aq). The atomic weights used were those recommended by the IUPAC Commission.[6] The masses of the sample and auxiliary compounds were reduced to vacuum, taking into consideration their densities (see Table S1, Supporting Information). For converting the energy of the actual bomb process to that of the isothermal process and reducing to standard states, the conventional procedure[4] was applied. Results of the combustion experiments for formamide are summarized in Table 1.

2.3. Vapor Pressure Measurements. Transpiration Method. Vapor pressures and enthalpies of vaporization, $\Delta_l^g H_m$, of formamide were determined using the method of transference in a saturated stream of nitrogen (transpiration method). The method has been described before[5] and has proven to give results in agreement with other established techniques for determining vapor pressures and enthalpies of vaporization of pure substances from the temperature dependence of the vapor pressure. The mass, m_i, of transported compound was determined by GC analysis using the undecane as external standard. The saturation vapor pressure p_i^{sat} at each temperature T_i was calculated from the amount of product collected within a definite 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 $\ln(p_i^{sat})$ 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 according to

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

where R = 8.314472 J·K^{-1}·mol^{-1}; m_i is the mass of the transported compound; M_i is the molar mass of the compound; and V_i is the volume contribution of the substance i to the gaseous phase. V_{N2} is the volume of transporting gas, and T_a is the temperature of the soap bubble meter. V_{N2} was determined from flow rate and time measurements. Experimental results and parameters a and b are listed in Table 2.

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

T[a]	m[b]	$V_{(N2)}$[c]	gas flow	p[d]	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$
K	mg	dm^3	dm^3/h	Pa	Pa	kJ·mol^{-1}
formamide $\Delta_l^g H_m(298.15\ K) = (62.19 \pm 0.28)$ kJ·mol^{-1}						
$\ln(p/Pa) = \frac{265.63}{R} - \frac{73696.25}{R\cdot(T, K)} - \frac{38.6}{R}\ln\left(\frac{T, K}{298.15}\right)$						
303.4	7.95	30.75	4.50	14.3	0.1	61.99
308.2	4.92	13.50	4.50	20.1	−0.6	61.80
313.2	7.47	13.48	2.91	30.5	0.1	61.61
318.2	11.26	13.53	2.62	45.5	1.4	61.42
323.2	8.65	7.49	2.90	63.6	0.5	61.22
328.2	4.38	2.62	2.62	91.5	2.2	61.03
333.2	7.88	3.47	2.60	124.3	−0.6	60.84
338.2	5.31	1.73	2.60	167.4	−5.3	60.64
343.2	8.19	1.95	2.60	229.7	−6.6	60.45
348.2	9.88	1.73	2.60	312.1	−8.1	60.26
353.3	5.86	0.708	2.66	454.3	22.0	60.06
358.2	5.37	0.539	2.16	546.8	−24.7	59.87
363.2	6.34	0.443	1.66	780.3	26.8	59.68
368.1	10.97	0.606	2.60	985.5	5.6	59.49
368.1	10.97	0.606	2.60	985.5	5.6	59.49
373.2	21.01	0.910	2.60	1271.0	−6.5	59.29
376.0	17.42	0.650	2.60	1475.6	2.8	59.18

[a] Temperature of saturation (± 0.1 K). [b] Mass of transferred sample (± 0.0001 g) condensed at T = 243 K. [c] Volume of nitrogen (± 0.001 dm^3) was used to transfer mass m of sample. [d] Vapor pressure at temperature T calculated from m and the residual vapor pressure at the cooling temperature T = 243 K.

The latter was calculated from the linear correlation between $\ln[m/V_{(N2)}]$ against T^{-1} iteratively. Vapor pressures derived from the transpiration method were reliable within (1 to 3) %, and their accuracy was governed by reproducibility of the GC analysis. We have checked experimental and calculation procedure with measurements of vapor pressures of n-alcohols.[7] The uncertainty of the GC analysis of transported mass of the material, δm_i = (1 to 3) %, was the main contributor to the total experimental error of vapor pressure data, δp_i = (1 to 3) %, measured by the transpiration method. To assess the uncertainty of the vaporization enthalpy, the experimental data were approximated with the linear equation $\ln(p_i^{sat}) = f(T^{-1})$ using the

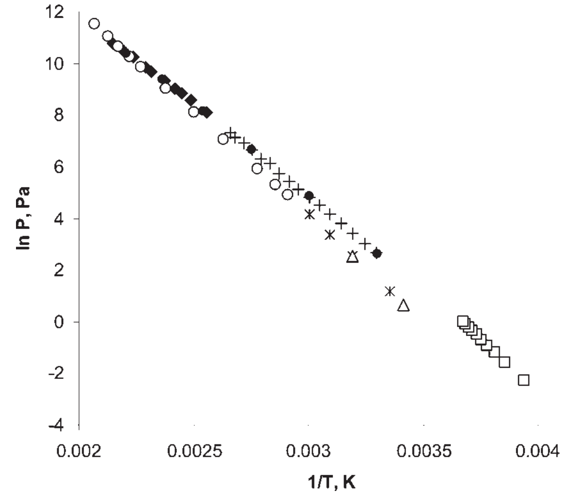

Figure 1. Experimental vapor pressures of formamide: ●, ref 12; ■, ref 9; ○, ref 8; Δ, ref 10; □, ref 13; *, ref 11; ×, this work.

method of least-squares. The uncertainty in the enthalpy of vaporization was assumed to be identical to the average deviation of experimental $\ln(p_i^{\mathrm{sat}})$ values from this linear correlation, and uncertainties in values of $\Delta_l^g C_p$ were not taken into account.

3. RESULTS AND DISCUSSION

3.1. Enthalpy of Formation of Formamide. The mean value for the standard specific energy of combustion $\Delta_c u° = -(12\,700.4 \pm 3.0)\ \mathrm{J \cdot g^{-1}}$ and the molar combustion enthalpy $\Delta_c H_m° = -(571.4 \pm 0.3)\ \mathrm{kJ \cdot mol^{-1}}$ have been obtained from the data listed in Table 1. To derive the molar standard formation enthalpy $\Delta_f H_m°(\mathrm{liq}) = -(250.8 \pm 0.3)\ \mathrm{kJ \cdot mol^{-1}}$ of formamide from the measured combustion enthalpy $\Delta_c H_m°$, the molar enthalpies of formation of $H_2O(l)$, $-(285.830 \pm 0.042)\ \mathrm{kJ \cdot mol^{-1}}$, and $CO_2(g)$, $-(393.51 \pm 0.13)\ \mathrm{kJ \cdot mol^{-1}}$, were taken, as assigned by CODATA.[8] The total uncertainty was calculated according to the guidelines presented by Olofsson.[9] The uncertainty assigned to $\Delta_f H_m°$ is twice the overall standard deviation and includes the uncertainties from calibration, from the combustion energies of the auxiliary materials, and of the enthalpies of formation of the reaction products H_2O and CO_2.

3.2. Enthalpy of Vaporization of Formamide. Although there are several reports of the dependence of vapor pressure with temperature of formamide in the literature,[10−16] most authors did not calculate enthalpy of vaporization at T = 298.15 K from their results. For this reason, our own data and original published experimental $p-T$ results[10−15] were fitted in this work using the following equation[7]

$$R \ln p_i^{\mathrm{sat}} = a + \frac{b}{T} + \Delta_l^g C_p \ln\left(\frac{T}{T_0}\right) \qquad (2)$$

where a and b are adjustable parameters. 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 vaporization enthalpy at temperature T is derived

$$\Delta_l^g H_m(T) = -b + \Delta_l^g C_p \cdot T \qquad (3)$$

where the value of $\Delta_l^g = -38.6\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ has been derived from the experimental[17] isobaric molar heat capacity $C_p^l = 107.6\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ at 298.15 K of the liquid formamide according to the procedure suggested by Chickos and Acree.[18]

Table 3. Compilation of Data on Enthalpies of Vaporization $\Delta_l^g H_m$ of Formamide ($\mathrm{kJ \cdot mol^{-1}}$)

technique[a]	temperature range, K	$\Delta_l^g H_m(T)$	$\Delta_l^g H_m(298\ \mathrm{K})$[b]	ref
E	343.6 to 483.6		69.1	8
E	391.0 to 465.5	54.6	59.5 ± 0.2	9
K	293.1 to 313.1	72.8	73.0	10
K	398.1 to 333.1	70.2	70.8 ± 0.3	11
N/A			65.0	1
N/A	303.1 to 453.1	59.3	62.0 ± 0.7	12
TE+K	251 to 273		62.7 ± 0.7[c]	13
C	298.15		60.1 ± 0.6	14
T	303.4 to 376.0	60.6	**62.2 ± 0.3**[d]	this work

[a] Techniques: E = Ebulliometry; K = mass loss Knudsen method; C = Calvet calorimetry with Knudsen cell; TE+K = combined torsion-effusion method and mass loss Knudsen method; T = transpiration; N/A = not available. [b] Original vapor pressures available in the literature were treated using eqs 2 and 3 to evaluate enthalpy of vaporization at T = 298.15 K. [c] Enthalpy of vaporization derived from the data in ref 13 for the enthalpy of sublimation, $\Delta_{cr}^g H_m$, of formamide (see Supporting Information). [d] Selected in this work for the thermodynamic calculations.

Table 4. Thermochemical Data at T = 298.15 K ($P°$ = 0.1 MPa) for Formamide ($\mathrm{kJ \cdot mol^{-1}}$)

$\Delta_c H_m°$	$\Delta_f H_m°(\mathrm{liq})$	$\Delta_l^g H_m$	$\Delta_f H_m°(\mathrm{g})$
−571.4 ± 0.3	−250.8 ± 0.3	62.2 ± 0.3	−188.6 ± 0.4

Available vapor pressures are presented graphically in Figure 1. Experimental vapor pressures available from the literature were treated using eqs 2 and 3, and results are listed in Table 3. As can be seen from this table, the spread of the enthalpies of vaporization measured indirectly (derived from the temperature dependence of the vapor pressure) by diverse techniques is unexpectedly large and lies between (59.5 and 73) $\mathrm{kJ \cdot mol^{-1}}$. However, the possible uncertainties by Δ_l^g could affect the result of calculation of vaporization enthalpy at the reference temperature by (0.5 to 1) $\mathrm{kJ \cdot mol^{-1}}$ depending on the temperature range of extrapolation.

Only one direct measurement of vaporization enthalpy $\Delta_l^g H_m$(298.15 K) = (60.1 ± 0.6) $\mathrm{kJ \cdot mol^{-1}}$ using the Calvet calorimeter with the Knudsen effusion cell at saturation pressure is available in the literature.[16] The best documented set of vapor pressure measurements was measured by the combined torsion-effusion technique.[15] However, these measurements were performed on the solid sample, and we have recalculated for the $\Delta_l^g H_m$(298.15 K) = (62.7 ± 0.7) $\mathrm{kJ \cdot mol^{-1}}$ using the experimental[17] enthalpy of fusion of formamide (see Supporting Information). Our new result for vaporization enthalpy $\Delta_l^g H_m$(298.15 K) = (62.2 ± 0.3) $\mathrm{kJ \cdot mol^{-1}}$ is in excellent agreement with those from the torsion-effusion technique[15] and the evaluation by DIPPR[14] (Table 3), and we selected this value for further thermodynamic calculations.

3.3. Study of Dimerization of Formamide in the Gaseous Phase. To understand the spread of the enthalpies of vaporization derived from the temperature dependence of the vapor pressure, we decided to study equilibrium of dimerization of formamide in the gaseous phase using ab initio methods. Indeed,

Table 5. Results of Calculation of the Standard Enthalpy of Formation $\Delta_f H_m°(g)$ for Formamide in the Gaseous Phase at 298.15 K ($kJ \cdot mol^{-1}$)

method	$\Delta_f H_m°(g)$	Δ	method	$\Delta_f H_m°(g)$	Δ
MP2(full)/ 6-311++G(3df,3pd)	−229.49	40.89	B3LYP/aug-cc-pV5Z	−190.3	1.7
B3LYP/6-311++(3df,3pd)	−195.4	6.8	MP4SDTQ/6-311++G(3df,3pd)	−183.91	−4.69
G1	−189.8	1.2	CBS-4O	−200.85	12.25
G2	−194.76	6.16	CBS-4M	−200.16	11.56
G2MP2	−196.08	7.48	CBS-Lq	−181.39	−7.21
G3	−191.46	2.86	CBS-Q	−187	−1.6
G3MP2	−185.45	−3.15	CBS-QB3	−184.96	−3.64
G3B3	−187.69	−0.91	CBS-APNO	−188.49	−0.11
G3MP2B3	−181.59	−7.01	W1U	−194.11	5.51
G4	−187.99	−0.61			

it is well established[19−21] that formamide is able to undergo the self-association in the gaseous phase, and maybe this process could affect the vaporization process. Two kinds of dimers, linear and cyclic (see Tables S2 and S3, Supporting Information), are possible according to quantum mechanical calculations.[21] However, the cyclic dimer is predominant in the gaseous phase.[21] The equilibrium constant K of the dimerization (two molecule formamide = dimer) is related to the degree of dimerization α by the following equation (where α is the fraction of the molecules that are H-bonded, $P° = 101.325$ kPa, and P is the total pressure)[22]

$$K = \frac{\alpha(1 - \alpha/2)P°}{2(1 - \alpha)^2 P} \qquad (4)$$

Results from ab initio calculations of the equilibrium constants K for acetic acid (Table S2, Supporting Information) and formamide (Table S3, Supporting Information) are collected in Table S4 (Supporting Information). As can be seen from Table S4 (Supporting Information), the G3(MP2) method is able to calculate the equilibrium constant K for acetic acid (where reliable data are available) in excellent agreement with experiment[23] (column 4). Ab initio calculations of the equilibrium constant K (column 3) and the degree of dimerization α (column 5) for formamide are therefore also likely to be reliable. In contrast to acetic acid, formamide in the gaseous phase predominantly consists of monomeric species; thus, any corrections of the vaporization enthalpies derived indirectly from vapor pressure measurements and listed in Table 3 are not necessary.

3.4. Calculation of the Gaseous Enthalpies of Formation. Values of vaporization enthalpy of formamide, measured in this work (Table 3), can now be used together with the result from our combustion experiments for calculation of the gaseous standard enthalpy of formation, $\Delta_f H_m°(g)$, at 298.15 K. The resulting value of $\Delta_f H_m°(g)$ of formamide is given in the last column in Table 4. Having now well-established experimental data, it was interesting to test some popular first-principles methods[24−27] like B3LYP, MPn, W1U, CBS-n, and Gn to calculate the enthalpy of formation of formamide properly. Standard quantum mechanical calculations were performed with the Gaussian 03 Rev.04 series of programs.[28] We have calculated the enthalpy of formation of formamide using the atomization reaction. Results of calculations are collected in Table 5, and the differences Δ (experimental − calculated) are discussed. It has turned out that noncomposite methods B3LYP and MPn were mostly inaccurate with the differences of (17 to 30) $kJ \cdot mol^{-1}$. In contrast, the most precise time-consuming method W1U was not especially successful for calculation of enthalpy of formation of formamide, which was predicted to be 5.5 $kJ \cdot mol^{-1}$ more positive. The composite methods selected for calculations in this study were able to reproduce the experimental result substantially more accurately with the maximal deviation by 7 $kJ \cdot mol^{-1}$ for the G2(MP2) method (one of the oldest composite methods). The most accurate (but the most time-consuming) method from the Gn family is the G4 method. This method is generally able to predict enthalpies of formation with the average uncertainties of 3.5 $kJ \cdot mol^{-1}$. These deviations were reported[29] from comparison with the G3/05 test set. The enthalpy of formation of formamide calculated by this method is only 0.6 $kJ \cdot mol^{-1}$ less negative. Surprisingly, two other methods from Gn families G3B3 and G4 were more accurate for calculation of enthalpy of formation of formamide with the deviations of (0.9 and 0.6) $kJ \cdot mol^{-1}$ (see Table 4). Perhaps, the reason for results discrepancy among Gn methods could be due to differences in the first two steps by these composite methods. As a matter of fact, the geometry optimization and frequency calculations by G3B3 and G4 methods are performed with the B3LYP methods. In contrast, the same two steps by G3 are performed by a simple HF procedure. In the family of the extrapolation methods CBS-n the best result was obtained with the most powerful CBS-APNO method. The difference with the experiment is only 0.1 $kJ \cdot mol^{-1}$. The quantum chemical results for formamide obtained in this work are part of a broad investigation of thermochemical properties of molecular and ionic compounds including the experimental and computational results. These studies help to localize suitable methods for prediction of enthalpies of formation for the aliphatic amides of the larger size.

4. CONCLUSIONS

The purpose of this work was to establish a consistent set of experimental and calculated thermochemical quantities for formamide. New experimental results from combustion calorimetry and vapor pressure measurements have strongly supported earlier data from Dow Chemical Co. The enthalpy of formation of formamide in the gaseous state at 298.15 K derived from the CBS-APNO and G4 methods is in very good agreement with the experimental value. These methods could be basically recommended for calculations of the thermodynamic properties of the chemical family of amides.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Auxiliary quantities of the materials used in the present study (TABLE S1); G3(MP2) calculations of the equilibrium constant of the dimerization of acetic acid at 298.15 K, gas phase (Tables S2); G3(MP2) calculations of the equilibrium constant of the dimerization of formamide at 298.15 K, gas phase (Table S3); G3(MP2) calculations of the equilibrium constant of dimerization and the degree of dimerization at 298.15 K in the gas phase (Table S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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