# Thermodynamic Analysis of Strain in the Five-Membered Oxygen and Nitrogen Heterocyclic Compounds

Sergey P. Verevkin and Vladimir N. Emel'yanenko*

Department of Physical Chemistry, University of Rostock, Dr-Lorenz-Weg 1, D-18059, Rostock, Germany

Andrey A. Pimerzin and Elena E. Vishnevskaya

Chemical Department, Samara State Technical University, Molodogvardeyskaya 244, Samara 443100, Russia

Ⓢ Supporting Information

**ABSTRACT:** Cyclopentane is conventionally strained. Replacement of a carbon atom by a heteroatom obviously impacts angular strain in the five-membered ring compounds. Changes of strains in the five-membered cycles are also caused by a double bond or attached benzene rings. We studied the thermochemical properties of Indane, 2,3-dihydrobenzofuran, indoline, $N$-methyl-indoline, carbazole, and $N$-ethyl-carbazole to obtain a better quantitative understanding of the energetics associated with these compounds containing five-membered ring units. We used combustion calorimetry, transpiration method, and high-level first-principles calculations to derive gaseous enthalpies of formation of the five-membered heterocyclic compounds. Our new values together with the selected values for parent heterocyclic compounds, available from the literature, were used for calculation of the strain energies $H_S$ of five-membered C-, N-, and O-containing cycles. Quantitative analysis of the resulting stabilization or destabilization of a molecule due to interaction of benzene rings with the heteroatom has been performed.
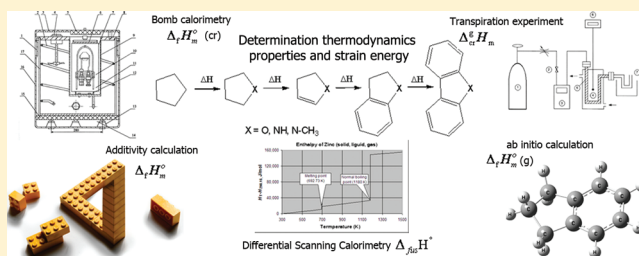
## 1. INTRODUCTION

Enthalpies of formation are needed for determination of reaction and process energies, for development of elementary reaction mechanisms, for evaluation of reaction pathways, and for calculation of chemical equilibrium constants. One of the aims of the experimental work in thermochemistry has been to build a framework of experimental data from which one may study the relation between energy content and molecular structure and calculate values for the enthalpies of formation of many hundreds of compounds without need for further experimental measurements. Heterocycles are among the important groups of compounds for which experimental data suitable for a basic framework of this kind are needed. The significance of heterocyclic compounds and their derivatives as environmental pollutants has led to attempts to derive their thermodynamic properties in order to examine their general stability and conditions of formation and assess their possible concentration as a potential pollutant. Recent experimental studies by Pilcher et al.,[1,2] Ribeiro da Silva et al.,[3,4] Steele and Chirico,[5−9] and Matos et al.[10−12] on N- and O-containing heterocycles, investigations by Jimenez and Roux on carbazoles[13] and imides,[14] as well as results of Sabbah on dibenzofuran[15] and acridine[16] have contributed to extension of our knowledge of the thermochemical properties of heterocyclic compounds. The present paper follows this course and describes a systematic investigation of the thermochemistry of O- and N-heterocyclic five-membered rings attached at first to one and then to two benzene rings (see Figure 1). In collecting experimental data from the literature we noticed that the vapor pressures of the low volatile compounds of interest (see Table 1) were measured at elevated temperatures (usually close to the boiling point). Enthalpies of vaporization, derived from such data using the Clausius−Clapeyron equation, could be affected by extrapolation to the reference temperature 298 K. One of the advantages of the transpiration method applied in this work is the ability to study the vapor pressures of very low volatile compounds at ambient temperatures, and very often the desired reference temperature could be included in the experimental temperature range. For this reason we focused our experimental efforts on determination of reliable vaporization (or sublimation) enthalpies. Having collected a set of reliable experimental thermodynamic properties for five-membered compounds (Tables 1−4) we used the high-level composite method G3MP2 to test their consistency. By combining new experimental data with literature data it was possible to evaluate the changes of strain energy from cyclopentane ring to Indane and fluorene and to compare these strains with the corresponding changes in their O- and N- heterocyclic analogues.
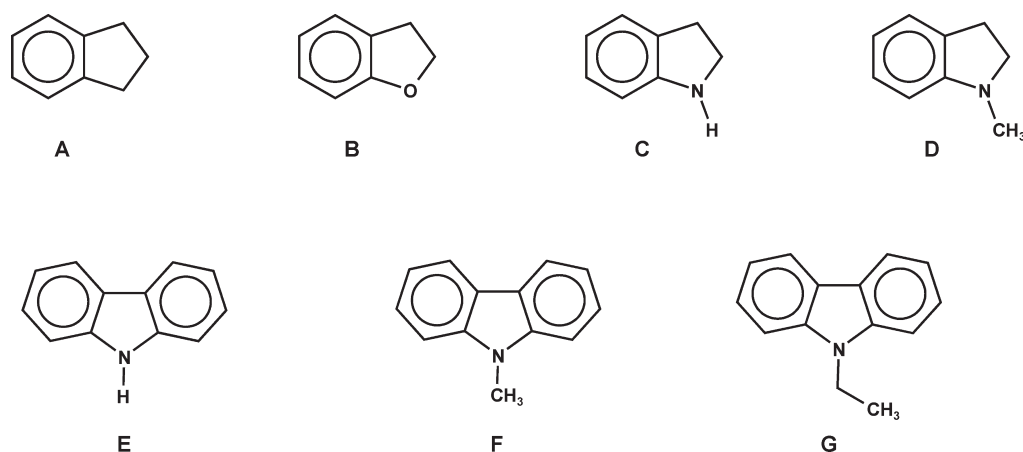
**Figure 1.** Structures of investigated compounds: Indane (A), 2,3-dihydrobenzofuran (B), indoline (C), N-methyl-indoline (D), cabazole (E), N-methyl-carbazole (F), and N-ethyl-carbazole (G).

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** All compounds were purchased from Aldrich or Acros Ltd. Glc analyses of the as-purchased samples gave an average mass fraction of 0.99, in agreement with specifications. Liquid compounds were fractionally distilled under flowing dry $N_2$, after being dried with molecular sieves (0.4 nm). Solid compounds were purified by repeated crystallization from petroleum ether or ethanol and then finally sublimed under reduced pressure to remove any traces of solvent. Determination of purity was carried out by glc. No impurities ($\geq 0.01$ mass percent) could be detected in samples used in this study. For all solid compounds, the mole fraction 0.9998 was additionally established by dsc measurements of the melting process.[17] To avoid traces of water in the liquid samples for combustion experiments, the purified samples were dried over molecular sieves and distilled once more prior to combustion. The samples were stored cold in the dark either at reduced pressure or in a nitrogen atmosphere.

**2.2. Transpiration Method.** Vapor pressures, enthalpies of sublimation, $\Delta_{cr}^{g}H_m$, and enthalpies of vaporization, $\Delta_l^{g}H_m$, of the five-membered compounds were determined using the method of transpiration in a saturated stream of nitrogen. The method has been described in detail before[18,19] and was proven to give results in agreement with other established techniques. The temperature dependence of the vapor pressures was used to determine the enthalpies of sublimation of the pure substances. A sample of approximately 0.5 g of the sample was mixed with glass beads and placed in a thermostatted U-tube of length 40 cm and diameter 0.5 cm. Preheated nitrogen stream was passed through the U-tube at constant temperature ($\pm 0.1$ K). The flow rate of the nitrogen stream was measured using a soap film bubble flow meter ($\pm 0.2-0.3\%$) and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. The material transported was condensed in a cold trap. The amount of condensed product was determined using GC equipped with a flame ionization detector and capillary column HP-5 or SE-30. This amount was determined by GC analysis using an external standard (hydrocarbon $n\text{-}C_nH_{2n+2}$). The saturated vapor pressure $p_i^{sat}$ at each temperature $T_i$ was calculated from the amount of product collected within a definite period of time. Assuming that Dalton's law of partial pressures

when applied to the nitrogen stream saturated with the substance $i$ of interest is valid, values of $p_i^{sat}$ were calculated

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

where $R = 8.31447 \text{ J·K}^{-1}\text{·mol}^{-1}$, $m_i$ is the mass of the transported compound, $M_i$ is the molar mass of the compound, and $V_i$ is its volume contribution to the gas phase. $V_{N2}$ is the volume of transporting gas, and $T_a$ is the temperature of the soap film bubble flow meter. The volume of transporting gas $V_{N2}$ was determined from the flow rate and time measurements. The following equation

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

was fitted to the experimental $p,T$ data using $a$ and $b$ as adjustable parameters. $T_0$ appearing in eq 2 is an arbitrarily chosen reference temperature (which in this case is 298 K). Consequently, from eq 3 the expression for the enthalpy of sublimation at temperature $T$ is

$$\Delta_{cr}^{g}H_m(T) = -b + \Delta_{cr}^{g} C_p T \quad (3)$$

Values of $\Delta_{cr}^{g} C_p$ have been derived from the experimental isobaric molar heat capacities of the solid compounds, $C_p^{cr}$, calculated according to the procedure developed by Chickos.[20,21] Equations 1−3 are also valid for the study of the liquid samples. For this case the enthalpy of vaporization is derived from eq 3 by using appropriate values of $C_p^{l}$ and $\Delta_l^{g} C_p$. Experimental results and parameters $a$ and $b$ are listed in Table 2. We checked the experimental and calculation procedures with measurements of vapor pressures of $n$-alcohols.[19] It turned out that vapor pressures derived from the transpiration method were reliable within 1−3%, and their accuracy was governed by the reproducibility of the GC analysis. In order to assess the uncertainty of the vaporization enthalpy, the experimental data were approximated with the linear equation $\ln(p_i^{sat}) = f(T^{-1})$ using the method of least squares. The uncertainty in the enthalpy of sublimation was assumed to be identical with the deviation of experimental $\ln(p_i^{sat})$ values from this linear correlation. Experimental results are presented in Table 2.

**Table 1. Compilation of Data on Enthalpies of Vaporization $\Delta_l^g H_m$ and Sublimation $\Delta_{cr}^g H_m$ Enthalpies of the 5-Membered Compounds under Study**

| compounds | technique[a] | T range, K | $C_p^l$ or $C_p^{cr}$ ($\Delta_l^g C_p$ or $\Delta_{cr}^g C_p$),[b] J·mol$^{-1}$·K$^{-1}$ | $\Delta_l^g H_m$ or $\Delta_{cr}^g H_m$ ($T_{av}$), kJ·mol$^{-1}$ | $\Delta_l^g H_m$ or $\Delta_{cr}^g H_m$ (298.15K),[c] kJ·mol$^{-1}$ | ref |
|---|---|---|---|---|---|---|
| Indane (l), 496-11-7 | E | 355.0−482.7 | 190.3 [30] | 43.1 | 49.9 ± 0.1 | 54 |
| | C | 381.7−451.0 | (−59.6) | 43.0 | 49.9 ± 0.2 | 55 |
| | E | 374.3−465.6 | | 42.4 | 49.4 ± 1.2 | 56 |
| | T | 284.0−338.2 | | 48.4 | **49.0 ± 0.2** | this work |
| indoline (l), 496-15-1 | C | 329.1 | 232.6 | 65.6 | 61.9 ± 1.7 | 35 |
| | T | 280.6−338.3 | (−71.1) | 60.2 | **60.9 ± 0.2** | this work |
| N-methyl-indoline (l), 824-21-5 | T | 295.6−338.2 | 238.5 (−72.6) | 62.9 | **64.2 ± 0.4** | this work |
| 2,3-dihydro-benzofurane (liq), 496-16-2 | E | | 188.6 [33] | | 53.3 ± 0.1 | 33 |
| | T | 278.7−333.3 | (−59.6) | 52.7 | **53.2 ± 0.2** | this work |
| carbazole (cr), 86-74-8 | N/A | | 190.8[57] | | 84.5 ± 0.8 | 58 |
| | S | 360−370 | (−29.4) | 108.8 | 110.8 | 59 |
| | C | 353.15 | | 96.1 | 97.7 ± 0.2 | 36 |
| | K | 346.6−364.0 | | 101.4 | 103.1 ± 1.37 | 37 |
| | T | 348.0−382.9 | | 102.1 | **104.3 ± 0.5** | this work |
| carbazole (liq) | S | 522.5−642.3 | 286.6 | 63.1 | **87.3 ± 0.1** | 60 |
| | S | 525.8−626.6 | (−85.1) | 63.9 | 87.8 ± 0.2 | 61 |
| N-methyl-carbazole (cr) | K | 312.8−332.6 | 217.8[65] (−33.4) | 94.9 | **95.8 ± 0.3** | 37 |
| N-methyl-carbazole (liq), 1484-12-4 | E | 317.2−470.6 | 292.5 (−86.6) | 72.1 | **82.6 ± 0.5** | 62 |
| | GC | | | | 79.4 ± 3.2 | 63 |
| N-ethyl-carbazole (cr), 86-28-2 | K | 310.0−328.8 | 238.2 [37] | 98.3 | 99.1 ± 0.2 | 37 |
| | T | 313.3−340.9 | (−36.5) | 96.0 | **97.1 ± 1.0** | this work |
| N-ethyl-carbazole (l) | T | 347.8−373.8 | 293.8 | 74.8 | 80.2 ± 1.01.5 | 64 |
| | T | 344.2−383.2 | (−87.0) | 78.3 | **83.9 ± 0.5** | this work |

[a] Techniques: E = ebulliometry; S = static method; C = calorimetry; T = transpiration; K = Knudsen-effusion method; GC, gas−liquid chromatographic correlation method. [b] Values of $\Delta_l^g C_p$ have been derived from the isobaric molar heat capacity of the liquid esters $C_p^l$ according to a procedure developed by Chickos and Acree.[20,21] [c] Vapor pressure data available in the literature were treated using eqs 2 and 3 in order to evaluate the enthalpy of vaporization at T = 298 K in the same way as our own results in Table 1.

**2.3. Combustion Calorimetry.** For measurements of the enthalpies of combustion of 2,3-dihydro-benzofuran and indoline an isoperibolic calorimeter with a static bomb and a stirred water bath was used. The samples were placed (under an inert atmosphere in a glovebox) in polythene capsules and burned in oxygen at 3.04 MPa pressure. The detailed procedure has been described previously.[22,23] The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but neither was detected. The energy equivalent of the calorimeter $\varepsilon_{calor}$ was determined with a standard reference sample of benzoic acid (sample SRM 39j, NIST). The working procedure has been tested with combustion experiments on two reference materials, nicotinic acid and 3-methoxy-benzoic acid, successfully. For reduction of the data to standard conditions, conventional procedures[24] were used. The densities of the liquid compounds were taken from the Aldrich catalog. Corrections for nitric acid formation were based on titration with 0.1 mol·dm$^{-3}$ NaOH (aq). We used the value −59.7 kJ·mol$^{-1}$ for the molar energy of formation of 0.1 mol·dm$^3$ HNO$_3$ from N$_2$, O$_2$, and H$_2$O (l).[25]

**2.4. Differential Scanning Calorimetry.** The melting temperature and enthalpy of fusion of N-ethyl-carbazole were determined with a Perkin-Elmer DSC-2C. The temperature scale of the DSC was calibrated by measuring the melting temperatures of the recommended high-purity standards: benzoic acid, tin, and indium.[17] The power scale was calibrated using sapphire as a standard material.

**2.5. Computations.** Standard first-principles molecular orbital calculations were performed with the Gaussian 03 Rev.04 series of programs.[27] Energies were obtained at the G3MP2 level of theory. G3 theory is a procedure for calculating energies of molecules containing atoms of the first and second row of the periodic table based on ab initio molecular orbital theory. A modification of G3 theory that uses reduced orders of Moller−Plesset perturbation theory is G3(MP2) theory.[28] This method saves considerable computational time compared to G3 theory with some loss in accuracy but is much more accurate that G2MP2 theory. For all the species included in this study, full geometry optimizations were carried out at the HF/6-31G(d)

**Table 2. Vapor Pressures, $p$, Vaporization Enthalpy, $\Delta_l^g H_m$, and Sublimation Enthalpy, $\Delta_{cr}^g H_m$, Obtained by the Transpiration Method**

| $T,^a$ K | $m,^b$ mg | $V_{(N2)},^c$ dm$^3$ | gas flow, dm$^3$/h | $p,^d$ Pa | $(p_{exp} - p_{calcd})$, Pa | $\Delta_l^g H_m$ or $\Delta_{cr}^g H_m$, kJ·mol$^{-1}$ |
|---|---|---|---|---|---|---|

Indane; $\Delta_l^g H_m$ (298.15 K) = (49.01 ± 0.20) kJ·mol$^{-1}$,

$$\ln(p/\text{Pa}) = \frac{266.85}{R} - \frac{66\,775.57}{R(T,\text{K})} - \frac{59.6}{R}\ln\left(\frac{T,\text{K}}{298.15}\right)$$

| $T,^a$ K | $m,^b$ mg | $V_{(N2)},^c$ dm$^3$ | gas flow, dm$^3$/h | $p,^d$ Pa | $(p_{exp} - p_{calcd})$, Pa | $\Delta_l^g H_m$ or $\Delta_{cr}^g H_m$, kJ·mol$^{-1}$ |
|---|---|---|---|---|---|---|
| 284.0 | 1.28 | 0.424 | 1.02 | 65.0 | 0.9 | 49.85 |
| 285.7 | 5.98 | 2.040 | 2.45 | 72.2 | −0.4 | 49.75 |
| 286.8 | 1.61 | 0.438 | 1.05 | 78.8 | 0.1 | 49.69 |
| 287.7 | 4.83 | 1.412 | 1.88 | 81.8 | −2.3 | 49.63 |
| 288.5 | 1.27 | 0.298 | 1.05 | 90.6 | 1.6 | 49.58 |
| 290.7 | 4.65 | 1.088 | 1.09 | 102.1 | −2.0 | 49.45 |
| 291.4 | 1.39 | 0.260 | 1.04 | 111.8 | 2.4 | 49.41 |
| 294.4 | 4.59 | 0.815 | 1.09 | 134.2 | −0.4 | 49.23 |
| 296.6 | 2.07 | 0.285 | 1.01 | 153.6 | −2.6 | 49.10 |
| 298.5 | 4.74 | 0.634 | 1.09 | 176.8 | −0.4 | 48.99 |
| 299.7 | 3.77 | 0.414 | 0.99 | 191.4 | −0.4 | 48.92 |
| 301.6 | 5.02 | 0.551 | 1.10 | 213.5 | −3.6 | 48.80 |
| 304.6 | 4.31 | 0.345 | 1.04 | 262.2 | −0.6 | 48.62 |
| 305.6 | 4.08 | 0.351 | 1.11 | 277.9 | −2.0 | 48.56 |
| 309.4 | 4.42 | 0.261 | 1.04 | 354.2 | 0.4 | 48.34 |
| 309.6 | 4.93 | 0.328 | 1.09 | 352.0 | −6.1 | 48.33 |
| 313.2 | 5.96 | 0.312 | 1.10 | 437.9 | −6.2 | 48.11 |
| 313.5 | 6.41 | 0.293 | 1.03 | 457.6 | 5.5 | 48.09 |
| 314.0 | 5.87 | 0.256 | 1.02 | 479.7 | 14.2 | 48.06 |
| 314.4 | 6.65 | 0.294 | 1.04 | 472.2 | −4.3 | 48.04 |
| 316.3 | 7.62 | 0.330 | 1.09 | 520.3 | −11.9 | 47.93 |
| 318.3 | 7.88 | 0.262 | 1.05 | 626.6 | 30.0 | 47.81 |
| 318.7 | 12.05 | 0.450 | 1.08 | 607.1 | −3.2 | 47.78 |
| 319.3 | 4.70 | 0.150 | 1.00 | 653.8 | 22.4 | 47.75 |
| 320.1 | 8.35 | 0.256 | 1.02 | 682.0 | 21.6 | 47.70 |
| 321.2 | 9.68 | 0.308 | 1.09 | 695.8 | −6.4 | 47.64 |
| 323.3 | 5.99 | 0.158 | 1.05 | 793.6 | 5.3 | 47.51 |
| 323.7 | 12.90 | 0.347 | 1.10 | 811.0 | 5.3 | 47.49 |
| 325.3 | 10.69 | 0.271 | 1.08 | 869.4 | −9.3 | 47.39 |
| 326.4 | 11.79 | 0.258 | 1.03 | 953.2 | 21.0 | 47.33 |
| 328.2 | 13.86 | 0.288 | 1.08 | 1046.8 | 21.2 | 47.22 |
| 328.3 | 12.94 | 0.263 | 1.05 | 1024.3 | −6.7 | 47.21 |
| 331.2 | 27.15 | 0.458 | 1.72 | 1236.9 | 37.6 | 47.04 |
| 333.2 | 17.34 | 0.280 | 1.05 | 1291.3 | −37.4 | 46.92 |
| 333.3 | 16.80 | 0.262 | 1.05 | 1331.0 | −4.5 | 46.91 |
| 337.5 | 32.69 | 0.429 | 1.72 | 1588.3 | −59.6 | 46.66 |
| 338.2 | 18.45 | 0.233 | 1.00 | 1648.0 | −57.5 | 46.62 |

2,3-dihydrobenzofuran; $\Delta_l^g H_m$ (298.15 K) = (53.23 ± 0.22) kJ·mol$^{-1}$,

$$\ln(p/\text{Pa}) = \frac{274.58}{R} - \frac{71\,002.02}{R(T,\text{K})} - \frac{59.6}{R}\ln\left(\frac{T,\text{K}}{298.15}\right)$$

| $T,^a$ K | $m,^b$ mg | $V_{(N2)},^c$ dm$^3$ | gas flow, dm$^3$/h | $p,^d$ Pa | $(p_{exp} - p_{calcd})$, Pa | $\Delta_l^g H_m$ or $\Delta_{cr}^g H_m$, kJ·mol$^{-1}$ |
|---|---|---|---|---|---|---|
| 278.7 | 1.52 | 1.85 | 2.10 | 17.3 | −0.2 | 54.39 |
| 283.5 | 1.68 | 1.36 | 2.10 | 25.7 | −0.3 | 54.11 |
| 288.6 | 1.98 | 1.09 | 2.10 | 38.0 | −1.1 | 53.80 |
| 290.5 | 2.92 | 1.32 | 1.14 | 45.6 | 0.4 | 53.69 |
| 293.4 | 1.88 | 0.666 | 2.10 | 58.5 | 2.2 | 53.52 |
| 294.5 | 5.57 | 1.88 | 1.61 | 61.0 | 0.0 | 53.45 |

## Table 2. Continued

| $T,^a$ K | $m,^b$ mg | $V_{(N2)},^c$ dm$^3$ | gas flow, dm$^3$/h | $p,^d$ Pa | $(p_{exp} - p_{calcd})$, Pa | $\Delta_l^g H_m$ or $\Delta_{cr}^g H_m$, kJ·mol$^{-1}$ |
|---|---|---|---|---|---|---|
| 298.3 | 1.91 | 0.489 | 2.10 | 80.4 | −0.3 | 53.23 |
| 298.7 | 5.61 | 1.36 | 1.95 | 84.5 | 1.5 | 53.20 |
| 301.7 | 5.72 | 1.14 | 1.96 | 102.5 | −0.1 | 53.02 |
| 303.3 | 1.91 | 0.351 | 2.10 | 111.9 | −2.8 | 52.93 |
| 304.6 | 6.10 | 0.976 | 1.95 | 128.0 | 2.5 | 52.85 |
| 307.6 | 7.35 | 0.958 | 1.92 | 157.0 | 3.2 | 52.67 |
| 308.4 | 1.92 | 0.246 | 2.10 | 160.2 | −2.0 | 52.62 |
| 311.4 | 6.64 | 0.700 | 1.14 | 193.9 | −3.7 | 52.45 |
| 313.5 | 1.61 | 0.139 | 2.10 | 237.9 | 11.6 | 52.32 |
| 313.6 | 8.99 | 0.804 | 1.93 | 228.3 | 0.6 | 52.31 |
| 313.6 | 10.38 | 0.932 | 1.36 | 226.7 | −1.1 | 52.31 |
| 314.3 | 9.57 | 0.852 | 1.70 | 231.6 | −6.5 | 52.27 |
| 316.3 | 9.31 | 0.691 | 1.18 | 274.4 | 4.2 | 52.15 |
| 316.8 | 9.04 | 0.655 | 1.57 | 281.7 | 2.8 | 52.12 |
| 318.3 | 7.04 | 0.468 | 1.12 | 307.4 | 1.3 | 52.03 |
| 318.8 | 7.65 | 0.500 | 1.20 | 311.4 | −4.2 | 52.00 |
| 319.3 | 8.25 | 0.506 | 1.21 | 332.8 | 7.3 | 51.97 |
| 321.4 | 14.06 | 0.795 | 1.70 | 364.5 | −5.4 | 51.85 |
| 323.3 | 8.81 | 0.433 | 1.30 | 414.5 | 0.0 | 51.74 |
| 323.4 | 8.31 | 0.420 | 1.20 | 402.9 | −14.1 | 51.73 |
| 325.4 | 14.10 | 0.628 | 1.35 | 462.4 | −6.8 | 51.61 |
| 327.8 | 10.53 | 0.403 | 1.21 | 532.5 | −7.0 | 51.47 |
| 328.3 | 10.94 | 0.398 | 1.14 | 559.9 | 4.6 | 51.44 |
| 329.3 | 12.09 | 0.426 | 1.28 | 584.5 | −3.5 | 51.38 |
| 333.3 | 13.56 | 0.378 | 1.16 | 730.4 | −5.8 | 51.14 |
| 333.3 | 12.30 | 0.333 | 1.21 | 752.4 | 16.3 | 51.14 |

indoline; $\Delta_l^g H_m$ (298.15 K) = (60.94 ± 0.21) kJ·mol$^{-1}$,

$$\ln(p/\text{Pa}) = \frac{295.85}{R} - \frac{82\,133.65}{R(T, \text{K})} - \frac{71.1}{R} \ln\left(\frac{T, \text{K}}{298.15}\right)$$

| | | | | | | |
|---|---|---|---|---|---|---|
| 280.6 | 1.16 | 9.82 | 5.36 | 2.49 | 0.05 | 62.19 |
| 283.8 | 1.20 | 7.50 | 4.50 | 3.34 | 0.05 | 61.96 |
| 285.5 | 0.96 | 5.16 | 1.91 | 3.88 | 0.03 | 61.84 |
| 288.5 | 1.53 | 6.21 | 3.72 | 5.13 | 0.08 | 61.62 |
| 291.8 | 1.63 | 5.06 | 1.91 | 6.65 | −0.10 | 61.39 |
| 293.6 | 1.27 | 3.39 | 2.54 | 7.77 | −0.11 | 61.26 |
| 296.6 | 1.22 | 2.54 | 2.54 | 9.91 | −0.24 | 61.05 |
| 298.4 | 1.80 | 3.15 | 1.91 | 11.77 | −0.02 | 60.92 |
| 300.6 | 1.13 | 1.68 | 2.52 | 13.90 | −0.20 | 60.76 |
| 303.4 | 1.11 | 1.28 | 1.91 | 17.90 | 0.26 | 60.57 |
| 305.4 | 1.55 | 1.48 | 2.54 | 21.60 | 0.96 | 60.42 |
| 308.3 | 1.43 | 1.16 | 1.98 | 25.61 | −0.21 | 60.22 |
| 308.9 | 2.38 | 1.93 | 1.91 | 25.35 | −1.67 | 60.17 |
| 313.8 | 3.28 | 1.78 | 1.91 | 37.94 | −0.98 | 59.83 |
| 315.3 | 2.58 | 1.23 | 2.54 | 43.29 | −0.11 | 59.72 |
| 318.6 | 1.69 | 0.630 | 1.91 | 55.15 | 0.22 | 59.48 |
| 320.3 | 2.07 | 0.685 | 2.06 | 62.37 | 0.49 | 59.36 |
| 323.6 | 1.86 | 0.497 | 1.91 | 77.08 | −0.56 | 59.13 |
| 325.3 | 2.76 | 0.659 | 1.98 | 86.42 | −0.66 | 59.01 |
| 328.3 | 2.41 | 0.456 | 1.30 | 108.7 | 2.4 | 58.80 |
| 328.6 | 3.25 | 0.630 | 1.91 | 106.1 | −2.2 | 58.77 |
| 333.3 | 3.45 | 0.469 | 1.41 | 151.4 | 4.7 | 58.44 |
| 335.3 | 2.99 | 0.363 | 1.09 | 169.7 | 3.4 | 58.30 |

## Table 2. Continued

| $T$,$^a$ K | $m$,$^b$ mg | $V_{(N2)}$,$^c$ dm$^3$ | gas flow, dm$^3$/h | $p$,$^d$ Pa | $(p_{exp} - p_{calcd})$, Pa | $\Delta_l^g H_m$ or $\Delta_{cr}^g H_m$, kJ·mol$^{-1}$ |
|---|---|---|---|---|---|---|
| 338.3 | 2.81 | 0.291 | 1.09 | 199.05 | −1.08 | 58.08 |

*N*-methyl-indoline; $\Delta_l^g H_m$ (298.15 K) = (64.16 ± 0.43) kJ·mol$^{-1}$,

$$\ln(p/\text{Pa}) = \frac{301.30}{R} - \frac{85\,805.13}{R(T,\text{K})} - \frac{72.6}{R}\ln\left(\frac{T,\text{K}}{298.15}\right)$$

| | | | | | | |
|---|---|---|---|---|---|---|
| 295.6 | 0.81 | 3.73 | 3.18 | 4.01 | −0.03 | 64.35 |
| 298.6 | 0.85 | 3.11 | 3.98 | 5.07 | −0.18 | 64.13 |
| 298.6 | 0.93 | 3.28 | 3.18 | 5.27 | 0.02 | 64.13 |
| 300.6 | 0.98 | 2.90 | 3.00 | 6.25 | 0.01 | 63.99 |
| 303.4 | 0.92 | 2.10 | 3.15 | 8.14 | 0.23 | 63.78 |
| 305.4 | 1.16 | 2.35 | 3.00 | 9.12 | −0.20 | 63.64 |
| 307.8 | 1.02 | 1.57 | 3.15 | 11.97 | 0.64 | 63.46 |
| 308.2 | 0.90 | 1.41 | 2.41 | 11.84 | 0.14 | 63.43 |
| 310.0 | 0.69 | 0.941 | 2.09 | 13.50 | −0.01 | 63.30 |
| 313.4 | 1.02 | 1.050 | 3.15 | 17.98 | 0.35 | 63.06 |
| 318.3 | 1.10 | 0.804 | 2.41 | 25.37 | −0.19 | 62.70 |
| 318.3 | 1.06 | 0.787 | 3.15 | 24.83 | −0.74 | 62.70 |
| 323.4 | 1.22 | 0.625 | 2.50 | 36.12 | −0.98 | 62.33 |
| 328.2 | 1.47 | 0.522 | 2.09 | 52.07 | 0.04 | 61.98 |
| 333.2 | 1.10 | 0.283 | 1.13 | 72.02 | −1.08 | 61.62 |
| 338.2 | 1.43 | 0.255 | 1.02 | 104.0 | 2.5 | 61.26 |

carbazole; $\Delta_{cr}^g H_m$ (298.15 K) = (104.3 ± 0.46) kJ·mol$^{-1}$

$$\ln(p/\text{Pa}) = \frac{307.13}{R} - \frac{112\,797.59}{R\cdot(T,\text{K})} - \frac{29.4}{R}\ln\left(\frac{T,\text{K}}{298.15}\right)$$

| | | | | | | |
|---|---|---|---|---|---|---|
| 348.0 | 0.31 | 63.54 | 6.29 | 0.072 | 0.00 | 102.57 |
| 349.1 | 0.48 | 85.17 | 6.39 | 0.083 | 0.00 | 102.54 |
| 353.1 | 0.36 | 41.84 | 7.05 | 0.13 | 0.00 | 102.42 |
| 353.2 | 0.35 | 41.43 | 3.60 | 0.13 | 0.00 | 102.41 |
| 354.2 | 0.83 | 84.58 | 6.06 | 0.14 | 0.01 | 102.39 |
| 356.1 | 0.32 | 27.74 | 6.35 | 0.17 | 0.01 | 102.33 |
| 359.1 | 0.38 | 25.34 | 6.39 | 0.22 | 0.00 | 102.24 |
| 362.1 | 0.35 | 17.55 | 6.30 | 0.30 | 0.00 | 102.15 |
| 365.2 | 0.43 | 16.46 | 6.02 | 0.38 | −0.01 | 102.06 |
| 367.1 | 0.41 | 12.63 | 6.48 | 0.47 | 0.00 | 102.01 |
| 370.1 | 0.35 | 8.70 | 6.26 | 0.60 | −0.02 | 101.92 |
| 373.0 | 0.51 | 9.45 | 6.23 | 0.80 | 0.00 | 101.83 |
| 376.2 | 0.58 | 8.03 | 6.26 | 1.06 | 0.01 | 101.74 |
| 379.0 | 0.42 | 4.73 | 6.30 | 1.32 | −0.02 | 101.66 |
| 379.1 | 0.67 | 7.26 | 6.22 | 1.37 | 0.02 | 101.65 |
| 381.0 | 0.45 | 4.16 | 6.23 | 1.58 | −0.01 | 101.60 |
| 382.8 | 0.76 | 6.02 | 6.23 | 1.86 | 0.02 | 101.54 |
| 382.9 | 0.70 | 5.55 | 6.28 | 1.86 | 0.00 | 101.54 |

*N*-ethyl-carbazole; $\Delta_l^g H_m$ (298.15 K) = (83.90 ± 0.47) kJ·mol$^{-1}$,

$$\ln(p/\text{Pa}) = \frac{336.33}{R} - \frac{109\,843.93}{R(T,\text{K})} - \frac{87.0}{R}\ln\left(\frac{T,\text{K}}{298.15}\right)$$

| | | | | | | |
|---|---|---|---|---|---|---|
| 344.2 | 1.37 | 9.856 | 6.29 | 1.75 | 0.00 | 79.90 |
| 346.2 | 1.19 | 7.401 | 6.34 | 2.03 | −0.03 | 79.73 |
| 348.2 | 1.43 | 7.435 | 6.28 | 2.43 | 0.01 | 79.55 |
| 351.2 | 1.36 | 5.573 | 5.67 | 3.07 | 0.02 | 79.29 |

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**Table 2. Continued**

| $T,^a$ K | $m,^b$ mg | $V_{(N2)},^c$ dm$^3$ | gas flow, dm$^3$/h | $p,^d$ Pa | $(p_{exp} - p_{calcd})$, Pa | $\Delta_l^g H_m$ or $\Delta_{cr}^g H_m$, kJ·mol$^{-1}$ |
|---|---|---|---|---|---|---|
| 354.2 | 0.94 | 3.137 | 5.70 | 3.79 | −0.05 | 79.03 |
| 357.1 | 1.14 | 2.985 | 3.98 | 4.83 | 0.05 | 78.78 |
| 359.0 | 0.81 | 1.925 | 4.62 | 5.29 | −0.21 | 78.62 |
| 360.1 | 1.11 | 2.319 | 3.98 | 6.04 | 0.08 | 78.52 |
| 363.1 | 1.13 | 1.897 | 3.56 | 7.48 | 0.09 | 78.26 |
| 366.1 | 1.25 | 1.691 | 3.38 | 9.33 | 0.19 | 78.00 |
| 368.5 | 1.58 | 1.835 | 6.48 | 10.84 | 0.03 | 77.79 |
| 370.1 | 2.49 | 2.595 | 1.95 | 12.09 | 0.04 | 77.65 |
| 373.3 | 0.98 | 0.811 | 1.95 | 15.28 | 0.32 | 77.37 |
| 375.3 | 1.17 | 0.850 | 1.82 | 17.40 | 0.31 | 77.20 |
| 378.0 | 1.04 | 0.641 | 1.54 | 20.51 | 0.13 | 76.96 |
| 380.0 | 0.82 | 0.461 | 1.54 | 22.52 | −0.67 | 76.79 |
| 383.2 | 0.82 | 0.375 | 1.32 | 27.74 | −0.66 | 76.51 |

$N$-ethyl-carbazole; $\Delta_{cr}^g H_m$ (298.15 K) = (97.08 ± 0.96) kJ·mol$^{-1}$,

$$\ln(p/\text{Pa}) = \frac{324.15}{R} - \frac{107\,958.90}{R(T,\text{K})} - \frac{36.5}{R} \ln\left(\frac{T,\text{K}}{298.15}\right)$$

| | | | | | | |
|---|---|---|---|---|---|---|
| 313.3 | 0.76 | 144.8 | 1.45 | 0.066 | −0.002 | 96.53 |
| 318.3 | 1.01 | 104.8 | 1.45 | 0.122 | −0.001 | 96.34 |
| 322.6 | 1.10 | 68.4 | 1.45 | 0.203 | 0.004 | 96.19 |
| 328.1 | 1.23 | 40.8 | 1.45 | 0.380 | 0.017 | 95.99 |
| 333.2 | 1.67 | 33.8 | 1.45 | 0.623 | 0.002 | 95.80 |
| 336.4 | 1.63 | 24.0 | 1.45 | 0.852 | −0.011 | 95.68 |
| 339.5 | 1.52 | 16.2 | 1.45 | 1.18 | 0.00 | 95.57 |
| 340.9 | 1.99 | 19.0 | 1.45 | 1.32 | −0.04 | 95.52 |

$^a$ Temperature of saturation. $^b$ Mass of transferred sample condensed at $T$ = 243.15 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 the cooling temperature $T$ = 243.15 K.

**Table 3. Compilation of Experimental Data on Enthalpies of Fusion, $\Delta_l^g H_m$, kJ·mol$^{-1}$**

| compound | $T_{fus}$, K | $\Delta_{cr}^l H_m$ at $T_{fus}$ | $\Delta_{cr}^l H_m{}^a$ at 298.15 K | $\Delta cr^g H_m{}^b$ at 298.15 K | $\Delta_l^g H_m{}^b$ at 298.15 K | $\Delta_{cr}^l H_m{}^c$ at 298.15 K |
|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| carbazole | 518.3 [66] | 27.1 ± 0.5[66] | 14.7 ± 0.5 | 104.3 ± 0.5 | 87.3 ± 0.1 | 17.0 ± 0.5 |
| | 521.1[57] | 27.2 | 14.8 | | | |
| $N$-Me-carbazole | 362.49 [65] | 17.15 [65] | 13.7 | 95.8 ± 0.3 | 82.6 ± 0.5 | 13.2 ± 0.6 |
| $N$-Et-carbazole | 343.1 | 15.10 ± 0.4 | 12.8 ± 0.4 | 97.1 ± 1.0 | 83.9 ± 0.5 | 13.2 ± 1.1 |

$^a$ Calculated according to procedure develpoed by Chickos and Acree.[20,21] The experimental enthalpies of fusion $\Delta_{cr}^l H_m$ measured at $T_{fus}$ and adjusted to 298 K (see text). $^b$ Taken from Table 1. $^c$ Calculated as the difference between columns 5 and 6 in this table.

level. The corresponding harmonic vibrational frequencies were evaluated at the same level of theory to confirm that the optimized structures found correspond to potential energy minima and to evaluate the corresponding zero-point vibrational energies, ZPE, and the thermal corrections at 298 K. ZPE values were scaled by the empirical factor 0.8929. All minima found at the HF/6-31G(d) level were again fully reoptimized at the MP2(FULL)/6-31G(d) level. G3MP2 theory uses geometries from second-order perturbation theory and scaled zero-point energies from Hartree−Fock theory followed by a series of single-point energy calculations at the MP2(Full), QCISD-(T), and MP2/GTMP2Large levels of theory (for details, see 28). The enthalpy value of the studied compound at $T$ = 298 K was evaluated according to standard thermodynamic procedures.[29]

## 3. RESULTS AND DISCUSSION

Considerable activity has taken place with respect to the thermochemical properties measurements on the compounds of interest presented in Figure 1. However, the mutual consistency of the data sets available from the literature is less than desired, especially for the values of the enthalpies of sublimation (see Table 1) and enthalpies of formation (see Table 4). Additional thermochemical research should help to provide validity to the results previously generated on these compounds.

Extended vapor pressure measurements on the five-membered compounds **A−G** have been performed in this work in the temperature ranges possibly close to the reference temperature 298 K. Molar enthalpies of sublimation and vaporization of the compounds under study (Figure 1) were obtained from the temperature dependence of the vapor pressure. The vapor

**Table 4. Thermochemical Results at $T$ = 298.15 K ($p°$ = 0.1 MPa), kJ·mol$^{-1}$**

| compound | | $\Delta_f H_m°$ (l or cr) | $\Delta_l^g H_m$ or $\Delta_{cr}^g H_m{}^c$ | $\Delta_f H_m°$ (g) |
|---|---|---|---|---|
| Indane (l) | A | 11.7 ± 1.8 [32] | 49.0 ± 0.2 | 60.7 ± 1.8 |
| 2,3-dihydro-benzofuran (l) | B | −99.8 ± 0.7 [33] | | |
| | | −100.6 ± 1.9 | 53.2 ± 0.2 | |
| | | **-100.2 ± 1.4 (average)** | | −47.0 ± 1.4 |
| indoline (l) | C | 58.1 ± 2.4 [35] | | |
| | | 63.4 ± 2.2 | 60.9 ± 0.2 | |
| | | **60.8 ± 2.3 (average)** | | 121.7 ± 2.3 |
| N-methyl-indoline (l) | D | | 64.2 ± 0.4 | (114.1)$^b$ |
| carabazole | E | **101.7 ± 2.8** [37] | 104.3 ± 0.5 | 206.0 ± 2.9 |
| | | 111.8 ± 3.5 [36]$^c$ | | |
| N-methyl-carbazole (cr) | F | 104.1 ± 1.0 [62] | 95.8 ± 0.3 | 199.9 ± 1.0 |
| N-ethyl-carbazole (cr) | G | 70.6 ± 2.6 [37] | 97.1 ± 1.0 | 167.7 ± 2.8 |

$^a$ Selected values from Table 3. $^b$ Calculated using the G3MP2 (see text). $^c$ This value was disregarded (see text).

pressures of compounds **A**−**G** were studied earlier (see references in Table 1), but enthalpies of sublimation or vaporization were not always derived from those literature data in the original work. Equations 2 and 3 were applied in this work to each available experimental data set in order to develop enthalpy of sublimation or vaporization values and to provide a consistent comparison between literature results and the present work (Table 1).

Results of combustion experiments on 2,3-dihydro-benzofuran (**B**) and indoline (**C**) are summarized in Table 4. The values of the standard specific energy of combustion, $\Delta_c u°$, the standard molar enthalpy of combustion, $\Delta_c H_m°$, and the standard molar enthalpy of formation in the crystalline state $\Delta_f H_m°$(cr) were based on the reactions

$$C_8H_8O + 9.5O_2 = 8CO_2 + 4H_2O \qquad (4)$$

$$C_8H_9N + 10.25O_2 = 8CO_2 + 4.5H_2O + 0.5N_2 \qquad (5)$$
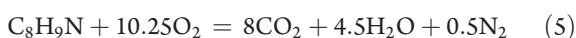
Values of the molar enthalpies of formation, $\Delta_f H_m°$(l) of the compounds under study have been obtained[24] from the enthalpic balance for reactions 4 or 5 above according to Hess's law using the molar enthalpies of formation of $H_2O$(l) and $CO_2$(g) as assigned by CODATA.[26] A summary of typical combustion experiments with the heterocyclic compounds is given in Table S1, Supporting Information. The individual values of the standard specific energies of combustion $\Delta_c u°$, are given as follows (in J·g$^{-1}$): for 2,3-dihydro-benzofuran (**B**) 34 855.1, 34 830.2, 34 860.3, 34 840.2, 34 853.3 and for indoline (**C**) 37 707.3, 37 725.3, 37 695.4, 37 686.2, 37 718.1. The mean values of $\Delta_c u°$ and $\Delta_c H_m°$ with their standard deviation are presented in Table S1, Supporting Information. The uncertainties assigned to $\Delta_f H_m°$ are twice the overall standard deviation and include the uncertainties from calibration and from the combustion energies of the auxiliary materials and the uncertainties of the enthalpies of formation of the reaction products $H_2O$ and $CO_2$.

**3.1. Comparison with Earlier Literature Values.** *Indane (A).* Determination of the standard molar enthalpy of formation $\Delta_f H_m°$(l) of Indane was made by Stull et al.[30] and Good[31] using combustion calorimetry. The results were in close agreement, and the averaged value $\Delta_f H_m°$(l) = (11.7 ± 1.8) kJ·mol$^{-1}$ was recommended by Roux et al.[32] recently. Available vapor pressure measurements for Indane were performed at temperatures close to the boiling point (see Table 1 and Figure S1, Supporting

Information). We derived $\Delta_l^g H_m$(298.15 K) = (49.0 ± 0.2) kJ·mol$^{-1}$ of Indane by the transpiration method in the temperature range 284−382 K, and this value is a good agreement with the available ebulliometric and calorimetric result (Table 1), but our value is more preferable because it is not affected by extrapolation to the reference temperature in comparison with the literature data.

*2,3-Dihydro-Benzofuran (B).* Previous determination of the standard molar enthalpy of formation $\Delta_f H_m°$(l) of 2,3-dihydro-benzofuran was made by Steele and Chirico by means of combustion calorimetry.[33] Unfortunately the NIPER report[33] is not in the open literature and no experimental details were available. For this reason we performed our own thermochemical studies on this compound. Our new value $\Delta_f H_m°$(l) = −(100.6 ± 1.9) kJ·mol$^{-1}$ for 2,3-dihydro-benzofuran is in excellent agreement with those measured by Steele and Chirico[33] (see Table 4). Also, the enthalpies of vaporization of 2,3-dihydrobenzofuran, measured by Steele and Chirico,[33] are in excellent agreement with this work as shown in Table 1.

*Indoline (C).* Previous determination of the standard molar enthalpy of formation $\Delta_f H_m°$(l) of indoline was also made by Steele and Chirico by means of combustion calorimetry.[34] Again, the NIPER report[34] and even the data from this report were not available. When our experimental study on the indoline was completed (but not published), the remarkable experimental and theoretical thermochemical study on this compound was published by Ribeiro da Silva et al.[35] Our results from combustion calorimetry are in agreement within the combined uncertainties. Enthalpies of vaporization are also in a close agreement; however, the vapor pressures of indoline have been measured in this work for the first time.

*N-Me-Indoline (D).* No experimental thermochemical data on this compound were found in the literature. Vapor pressures and vaporization enthalpies have been measured in this work for the first time.

*Carbazole (E).* There are two combustion results on carbazole available in the literature[36,37] (see Table 4) with the inacceptable difference of 10 kJ·mol$^{-1}$. It should be mentioned that combustion experiments by Sabbah and Antipine[36] were performed on the microcombustion calorimeter with the amount of sample around 5 mg. In contrast, combustion experiments by Jimenez et al.[37] were performed with the sample of about 0.7 g and even with addition of the auxiliary compound (benzoic acid) for completeness of combustion. In our opinion, the result by

Sabbah and Antipine[36] could be affected by incomplete combustion, which is difficult to detect using the very small sample. The spread of the sublimation enthalpies for carbazole in the range $84-110$ kJ·mol$^{-1}$ (see Table 1) prompted additional measurements. Our new value $\Delta_{cr}^{g}H_m(298.15\ K) = (104.3 \pm 0.5)$ kJ·mol$^{-1}$ strongly supports the most recent result from the Knudsen-effusion method (see Table 1, Figure S2, Supporting Information) and helps to resolve contradiction among the available data. An additional test for consistency of our new results will be given below by comparison of sublimation, vaporization, and fusion enthalpies of carbazole.

*N-Methyl-Carbazole (F).* Determination of the standard molar enthalpy of formation $\Delta_f H_m^{\circ}(cr)$ for this compound was made by Good[38] and Jimenez et al.[37] using combustion calorimetry. Results were in close agreement, and the average value of $\Delta_f H_m^{\circ}(cr) = (104.1 \pm 1.0)$ kJ·mol$^{-1}$ has been evaluated by Steel et al.[39] (see Table 4). The enthalpy of sublimation for this compound measured by the Knudsen technique[37] is consistent with the vaporization and fusion enthalpies as shown below.

*N-Ethyl-Carbazole (G).* Enthalpies of combustion, vapor pressures, enthalpies of sublimation, and enthalpies of formation of carbazole, *N*-methyl-carbazole, and *N*-ethyl-carbazole have been measured by Jimenez et al.[37] Only their determination of the standard enthalpy of formation $\Delta_f H_m^{\circ}(cr) = (70.6 \pm 2.6)$ kJ·mol$^{-1}$ and enthalpy of sublimation $\Delta_{cr}^{g}H_m(298.15\ K) = (99.1 \pm 0.2)$ kJ·mol$^{-1}$ of *N*-ethyl-carbazole are available in the literature. In the course of our investigation of the relationship between the enthalpy of vaporization and the molecular surface in our previous work[40] we detected slight inconsistency of the sublimation enthalpy for *N*-ethyl-carbazole with those for carbazole and *N*-methyl-carbazole. Thus, we decided to perform measurements of the vapor pressure of *N*-ethyl-carbazole using the transpiration technique. Our new value of $\Delta_{cr}^{g}H_m(298.15\ K) = (97.1 \pm 1.0)$ kJ·mol$^{-1}$ is 2 kJ·mol$^{-1}$ lower in comparison with the value obtained from mass effusion measurements.[37] In order to support our result from the transpiration technique, we performed a consistency test for carbazole, *N*-methyl-carbazole, and *N*-ethyl-carbazole as described below.

**3.2. Enthalpies of Fusion of Carbazoles.** The melting temperatures and enthalpies of fusion of carbazole, *N*-methyl-carbazole, and *N*-ethyl-carbazole measured in the present work and those available from the literature are compiled in Table 3. No phase transitions other than melting of carbazoles under study have been detected. Experimental enthalpies of fusion measured by DSC (see Table 3) are obtained at the melting temperature $T_{fus}$. Because of the differences in the reference temperatures, the experimental enthalpies of fusion have to be adjusted to $T = 298$ K. The adjustment was calculated from the equation[41]

$$\{\Delta_{cr}^{l}H_m(T_{fus}/K) - \Delta_{cr}^{l}H_m(298\ K)\}/(J·mol^{-1})$$
$$= \{(0.75 + 0.15 C_p^{cr})[(T_{fus}/K - 298\ K]$$
$$- (10.58 + 0.26 C_p^{l})[(T_{fus}/K) - 298\ K]\} \quad (6)$$

where the isobaric molar heat capacities $C_p^{cr}$ and $C_p^{l}$ of the solid and the liquid carbazoles are given in Table 1 and calculated according to the procedure developed by Chickos and Acree.[20,21] With this adjustment (the uncertainty of the correlation was not taken into account), the molar enthalpies of fusion, $\Delta_{cr}^{l}H_m(298\ K)$, were calculated (see Table 3).

**3.3. Consistency Test of the Vaporization, Sublimation, and Fusion Enthalpies of Carbazoles.** Since a significant

discrepancy between available experimental data for carbazoles has been found (see Table 1), additional arguments to support the reliability of our new vapor pressure measurements are required. A valuable test of the consistency of the experimental data on sublimation and vaporization enthalpies available for carbazoles (see Table 1) provides a comparison with the experimental values of enthalpy of fusion collected in Table 3. For example, in this work the sample of *N*-ethyl-carbazole was investigated by the transpiration method in both ranges, above and below its temperature of melting $T_{fus} = 343.1$ K. The value of $\Delta_{cr}^{g}H_m(298\ K) = (97.1 \pm 1.0)$ kJ·mol$^{-1}$ for *N*-ethyl-carbazole was obtained in this work from measurements in the temperature range $313.3-340.9$ K and the vaporization enthalpy for *N*-ethyl-carbazole $\Delta_{l}^{g}H_m(298\ K) = (83.9 \pm 0.5)$ kJ·mol$^{-1}$ from measurements in the temperature range $344.2-383.2$ K. To test of the consistency of the experimental data on vaporization and sublimation enthalpies measured in this work for *N*-ethyl-carbazole let us compare the enthalpy of fusion calculated as the difference $\Delta_{cr}^{l}H_m(298.15\ K) = \Delta_{cr}^{g}H_m - \Delta_{l}^{g}H_m$ (both values referring to $T = 298$ K) = $(13.2 \pm 1.1)$ kJ·mol$^{-1}$ with the $\Delta_{cr}^{l}H_m$ $(298\ K) = (12.8 \pm 0.4)$ kJ·mol$^{-1}$ of *N*-ethyl-carbazole measured by DSC (see Table 3). The enthalpy of fusion $\Delta_{cr}^{l}H_m$ calculated from the difference $\Delta_{cr}^{g}H_m - \Delta_{l}^{g}H_m$ measured in this work is in excellent agreement with those measured directly by calorimetry (and adjusted to $T = 298$ K). Thus, our new results for vaporization and sublimation enthalpies of *N*-ethyl-carbazole have been proven to be consistent. In the same way, we tested the experimental results for carbazole and *N*-methyl-carbazole (see Table 3, last column). Data on the vaporization, sublimation, and fusion enthalpy of *N*-methyl-carbazole were highly consistent. For carbazole, the enthalpy of fusion calculated according to the difference $\Delta_{cr}^{l}H_m(298\ K) = \Delta_{cr}^{g}H_m - \Delta_{l}^{g}H_m =$ $(17.0 \pm 0.5)$ kJ·mol$^{-1}$ is somewhat higher than those $\Delta_{cr}^{l}H_m$ $(298.15\ K) = (14.8 \pm 0.5)$ kJ·mol$^{-1}$ measured by calorimetry (and adjusted to $T = 298$ K). In our opinion, the data for carbazole is still consistent, and a possible reason for the observed discrepancy is due to the very long way of extrapolation (over 250 K) of the vaporization enthalpy of carbazole to the reference temperature $T = 298$ K.

**3.4. Calculation of the Gas-Phase Enthalpies of Formation: Quantum Chemical Calculations.** Values of the sublimation and vaporization enthalpies of compounds under study selected in Table 1 can now be used together with the results from combustion experiments (see Table 4) for further calculation of the gas standard enthalpies of formation, $\Delta_f H_m^{\circ}(g)$, at 298 K. The resulting experimental values of $\Delta_f H_m^{\circ}(g)$ are given in the last column in Table 4, and they can now be compared with the theoretical results from quantum chemical calculations.

First-principles molecular orbital methods for calculation of the enthalpy of formation of the compounds in Figure 1 have not been reported in the literature (except for indoline). We calculated using the G3MP2 the total energies $E_0$ at $T = 0$ K and enthalpies $H_{298}$ at $T = 298$ K (Table S2, Supporting Information). In standard Gaussian-*n* theories, theoretical standard enthalpies of formation, $\Delta_f H_m^{\circ}(g)$, are calculated through atomization reactions and bond separation reactions. In this work we applied the atomization procedure (AT) and the reactions in Table 5 for calculation of the enthalpies of the 5-membered heterocycles.

The results of the calculations are given in Table 6. The results calculated from the standard atomization procedure are

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**Table 5**

<table>
<tr><td colspan="2" align="center">reactions for Indane</td></tr>
<tr><td>compound + $x$CH$_4$ = $y$C$_2$H$_6$</td><td>BS1</td></tr>
<tr><td>compound + C$_4$H$_8$ = C$_6$H$_6$ + C$_5$H$_8$</td><td>BS2</td></tr>
<tr><td colspan="2" align="center">reactions for 2,3-dihydro-benzofuran</td></tr>
<tr><td>compound + $x$CH$_4$ = CH$_3$OH + $y$C$_2$H$_6$</td><td>BS1</td></tr>
<tr><td>compound + $x$CH$_4$ = CH$_3$−O−CH$_3$ + $y$C$_2$H$_6$</td><td>BS2</td></tr>
<tr><td colspan="2" align="center">reactions for carbazole and indoline</td></tr>
<tr><td>compound + $x$CH$_4$ = NH$_3$ + $y$C$_2$H$_6$</td><td>BS1</td></tr>
<tr><td>compound + $x$CH$_4$ = (CH$_3$)$_2$NH + $y$C$_2$H$_6$</td><td>BS2</td></tr>
<tr><td colspan="2" align="center">reactions for $N$-methyl-carbazole, $N$-ethyl-carbazole, $N$-methyl-indoline</td></tr>
<tr><td>compound + $x$CH$_4$ = NH$_3$ + $y$C$_2$H$_6$</td><td>BS1</td></tr>
<tr><td>compound + $x$CH$_4$ = (CH$_3$)$_3$N + $y$C$_2$H$_6$</td><td>BS2</td></tr>
</table>

**Table 6. Results of G3MP2 Calculation of the Standard Enthalpy of Formation $\Delta_f H_m^\circ(g)$ for the Molecules Studied in This Work in the Gaseous Phase at 298.15 K, kJ·mol$^{-1}$**

| compounds | | AT | AT(corr) | BS1 | BS2 | exp |
|---|---|---|---|---|---|---|
| indane | A | 53.1 | **63.0** | 60.9 | 60.8 | 60.7 ± 1.8 |
| 2,3-dihydro-benzofuran | B | −59.7 | -46.5 | −54.2 | −54.0 | −47.0 ± 1.4 |
| indoline | C | 115.9 | **125.3** | 119.9 | 116.4 | 121.7 ± 2.3 |
| $N$-methyl-indoline | D | 104.6 | **114.1** | 109.1 | 109.7 | |
| carbazole | E | 196.7 | **205.4** | 205.9 | 202.4 | 206.0 ± 2.9 |
| $N$-methyl-carbazole | F | 185.7 | **194.5** | 195.4 | 196.0 | 199.9 ± 1.0 |
| $N$-ethyl-carbazole | G | 153.6 | **162.7** | 163.8 | 164.5 | 167.7 ± 2.8 |

systematically less positive than those from the bond separation reactions for all compounds under study. At the same time, the selected bond separation is in a good agreement with the experimental values (see Table 6) except for 2,3-dihydro-benzofuran (B) and indoline (C). Such disagreement prompted our new thermochemical measurements on both compounds; however, our new results only supported the available experimental data;[33−35] thus, to confirm the experimental data for 2,3-dihydro-benzofuran (B) and indoline (C) we have to look for a possible improvement of the calculation procedure. Indeed, it is well established that the enthalpies of formation obtained from the first-principle calculations are very sensitive for the choice of the bond separation or isodesmic reactions used for this purpose.[42] The possible reasons are usually explained for different quality of the experimental data, involved in estimation, as well as a disbalance of electronic energies calculated for the reaction participants. To set an example, we calculated the gaseous enthalpy of formation, $\Delta_f H_m^\circ(g)$, of 2,3-dihydrobenzofuran, using four additional reactions (see Table S4, Supporting Information) with the dramatic spread of values from −52.6 to −62.0 kJ·mol$^{-1}$, which still remains in disagreement with the experimental value −(47.0 ± 1.4) kJ·mol$^{-1}$. In contrast to the bond separation reactions, the atomization reaction suggests the quality of the data on the right side (the constituted atoms) is the same for all compounds under study.[42] However, as mentioned above, the enthalpies of formation from the atomization procedure deviate systematically from the experimental values. It turns out that a remarkable linear correlation could be found between experimental values and those calculated by atomization enthalpies of formation (see Table S3 and Figure

**Table 7. Strain-Free Increments $\Gamma_i$ for Estimation of $\Delta_f H_m^\circ$ (g) at $T$ = 298 K of Hydrocarbons, Nitrogen, and Oxygen-Containing Compounds, kJ·mol$^{-1}$** [a]

| $\Gamma_i$ | value | $\Gamma_i$ | value | $\Gamma_i$ | value |
|---|---|---|---|---|---|
| CH$_3$[C] | −42.05[44] | CH$_3$[N] | −42.05[49] | C$_B$H[2C$_B$] | 13.72[47] |
| CH$_2$[2C] | −21.46[44] | CH$_2$[N, C] | −26.9[49] | C$_B$ [C, 2C$_B$] | 23.51[47] |
| CH[3C] | −9.04[44] | CH [N, 2C] | −20.0[49] | C$_B$ [3C$_B$] | 23.51[47] |
| C[4C] | −1.26[44] | C[N, 3C] | −16.1[49] | CH$_2$ [C$_d$] | 26.4[46] |
| CH$_2$[C$_d$, C] | −21.46[b] | NH$_2$[C] | 19.4[49] | C$_d$H [C$_d$, C] | 36.0[46] |
| CH [C$_d$, 2C] | −9.04[b] | NH[2C] | 64.1[49] | C$_d$ [C$_d$, 2C] | 42.7[46] |
| C [C$_d$, 3C] | −1.26[b] | N[3C] | 103.2[49] | C$_d$H[C$_d$, C$_B$] | 28.5[46] |
| CH$_2$[O, C] | −33.06[50] | C$_B$ [N, 2C$_B$] | 2.1[49] | C$_d$H[N, C$_d$] | 14.7[51] |
| O[2C] | −99.24[50] | NH$_2$[C$_B$] | 16.6[49] | | |
| C$_B$ [O, 2C$_B$] | 3.42[50] | NH[C$_B$, C] | 65.4[49] | C$_d$H[O, C$_d$] | 7.7[52] |
| | | N[C$_B$, 2C] | 115.2[49] | C$_d$[O, C$_d$, C] | 8.5[52] |

[a] C$_d$ represents a double-bonded C atom and C$_B$ the C atom in a benzene ring. [b] Strain-free increments were adopted to be equal to those in alkanes.[44]

S5, Supporting Information).

$$\Delta_f H_m^\circ(g)(exp)/kJ \cdot mol^{-1} = 0.992$$
$$\times \Delta_f H_m^\circ(g)(AT) + 10.3 \quad (7)$$

Using this correlation the "corrected" enthalpies of formation of the compounds under study have been calculated (see Table 6), and these values are now in good agreement with the experimental results. Having established this "modified atomization procedure" we could use eq 7 for estimation enthalpies of the parent compounds from the G3MP2 energies without creating any "suitable" bond separation or isodesmic reactions. However, to check the validity of this "corrected AT procedure" we calculated enthalpies of formation of the three recent experimental data[43] for the parent five-membered heterocycles: 1-methyl-indol, 2-methyl-indol, and 3-methyl-indol. The experimental data for these compounds have not been involved in development of eq 7, but we were able to predict their enthalpies of formation within the boundaries of the experimental uncertainties of 2−3 kJ·mol$^{-1}$ (see Table S6, Supporting Information). Thus, the results of first-principles calculations have helped to establish the thermodynamic consistency of the experimental results from the transpiration and from the combustion calorimetry. The G3MP2 method combined with the modified atomization procedure could be recommended for reliable calculations of $\Delta_f H_m^\circ(gas, 298$ K) of the heterocyclic compounds.

**3.5. Strain Effects in the Five-Membered Heterocycles.** The concept of "*strain energy*", $H_S$, in organic molecules is conceptually useful, because in the value of $H_S$ the sum of all nonbonded interactions in a molecule is collected. The concept of strain and strain energy provides a basis that helps correlate the structure, stability, and reactivity of molecules. Stability is always relative, and the strain energy, resonance energy, or conjugation could be derived only through comparison of the molecule in question with an appropriate reference (e.g., with a sum of increments) or with a model compound. The strain, $H_S$, of a molecule is conventionally defined as the difference between its experimental $\Delta_f H_m^\circ(g)$ and that for its corresponding hypothetically strain-free model,[44] calculated from group contributions
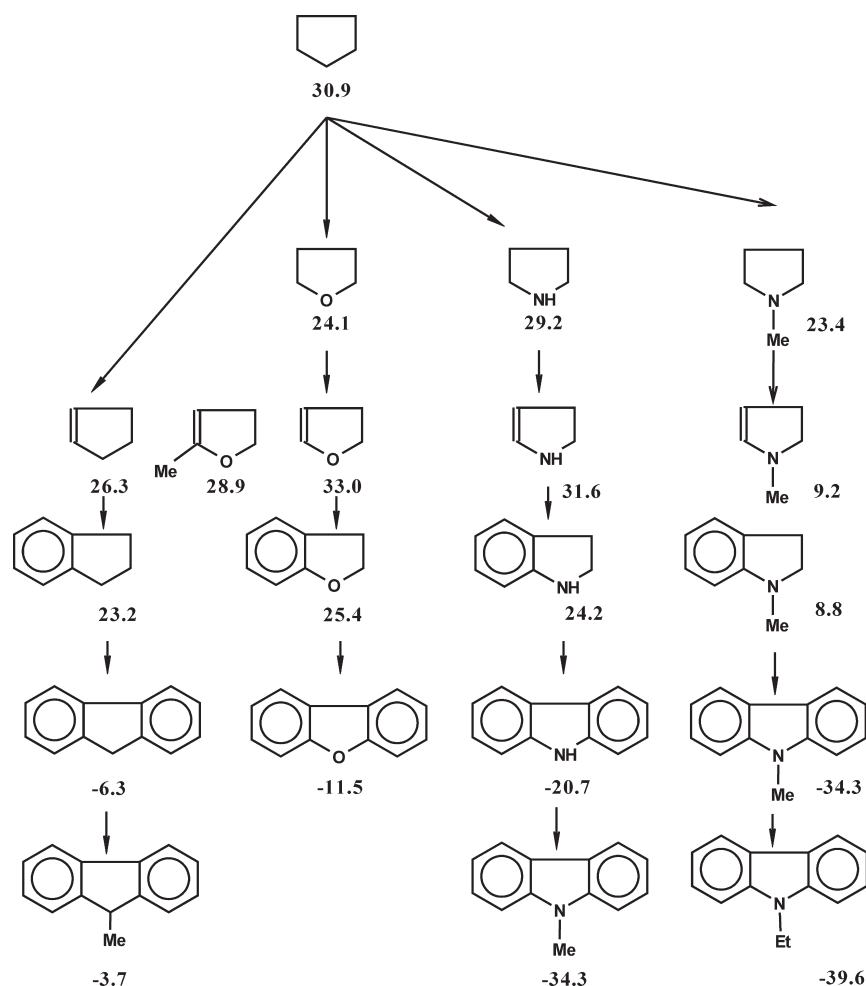
**Figure 2.** Strain Enthalpies $H_S$ (in kJ·mol$^{-1}$) of Five-Membered Rings Derivatives. The standard enthalpies of formation $\Delta_f H_m^\circ(g)$ values used to derive $H_S$ are given in Tables S2–S4, Supporting Information.

(increments)

$$H_S = \left(\Delta_f H_m^\circ(g) - \sum \text{increments } \Gamma_i\right)$$

A group is defined like by Benson[45,46] as a polyvalent atom in a molecule together with all of its ligands. The system of strain-free increments[44] is based on the standard enthalpies of formation $\Delta_f H_m^\circ(g)$ of simple homologous ("strainless) molecules. Their advantage with respect to the classic Benson[45,46] increments is the possibility of the determining of strain enthalpies. Schleyer et al.[44] established the values of "strain-free" increments only for hydrocarbons (see Table 7). Later, Beckhaus[47] extended this methodology to arenes for increments $C_B H[2C_B]$ and $C_B$ [C, $2C_B$], where $C_B$ represents the aromatic C atoms. As an example of calculations with the system of strain increments listed in Table 7 strain of cyclopropane, $H_S = 117.7$ kJ·mol$^{-1}$, can be calculated using its enthalpy of formation[48] $\Delta_f H_m^\circ(g) = 53.3$ kJ·mol$^{-1}$ and the sum of the strain-free increments $3 \times CH_2$-[2C] from Table 7.

Only strain-free group additivity increments for hydrocarbons[44] and arenes[47] were defined in the literature. The increments for other homologous series (ethers, alcohols, amines, etc.) have been adjusted to the strain-free hydrocarbon increments recently[49–53] (see Table 7). We use these group-additivity

parameters and the values of $\Delta_f H_m^\circ(g)$ of compounds from Table 4 derived in this study to derive the values of strain enthalpies $H_S$ of five-membered heterocycles. In order to obtain much broader basis for discussion of the structural effects in these compounds, the data for $\Delta_f H_m^\circ(g)$ of some structurally relevant compounds have been involved from the literature with an emphasis on the values recommended by Pedley et al.,[48] but the origin of the data has been carefully documented in Tables S3 and S4, Supporting Information.

Strains enthalpies, $H_S$, of five-membered heterocycles are presented in graphic form in Figure 2. Cyclopentane is conventionally strained by 30.9 kJ·mol$^{-1}$. Introduction of a heteroatom into a carbocyclic ring may affect the ring strain in several ways. Replacement of a carbon atom by an atom whose covalent radius is shorter than that of carbon obviously increases angular strain in small-ring compounds. On the other hand, nonbonded interactions might be expected to decrease as two methylene—methylene interactions are removed. The amount of this kind of strain release naturally depends on the extent of eclipsing of the methylene groups in the parent carbocyclic compound. In the case of a five-membered ring replacement of a methylene group by an oxygen (tetrahydrofurane, $H_S = 24.1$ kJ·mol$^{-1}$) or a nitrogen atom (pyrrolidine $H_S = 29.2$ kJ·mol$^{-1}$ and $N$-Me-pyrrolidine $H_S =$

23.4 kJ·mol$^{-1}$) causes only a small change in ring strain as shown in Figure 2. In cyclic compounds containing unsaturation there is an additional possibility of torsional strain or twisting of the olefinic link to permit ring formation. That is why 2,3-dihydrofuran derivatives and 2,3-dihydro-1$H$-pyrrole are somewhat more strained in comparison to tetrahydrofuran and pyrrolidine (Figure 2). It makes oneself conspicuous that strain in the unsaturated $N$-methylated cycle (2,3-dihydro-1-methyl-1$H$-pyrrole $H_S$ = 9.2 kJ·mol$^{-1}$) is 14 kJ·mol$^{-1}$ lower than in the saturated analogue ($N$-Me-pyrrolidine $H_S$ = 23.4 kJ·mol$^{-1}$).

In heterocyclic compounds containing fused benzene rings there is also the similar additional possibility of torsional strain or twisting of the cycle compared to the unsaturated five-membered ring. The near constancy of the difference of enthalpies of formation of phenyl and vinyl derivatives, i.e., C$_6$H$_5$X and CH$_2$=CHX, has been already established.[53] Is there any quantitative difference between strain caused in the cycle by a double bond or by attached benzene rings? Our experimental results on 2,3-dihydrobenzofuran and indoline have indicated a sizable stabilization of about 7 kJ·mol$^{-1}$ in these compounds compared to five-membered rings without a fused benzene ring. Taking into account that Indane ($H_S$ = 23.2 kJ·mol$^{-1}$) is destabilized to a similar extent as cyclopentene ($H_S$ = 26.3 kJ·mol$^{-1}$), the reason for the additional stabilization of 2,3-dihydrobenzofuran and indoline is suggested to be the conjugation of the ring with the heteroatom. Again, this attracts attention to the special pattern of strain in $N$-methyl-indoline ($H_S$ = 8.8 kJ·mol$^{-1}$) which is only slightly stabilized in comparison to the unsaturated $N$-methylated cycle (2,3-dihydro-1-methyl-1$H$-pyrrole $H_S$ = 9.2 kJ·mol$^{-1}$).

Further, does the fusion of the five-membered ring with the next benzene ring increase the amount of stabilization? Indeed, the results for fluorene ($H_S$ = −6.3 kJ·mol$^{-1}$) showed its stabilization of 30 kJ·mol$^{-1}$ in comparison to Indane ($H_S$ = 23.2 kJ·mol$^{-1}$). Dibenzofuran ($H_S$ = −11.5 kJ·mol$^{-1}$) is only of 37 kJ·mol$^{-1}$ more stabilized than 2,3-dihydrobenzofuran ($H_S$ = 25.4 kJ·mol$^{-1}$). 9-$H$-Carbazole ($H_S$ = −20.7 kJ·mol$^{-1}$) and 9-methyl-carbazole ($H_S$ = −34.3 kJ·mol$^{-1}$) are 43−45 kJ·mol$^{-1}$ more stable in comparison to indoline and $N$-methyl-indoline (see Figure 2). The general stabilization of these molecules is caused by the conjugation of both benzene rings with the heteroatom, which has entirely wiped out the original strain of the cyclopentane ring ($H_S$ = 30.9 kJ·mol$^{-1}$). It is worthy of mention that the amount of stabilization effect in the case of the N-containing heterocycles is large in comparison with O-containing compounds.

The stabilization of the N-alkylated carbazoles (e.g., $N$-methyl-carbazole, $H_S$ = −34.3 kJ·mol$^{-1}$) is even more profound than in carbazole itself (9-$H$-carbazole, $H_S$ = −20.7 kJ·mol$^{-1}$) in the same way that N-alkylated piperidines are strainless in comparison to piperidine ($H_S$ = 6.4 kJ·mol$^{-1}$) itself, as shown in our recent investigation of these compounds.[52] At the same time the $N$-ethyl-carbazole is 5.3 kJ·mol$^{-1}$ more stable in comparison to $N$-methyl-carbazole. The reason for such different stabilities of N-alkylated carbazoles is apparent from Figure 3. Indeed, the ethyl group in $N$-ethyl-carbazole is out of the ring plane and avoids the steric interactions with the rings.

Analysis of the strain in the ring compounds using the group-additivity procedure applied in this work is one of the traditional methods. However, similar knowledge could be obtained with the modern first-principles calculations. For example, we could use the bond separation reaction



$$\Delta_r H = -9.8 \text{ kJ·mol}^{-1} \tag{8}$$
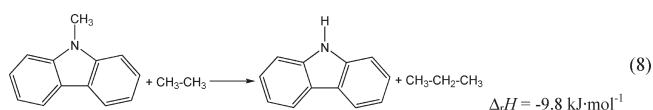
to compare stabilization of $N$-methyl-carbazole and 9-$H$-carbazole. The enthalpy of reaction (see eq 8) calculated using G3MP2 demonstrated that $N$-methyl-carbazole is about 9 kJ·mol$^{-1}$ more stable in comparison to carbazole (in agreement with the result obtained with increments in Figure 2). Thus, the group-additivity and first-principles calculations could be successfully combined for analysis of the strain in heterocyclic compounds.

Investigation of the compounds (Figures 1 and 2) covered a broad range of structures of heterocycles. Discussion of strains of these compounds given in Figure 2 have shown internal consistency of the data chosen for thermodynamic analysis. These experimental data could be recommended for validation of the modern first-principles calculations.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information.** Results from combustion calorimetry (Tables S1); data involved in calculation of the strain enthalpies (Tables S2−S4); plots of vapor pressure against reciprocal temperature for Indane, carbazole, and $N$-ethyl-carbazole (Figure S1−S3); reactions applied for calculation of the enthalpy of formation of 2,3-dihydrobenzofuran using the G3MP2 method (Figure S4); correlation of the enthalpies of formation of the aromatic compounds from the G3MP2 atomization procedure with the experimental data (Figure S5); proof of the corrected atomization procedure for calculation of the enthalpies of formation of the three methyl-indoles (Figure S6). This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

**Corresponding Author**
*Phone: +49 381 498 6508. Fax +49 381 498 6524. E-mail: vladzimir.yemelyanenko@uni-rostock.de.

## ■ ACKNOWLEDGMENT

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