


Thermodynamic Analysis of Strain in Heteroatom Derivatives of Indene

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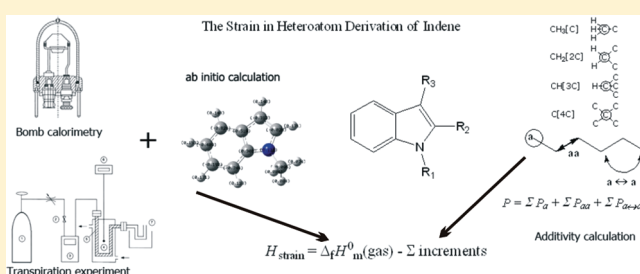
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 Supporting Information

ABSTRACT: Thermochemical properties of indene, 2,3-benzofuran, indole, and *N*-methylindole have been studied to obtain a better quantitative understanding of the energetics associated with these compounds containing five-membered ring units. We used combustion calorimetry, transpiration, and high-level first-principles calculations to derive gaseous enthalpies of formation of the five-membered heterocyclic compounds. Our new values together with selected values for the parent heterocyclic compounds, available from the literature were used for calculation of the strain enthalpies H_S of five-membered C, N, and O-containing cycles. The quantitative analysis of the resulting stabilization or destabilization of a molecule due to interaction of the benzene ring with the heteroatom has been performed.



1. INTRODUCTION

The concept of strain enthalpy (H_S) has aided our understanding of the energetics and reactivities of carbocycles and heterocycles.¹ Cyclopentane and cyclopentene are conventionally strained. Replacement of a carbon atom by a heteroatom obviously impacts angular strain in the five-membered ring compounds. A benzene ring fused to a nonaromatic five-membered ring also causes the alteration of strain. Changes in strain in saturated five-membered cycles have been reported just recently.² This study extends our previous work on manifestation of strain in cyclic compounds^{3,4} with experimental measurements and first-principles calculations of unsaturated five-membered cycles fused to benzene ring (indene derivatives). Indene and its derivatives are broadly used in clinical cancer prevention and therapy.⁵ These compounds could be obtained from synthetic pathway or from natural sources such as marine invertebrates. In any case for synthesis or for separation of compounds containing indene and indene heteroatom derivatives, knowledge of their thermodynamic properties would be useful. Enthalpies of formation, enthalpies of vaporization, enthalpies of fusion, and vapor pressures 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. The recent experimental work of Ribeiro da Silva et al.^{6,7} and Steele and Chirico⁸ on N- and O-containing heterocycles, have extended our knowledge of thermochemical properties of the heterocyclic compounds. The present paper follows this course and describes a systematic

investigation of the thermochemistry of O- and N-heterocyclic five-membered rings, detached at first to one and then to two benzene rings (Figures 1–3). We have focused our experimental efforts on the determination of the reliable vaporization (or sublimation) enthalpies and enthalpies of formation of the indene derivatives. We have also used the high-level composite method G3(MP2) to test the consistency of the experimental data on enthalpies of formation in the gas phase. By combining new experimental data with literature data, it was possible to evaluate the changes of strain energy in O- and N-heterocyclic analogues of indene.

2. EXPERIMENTAL SECTION

2.1. Materials. Samples of indene [CAS 95-13-6], 2,3-benzofuran [CAS 271-89-6], and indole [CAS 120-72-9] were purchased from Aldrich. *N*-methylindole [CAS 603-76-9] was from Alfa. Gas chromatography (GC) 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). A solid sample of indole was purified by repeated fractional sublimation under reduced pressure. The determination of purity was carried out

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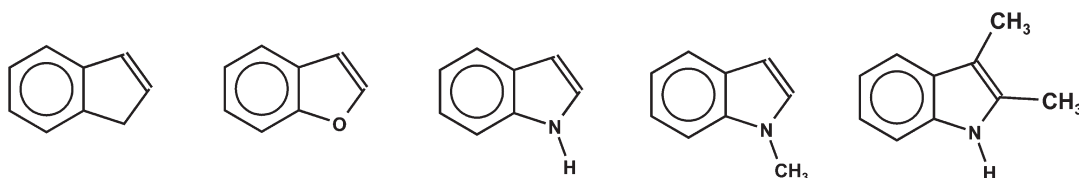


Figure 1. Structures of investigated compounds: indene, 2,3-benzofuran, indole, *N*-methylindole, and 2,3-dimethylindole.

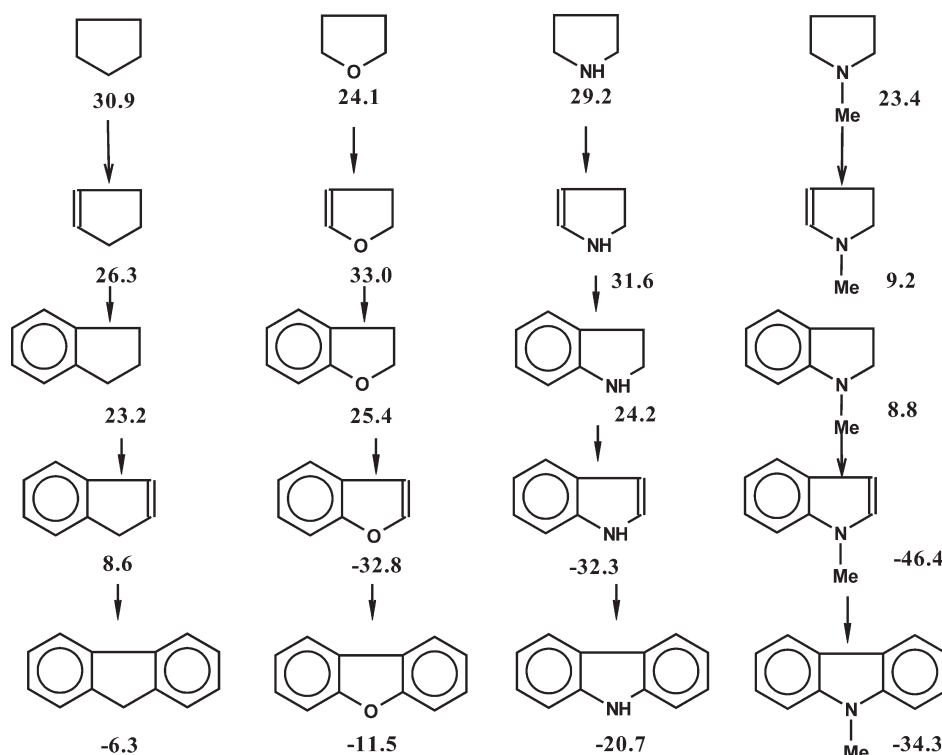


Figure 2. Strain enthalpies H_S ($\text{kJ}\cdot\text{mol}^{-1}$) of five-membered ring derivatives. The standard enthalpies of formation $\Delta_f H_m^\circ(\text{g})$ used to derive H_S are given in Tables S4 and S5 (Supporting Information).

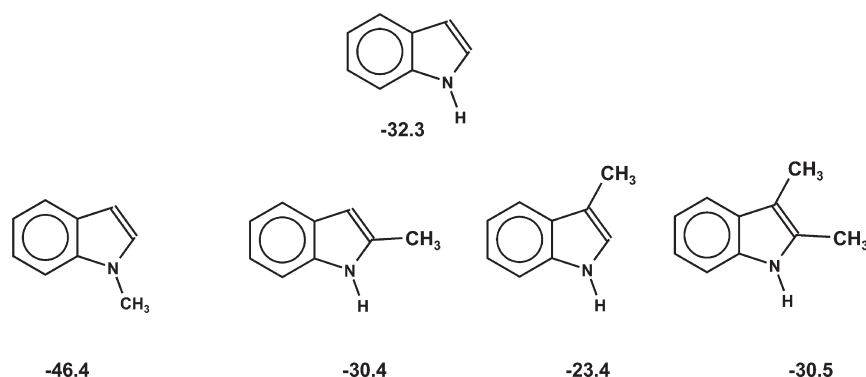


Figure 3. Strain enthalpies H_S ($\text{kJ}\cdot\text{mol}^{-1}$) of five-membered rings derivatives: *N*-methylindole, 2-methylindole, 3-methylindole, and 2,3-dimethylindole.

by GC. No impurities (≥ 0.01 mass %) could be detected in samples used in this study. For all solid compounds, mole fractions 0.9998 were additionally established by DSC measurements of the melting process. The samples were stored cold in the dark, either at reduced pressure or in a nitrogen atmosphere.

2.2. Transpiration Method. Vapor pressures and enthalpies of vaporization, $\Delta_f^\circ H_m$ or enthalpies of sublimation, $\Delta_{\text{cr}}^\circ H_m$, of the indene derivatives were determined using the method of transpiration in a saturated stream of nitrogen. The method has been described in detail before^{9,10} and has proven to give results in agreement with other established techniques. The saturated

Table 1. Vapor Pressures, p , Vaporization Enthalpy, $\Delta^{\text{f}}H_{\text{m}}$, and Sublimation Enthalpy, $\Delta^{\text{g}}_{\text{cr}}H_{\text{m}}$, Obtained by the Transpiration Method

T^{a} (K)	m^{b} (mg)	$V_{\text{N}_2}^{\text{c}}$ (dm ³)	gas flow (dm ³ /h)	p^{d} (Pa)	$p_{\text{exp}} - p_{\text{calc}}$ (Pa)	$\Delta^{\text{f}}H_{\text{m}}$ or $\Delta^{\text{g}}_{\text{cr}}H_{\text{m}}$ (kJ·mol ⁻¹)	T^{a} (K)	m^{b} (mg)	$V_{\text{N}_2}^{\text{c}}$ (dm ³)	gas flow (dm ³ /h)	p^{d} (Pa)	$p_{\text{exp}} - p_{\text{calc}}$ (Pa)	$\Delta^{\text{f}}H_{\text{m}}$ or $\Delta^{\text{g}}_{\text{cr}}H_{\text{m}}$ (kJ·mol ⁻¹)
Indene; $\Delta^{\text{f}}H_{\text{m}}$ (298.15 K) = 50.29 ± 0.13 kJ·mol ⁻¹													
$\ln(p/\text{Pa}) = \frac{274.97}{R} - \frac{69311.80}{R \cdot (T, \text{K})} - \frac{63.8}{R} \ln\left(\frac{T, \text{K}}{298.15}\right)$													
274.6	6.0	4.64	5.26	29.2	1.0	51.80	300.3	4.7	0.524	1.57	193.3	2.2	50.16
276.5	5.3	3.50	5.26	33.7	0.7	51.67	303.2	3.2	0.301	1.39	222.6	-8.9	49.97
277.6	1.0	0.601	1.39	36.0	-0.1	51.60	303.5	6.4	0.571	1.43	238.7	2.5	49.95
283.0	1.2	0.462	1.39	54.1	-1.1	51.26	308.5	5.6	0.366	1.10	326.0	0.8	49.63
280.4	5.4	2.51	4.56	46.9	1.8	51.43	308.6	4.5	0.301	1.39	311.0	-16.2	49.63
284.5	6.5	2.28	4.56	62.2	0.3	51.16	313.4	6.0	0.293	1.10	438.5	-1.1	49.32
287.6	5.8	1.63	2.79	76.8	-1.3	50.97	318.0	9.4	0.343	1.03	584.8	7.1	49.03
287.6	1.4	0.393	1.39	76.6	-1.8	50.96	313.6	6.8	0.324	1.39	438.5	-7.6	49.30
290.3	5.6	1.25	2.08	96.5	1.3	50.79	318.2	15.5	0.558	1.10	589.2	4.7	49.01
291.2	8.2	1.75	5.26	100.7	-1.0	50.74	323.0	10.1	0.275	1.03	780.9	11.8	48.71
293.3	5.6	1.05	2.06	115.6	-2.5	50.60	323.1	13.7	0.373	1.49	781.1	7.7	48.70
292.6	1.7	0.324	1.39	110.0	-2.3	50.65	318.7	9.5	0.324	1.39	614.7	13.0	48.98
296.3	4.6	0.660	1.58	147.9	2.3	50.41	328.2	11.3	0.231	1.39	1032.3	8.1	48.38
297.6	2.2	0.301	1.39	156.7	-2.5	50.33	333.6	26.5	0.403	1.42	1377.9	14.5	48.03
298.5	4.7	0.595	1.43	170.4	1.1	50.27	338.7	26.2	0.308	1.42	1780.5	12.5	47.71
2,3-Benzofuran; $\Delta^{\text{f}}H_{\text{m}}$ (298.15 K) = 48.81 ± 0.33 kJ·mol ⁻¹													
$\ln(p/\text{Pa}) = \frac{266.23}{R} - \frac{65836.18}{R \cdot (T, \text{K})} - \frac{57.1}{R} \ln\left(\frac{T, \text{K}}{298.15}\right)$													
278.7	3.59	1.33	1.85	60.0	1.5	49.93	303.5	16.65	1.07	1.85	327.0	-4.9	48.51
283.6	3.80	0.999	1.85	83.0	-1.8	49.65	304.5	5.88	0.352	1.85	352.1	-1.5	48.45
288.4	6.89	1.22	1.85	121.2	1.1	49.37	308.7	4.07	0.185	1.85	462.0	3.6	48.21
293.4	4.78	0.611	1.85	166.9	-3.7	49.09	313.4	2.72	0.093	1.85	616.4	9.2	47.94
298.4	5.44	0.481	1.85	239.5	0.8	48.80							
Indole; $\Delta^{\text{g}}_{\text{cr}}H_{\text{m}}$ (298.15 K) = 73.94 ± 0.37 kJ·mol ⁻¹													
$\ln(p/\text{Pa}) = \frac{273.69}{R} - \frac{79958.60}{R \cdot (T, \text{K})} - \frac{20.2}{R} \ln\left(\frac{T, \text{K}}{298.15}\right)$													
290.4	1.06	26.00	2.00	0.86	-0.01	74.09	306.5	0.55	2.64	3.97	4.39	0.04	73.77
293.4	0.97	16.98	4.85	1.20	0.01	74.03	310.1	0.89	2.97	3.97	6.27	0.18	73.70
296.4	0.89	11.58	4.79	1.62	0.00	73.97	311.0	0.96	2.94	4.77	6.87	0.27	73.68
296.6	0.77	9.80	4.90	1.64	-0.01	73.97	309.3	13.59	51.23	2.25	5.57	-0.08	73.71
301.3	3.53	28.87	2.40	2.57	-0.07	73.87	311.1	0.77	2.40	3.90	6.75	0.09	73.68
298.6	0.62	6.39	4.79	2.05	0.03	73.93	306.6	0.71	3.34	4.77	4.48	0.09	73.77
298.6	0.81	8.66	4.90	1.95	-0.06	73.93	311.3	4.82	15.12	2.25	6.70	-0.09	73.67
300.6	0.60	5.09	3.97	2.47	0.01	73.89	313.3	13.59	35.91	2.25	7.95	-0.20	73.63
301.5	0.60	4.69	3.97	2.68	0.00	73.87	315.3	9.88	20.88	2.25	9.94	0.20	73.59
303.4	16.43	108.6	2.22	3.18	-0.05	73.83	315.3	0.58	1.20	4.79	10.09	0.35	73.59
301.6	1.02	7.76	4.90	2.77	0.06	73.87	317.3	19.76	36.89	2.30	11.25	-0.38	73.55
303.6	0.62	3.97	3.97	3.27	-0.03	73.83	318.2	1.31	2.16	3.82	12.72	0.13	73.53
306.3	1.12	5.45	1.45	4.33	0.07	73.77	312.9	0.67	1.72	3.97	8.17	0.32	73.64
305.5	10.50	56.68	2.22	3.89	-0.06	73.79	319.3	4.58	7.18	2.34	13.38	-0.47	73.51
308.2	1.06	4.36	3.97	5.11	0.01	73.73	320.3	1.22	1.71	3.79	15.03	-0.06	73.49
308.2	0.76	3.20	3.84	4.96	-0.14	73.73	321.3	5.56	7.21	2.34	16.21	-0.24	73.47
310.0	0.71	2.45	3.86	6.08	0.06	73.70	323.3	1.25	1.33	3.79	19.70	0.19	73.43
308.2	0.71	2.78	4.77	5.36	0.26	73.73	325.2	2.21	2.08	2.40	22.28	-0.60	73.39
307.4	10.13	47.02	2.22	4.53	-0.20	73.75							

Table 1. Continued

T^a (K)	m^b (mg)	$V_{N_2}^c$ (dm ³)	gas flow (dm ³ /h)	p^d (Pa)	$p_{\text{exp}} - p_{\text{calc}}$ (Pa)	$\Delta_f^s H_m$ or $\Delta_{\text{cr}}^s H_m$ (kJ·mol ⁻¹)	T^a (K)	m^b (mg)	$V_{N_2}^c$ (dm ³)	gas flow (dm ³ /h)	p^d (Pa)	$p_{\text{exp}} - p_{\text{calc}}$ (Pa)	$\Delta_f^s H_m$ or $\Delta_{\text{cr}}^s H_m$ (kJ·mol ⁻¹)
Indole; $\Delta_f^s H_m$ (298.15 K) = 65.30 ± 0.59 kJ·mol ⁻¹													
$\ln(p/\text{Pa}) = \frac{296.54}{R} - \frac{85841.99}{R \cdot (T, \text{K})} - \frac{68.9}{R} \ln\left(\frac{T, \text{K}}{298.15}\right)$													
328.3	2.60	1.84	2.40	29.6	-0.8	63.23	343.2	3.55	0.900	2.40	82.9	0.3	62.20
331.1	3.01	1.68	2.40	37.6	0.6	63.03	346.2	3.53	0.739	2.40	100.3	0.6	61.99
334.2	3.24	1.48	2.40	45.9	0.2	62.82	349.2	3.56	0.619	2.40	120.9	1.0	61.79
337.2	3.57	1.34	2.40	55.8	-0.1	62.61	352.2	3.43	0.499	2.40	144.4	0.7	61.58
340.2	3.53	1.08	2.40	68.7	0.6	62.41	355.2	2.55	0.319	2.40	167.5	-4.1	61.37
N-Methylindole; $\Delta_f^s H_m$ (298.15 K) = 64.31 ± 0.435 kJ·mol ⁻¹													
$\ln(p/\text{Pa}) = \frac{307.37}{R} - \frac{87625.05}{R \cdot (T, \text{K})} - \frac{78.2}{R} \ln\left(\frac{T, \text{K}}{298.15}\right)$													
295.6	0.81	3.73	3.18	4.01	-0.01	64.51	307.8	0.98	1.57	3.15	11.53	0.23	63.56
298.6	0.85	3.11	3.98	5.07	-0.16	64.28	313.4	1.02	1.05	3.15	17.98	0.39	63.12
298.6	0.93	3.28	3.18	5.27	0.04	64.28	318.3	1.10	0.804	2.41	25.37	-0.15	62.74
300.6	0.98	2.90	3.00	6.25	0.03	64.12	318.3	1.06	0.787	3.15	24.83	-0.69	62.74
303.4	0.92	2.10	3.15	8.14	0.26	63.90	323.4	1.22	0.625	2.50	36.12	-0.93	62.34
305.4	1.16	2.35	3.00	9.12	-0.18	63.75	328.2	1.47	0.522	2.09	52.07	0.12	61.96
308.2	0.90	1.41	2.41	11.84	0.17	63.53	333.2	1.10	0.283	1.13	72.02	-0.96	61.57
310.0	0.69	0.941	2.09	13.50	0.02	63.39	338.2	1.43	0.255	1.02	103.99	2.72	61.18
2,3-Dimethylindole; $\Delta_f^s H_m$ (298.15 K) = 86.75 ± 0.29 kJ·mol ⁻¹													
$\ln(p/\text{Pa}) = \frac{297.69}{R} - \frac{94739.26}{R \cdot (T, \text{K})} - \frac{26.8}{R} \ln\left(\frac{T, \text{K}}{298.15}\right)$													
313.2	0.33	11.22	4.99	0.50	0.02	86.35	343.3	0.58	1.10	4.41	8.78	0.11	85.54
318.2	0.43	9.20	4.42	0.79	-0.02	86.21	348.1	1.77	2.28	4.41	13.04	-0.02	85.41
323.2	0.23	2.94	4.42	1.30	-0.03	86.08	348.1	0.88	1.10	4.42	13.30	0.19	85.41
328.2	0.34	2.58	4.42	2.23	0.06	85.94	353.1	1.30	1.10	4.42	19.63	-0.29	85.28
325.6	0.58	5.87	4.82	1.67	-0.03	86.01	358.1	1.91	1.10	4.42	28.94	-0.89	85.14
333.2	0.39	1.84	4.42	3.58	0.11	85.81	363.2	2.95	1.10	4.42	44.64	0.32	85.01
338.1	0.35	1.10	4.41	5.30	-0.18	85.68	368.2	1.78	0.454	1.82	65.39	0.21	84.87
332.9	0.27	1.38	2.38	3.27	-0.10	85.82	373.2	2.79	0.484	1.82	96.42	2.23	84.74

^a Temperature at 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 condensation temperature, $T = 243.15$ K.

vapor pressure p_i^{sat} at different temperatures 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:

$$p_i^{\text{sat}} = m_i \cdot R \cdot T_a / V \cdot M_i \quad V = V_{N_2} + V_i \quad (V_{N_2} \gg V_i) \quad (1)$$

where $R = 8.31447 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; 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 gaseous phase. V_{N_2} 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_{N_2} was determined from the flow rate and time measurements.

2.3. Combustion Calorimetry. For measurements of the enthalpies of combustion of 2,3-benzofuran and indole, an isoperibolic macrocalorimeter 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.¹¹ The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon but neither was detected. The energy equivalent of the calorimeter ϵ_{calor} was determined with a standard reference sample of benzoic acid (sample SRM 39j, NIST). From eight experiments, ϵ_{calor} was measured to be $25112.6 \pm 1.9 \text{ J} \cdot \text{K}^{-1}$. For the reduction of the data to standard conditions, conventional procedures¹² were used. The densities of the liquid compounds were taken from the Aldrich catalogue. Corrections for nitric acid formation were based on titration with $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ NaOH(aq)}$. We used the value $-59.7 \text{ kJ} \cdot \text{mol}^{-1}$ for the molar energy of formation of $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ HNO}_3$ from N_2 , O_2 , and water.¹³ The atomic weights used were those recommended by the IUPAC commission.¹⁴

2.4. Phase Transitions in the Solid State. DSC Measurements. Information about the possible phase transitions in the sample under study is indispensable for the vapor pressure measurements

Table 2. Compilation of Data on Enthalpies of Vaporization $\Delta^{\text{f}}H_{\text{m}}$ and Sublimation $\Delta^{\text{g}}H_{\text{m}}$ Enthalpies of the Five-Membered Compounds under Study

compounds	technique ^a	T-range (K)	C_p^{l} or C_p^{cr} ($\Delta^{\text{f}}C_p$ or $\Delta^{\text{g}}C_p$) ^b (J·mol ⁻¹ ·K ⁻¹)	$\Delta^{\text{f}}H_{\text{m}}$ or $\Delta^{\text{g}}H_{\text{m}}$ (T_{av}) (kJ·mol ⁻¹)	$\Delta^{\text{f}}H_{\text{m}}$ or $\Delta^{\text{g}}H_{\text{m}}$ 298 K ^c (kJ·mol ⁻¹)	ref
indene (l)	E	369.2–457.0	186.9 (–63.8)	43.9	51.2 ± 0.3	20
	n/a	289.5–454.7			47.8	21
	T	274.6–338.7		49.8	50.3 ± 0.1	this work
2,3-benzofuran (l)	E		178.7 (–57.1)		48.4 ± 0.2	23
	T	278.7–313.4		49.0	48.8 ± 0.3	this work
					48.6 ± 0.2	(average)
indole (l)	T	328.3–355.2	224.4 (–68.9)	62.3	65.3 ± 0.6	this work
indole (cr)	K	291.7–319.0	129.5 (–20.2)	74.9	75.1	27
	VG	298–315		95.0	69.9 ± 0.9	28
	K	275–303		77.8	95.2	25
	K	275.2–291.1		78.4	77.6 ± 1.7	29
	K	290.4–325.2		73.7	78.1 ± 1.1	6
	T				73.9 ± 0.4	this work
					62.2 ± 1.6	7
N-methylindole(l)	C	334.3	260.1 (–78.2)	67.1	62.2 ± 1.6	7
	T	295.6–338.2		63.0	64.3 ± 0.4	this work
2,3-dimethylindole (cr)	T	313.2–373.2	173.7 (–26.8)	85.5	86.8 ± 0.3	this work

^a Techniques: E = ebulliometry; VG = viscosity gauge; C = calorimetry; T = transpiration; K = Knudsen-effusion method. ^b Values of $\Delta^{\text{f}}C_p$ have been derived from the isobaric molar heat capacity of the liquid esters C_p^{l} according to procedure developed by Chickos and Acree.^{18,19} ^c Vapor pressure data available in the literature were treated using eqs 2 and 3 to evaluate enthalpy of vaporization at $T = 298$ K in the same way as our own results in Table 1.

using the transpiration method. Such knowledge helps choosing of the temperature range for investigation and allows vapor pressure measurements within the range where the compound of interest exists in only a certain crystalline modification. That is why, prior to the transpiration experiments, the crystalline samples are usually studied by DSC. The thermal behavior of indole including its melting temperature and enthalpy of fusion was determined with a Perkin-Elmer DSC-2. The fusion temperature and enthalpies were determined as the peak onset temperature and by using a straight baseline for integration, respectively. The temperature and heat flow rate scale of the DSC was calibrated by measuring high-purity indium. The thermal behavior of each specimen was investigated during heating the sample at a cooling rate of 10 K·min⁻¹. The uncertainty for temperature is ±0.5 K and for enthalpy of fusion ±1 J·g⁻¹. The DSC measurements were repeated in triplicate and values agreed within the experimental uncertainties ±0.2 kJ·mol⁻¹ for the enthalpy of fusion and ±0.5 K for the melting temperature.

2.5. Computations. Standard-principles molecular orbital calculations were performed with the Gaussian 03 Rev.04 series of programs.¹⁵ Energies were obtained at the G3(MP2) level of theory. G3 theory is a procedure for calculating energies of molecules containing atoms of the first and second row of the periodic chart 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.¹⁶ This method saves considerable computational time compared to G3 theory with some loss in accuracy but is much more accurate than G2(MP2) theory. For all the species included in this study, full geometry optimizations were carried out at the HF/6-31G(d) 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 the minima found

at the HF/6-31G(d) level were again fully reoptimized at the MP2(FULL)/6-31G(d) level. G3(MP2) 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 ref 16). The enthalpy values of the compounds studied at $T = 298$ K, were evaluated according to standard thermodynamic procedures.¹⁷

3. RESULTS AND DISCUSSION

3.1. Vapor Pressure Vaporization and Sublimation Enthalpies. Experimental vapor pressures of indene derivatives measured in this work were treated with eqs 2 and 3, respectively

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

$$\Delta^{\text{g}}H_{\text{m}}(T) = -b + \Delta^{\text{g}}C_p \cdot T \quad (3)$$

where p_i^{sat} is vapor pressure, a and b are adjustable parameters (Table 1), T_0 is an arbitrarily chosen reference temperature (T_0 is 298.15 K in this work), and $\Delta^{\text{g}}C_p$ is the difference of the molar heat capacities of the gaseous and the liquid phase. Values of $\Delta^{\text{f}}C_p$ were calculated from isobaric molar heat capacity C_p^{l} of indene derivatives using the group contribution method of Chickos and Acree.^{18,19} Equations 1–3 are also valid for the study of the solid samples. For this case the enthalpy of sublimation is derived from eq 3 by using the appropriate values of C_p^{cr} and $\Delta^{\text{g}}C_p$. Experimental results, and parameters a and b are listed in Tables 1 and 2. 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 average deviation of experimental

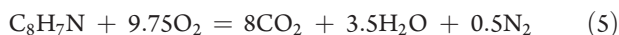
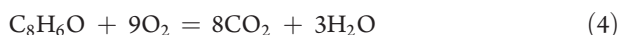
Table 3. Thermochemical Results at $T = 298.15$ K ($p^\circ = 0.1$ MPa), $\text{kJ} \cdot \text{mol}^{-1}$

compound	$\Delta_f H_m^\circ(\text{l or cr})$	$\Delta_f^\circ H_m$ or $\Delta_{\text{cr}}^\circ H_m$	$\Delta_f H_m^\circ(\text{g})$
indene (l)	110.4 ± 1.3 [20]	50.3 ± 0.1^a	160.7 ± 1.3
2,3-benzofuran (l)	-34.8 ± 0.6 [8] -35.3 ± 1.6 -35.1 ± 1.2 (average)	48.6 ± 0.2^a	13.5 ± 1.2
indole (cr)	86.7 ± 0.8 [23] 86.5 ± 1.3 86.6 ± 1.1 (average)	73.9 ± 0.4^a	160.5 ± 1.2
N-methylindole (l)	93.6 ± 2.3 [7]	64.3 ± 0.4^a	157.9 ± 2.3
2-methylindole (cr)	37.7 ± 2.7 [7]	88.7 ± 2.4 [7]	126.4 ± 3.6
3-methylindole (cr)	47.4 ± 2.3 [7]	90.4 ± 1.9 [7]	137.8 ± 3.0
2,3-dimethylindole	4.2 ± 1.0 [23]	86.8 ± 0.3^a	91.0 ± 1.1

^a Selected values from Table 1.

$\ln(p_i^{\text{sat}})$ values from this linear correlation (uncertainties in values of $\Delta_f^\circ C_p$ are not taken into account). This experimental and calculation procedure has been validated with measurements of vapor pressures of *n*-alkanols.⁹ 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. 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 sublimation was assumed to be identical with the deviation of experimental $\ln(p_i^{\text{sat}})$ values from this linear correlation.

3.2. Enthalpies of Formation from Combustion Calorimetry. Results of combustion experiments on 2,3-benzofuran and indole are summarized in Table 3. The values of the standard specific energy of combustion, $\Delta_c u^\circ$, the standard molar enthalpy of combustion, $\Delta_c H_m^\circ$, and the standard molar enthalpy of formation in the liquid or crystalline state $\Delta_f H_m^\circ(\text{l or cr})$ were based on the reactions:



Values of the molar enthalpies of formation, $\Delta_f H_m^\circ(\text{l or cr})$ of compounds under study have been obtained from the enthalpic balance for reactions 4 or 5 above according to Hess' law using the molar enthalpies of formation of $\text{H}_2\text{O}(\text{l})$ and $\text{CO}_2(\text{g})$ as assigned by CODATA.¹⁴ A summary of typical combustion experiments with the 2,3-benzofuran and indole is given in Tables S1 and S2 (Supporting Information). The individual values of the standard specific energies of combustion of 2,3-benzofuran, $\Delta_c u^\circ$, are given as follows (in $\text{J} \cdot \text{g}^{-1}$): 2,3-benzofuran: -33598.1 , 33589.2 , 33574.4 , 33585.1 , 33587.4 with the mean values of $\Delta_c u^\circ = -33586.8 \pm 3.8 \text{ J} \cdot \text{g}^{-1}$ and $\Delta_c H_m^\circ = -3970.3 \pm 1.2 \text{ kJ} \cdot \text{mol}^{-1}$. The individual values of the standard specific energies of combustion of indole, $\Delta_c u^\circ$, are given as follows (in $\text{J} \cdot \text{g}^{-1}$): 36128.8 , 36124.7 , 36140.5 , 36126.7 , 36146.3 , $\Delta_c u^\circ = -36133.4 \pm 4.2 \text{ J} \cdot \text{g}^{-1}$, and $\Delta_c H_m^\circ = -4235.0 \pm 1.3 \text{ kJ} \cdot \text{mol}^{-1}$. The uncertainties assigned to $\Delta_f H_m^\circ$ are twice the overall standard deviation and include the uncertainties from calibration, 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 .

3.3. Comparison with the Earlier Literature Values. *Indene.* The only previous determination of the standard molar enthalpy of formation $\Delta_f H_m^\circ(\text{l})$ of indene (Table 3) was made by Stull et al.²⁰ using combustion calorimetry. Very accurate vapor pressures were also reported by Stull et al.²⁰ but in the temperature range close to the boiling point. Earlier low temperature measurements were reported by Stull²¹ from the database of the Dow company; however, methods and purities of samples are unknown. Comparison of the available data with our own vapor pressures for indene are given in Figure S1 (Supporting Information). We obtained $\Delta_f^\circ H_m = (50.3 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}$ for indene by transpiration, and this value is slightly different (Table 2) from the value derived from the high-temperature by Stull et al.²⁰ In our opinion the difference is rather due to the long temperature adjustment to the reference temperature. In this case our data are more reliable, because the reference temperature 298 K was included within our experimental range measured by transpiration.

2,3-Benzofuran. Previous determinations of the standard molar enthalpy of formation $\Delta_f H_m^\circ(\text{l})$ of 2,3-benzofuran, were made by Steele and Chirico, by means of combustion calorimetry.⁸ Unfortunately details of this study are not available and the information is only cited by the NIST-database.²² Our new result $\Delta_f H_m^\circ(\text{l}) = -35.3 \pm 1.6 \text{ kJ} \cdot \text{mol}^{-1}$ from combustion calorimetry is in excellent agreement with the previous measurements by Steele and Chirico^{8,22} $\Delta_f H_m^\circ(\text{l}) = -34.8 \pm 0.6 \text{ kJ} \cdot \text{mol}^{-1}$ (Table 3). Also the enthalpy of vaporization of 2,3-benzofuran, reported by Steele and Chirico⁸ (apparently from the ebulliometry) is in excellent agreement with our result from the transpiration which was measured near the reference temperature (Table 2).

Indole. The most recent standard enthalpy of formation, $\Delta_f H_m^\circ(\text{cr})$, of indole was reported by Good²³ from combustion calorimetry. The earlier measurements of enthalpies of combustion^{25,26} have been disregarded according to a recommendation by Pedley et al.²⁴ We repeated combustion experiments on indole to check our procedures. Our new result for $\Delta_f H_m^\circ(\text{cr}) = 86.5 \pm 1.3 \text{ kJ} \cdot \text{mol}^{-1}$ strongly supports Good's²³ value of $86.7 \pm 0.8 \text{ kJ} \cdot \text{mol}^{-1}$. Determinations of the enthalpies of sublimation of indole have been made by a number of groups in recent years (Table 2). Scatter of the observed^{25–29} values $\Delta_{\text{cr}}^\circ H_m(298.15 \text{ K})$ ranges from 70 to 95 $\text{kJ} \cdot \text{mol}^{-1}$ (Table 2). The value of $\Delta_{\text{cr}}^\circ H_m$ for indole, $73.9 \pm 0.4 \text{ kJ} \cdot \text{mol}^{-1}$, measured in this work generally meets the average of the available values and it is very close to the result by Serpinski et al.²⁷ However, our sublimation enthalpy is slightly lower than the most recent Knudsen-effusion result by Ribeiro da Silva et al.⁶ The experimental vapor pressures for indole from effusion and transpiration methods are compared in Figure S2 (Supporting Information). Results from both studies are quite close; however, the relatively large scatter of the effusion data on the edges could cause some fluctuation of the sublimation enthalpy. To ascertain our transpiration results, the vapor pressures of indole above the melting point have been performed and the vaporization enthalpy together with the fusion enthalpy of indole have been used to obtain sublimation enthalpy of indole independently (see section 3.5).

2,3-Dimethylindole. The standard molar enthalpy of formation, $\Delta_f H_m^\circ(\text{cr})$, of indole was reported by Good²³ from combustion calorimetry. The molar enthalpy of sublimation for this compound was measured in this work for the first time (Tables 1 and 2).

3.4. Enthalpy of Fusion of Indole. The melting temperature $T_{\text{fus}} = 325.9$ K and the enthalpy of fusion $\Delta_{\text{cr}}^1 H_{\text{m}} = 10.6 \pm 0.2$ $\text{kJ} \cdot \text{mol}^{-1}$ have been measured for indole in the present study using DSC. No phase transitions other than melting have been detected. In general, the experimental enthalpy of fusion measured by DSC are obtained at the melting temperature T_{fus} . Because of the difference in the reference temperatures, the experimental enthalpy of fusion needs to be adjusted to $T = 298$ K. The adjustment was calculated from the equation:³⁰

$$\begin{aligned} & \{ \Delta_{\text{cr}}^1 H_{\text{m}}(T_{\text{fus}}/\text{K}) - \Delta_{\text{cr}}^1 H_{\text{m}}(298 \text{ K}) \} / (\text{J} \cdot \text{mol}^{-1}) \\ &= \{ (0.75 + 0.15C_p^{\text{cr}}) [(T_{\text{fus}}/\text{K}) - 298 \text{ K}] \\ & - \{ (10.58 + 0.26C_p^{\text{l}}) [(T_{\text{fus}}/\text{K}) - 298 \text{ K}] \} \end{aligned} \quad (6)$$

where the isobaric molar heat capacities, C_p^{cr} and C_p^{l} of the solid and the liquid carbazoles (given in Table 2) and calculated according to procedure developed by Chickos and Acree.^{18,19} With this adjustment (the uncertainty of the correlation was not taken into account), the molar enthalpy of fusion, $\Delta_{\text{cr}}^1 H_{\text{m}}(298 \text{ K}) = 9.2 \pm 0.2$ $\text{kJ} \cdot \text{mol}^{-1}$ was calculated.

3.5. Consistency Test of the Vaporization, Sublimation and Fusion Enthalpies of Indole. Because a significant discrepancy between available experimental data for indole has been found (Table 2), 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 measured for indole at $T = 298.15$ K (Tables 1 and 2) involves a comparison with the experimental enthalpy of fusion adjusted to the reference temperature. In this work the sample of indole was investigated by transpiration in both ranges, above and below its temperature of melting, $T_{\text{fus}} = 325.9$ K. The value of $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}(298 \text{ K}) = 73.9 \pm 0.4$ $\text{kJ} \cdot \text{mol}^{-1}$ was obtained in this work from measurements in the temperature range 290.4–325.2 K and the vaporization enthalpy for indole $\Delta_{\text{v}}^{\text{g}} H_{\text{m}}(298 \text{ K}) = 65.3 \pm 0.6$ $\text{kJ} \cdot \text{mol}^{-1}$ from measurements in the temperature range 328.3–355.2 K. The enthalpy of fusion calculated as the difference $\Delta_{\text{cr}}^1 H_{\text{m}}(298.15 \text{ K}) = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}} - \Delta_{\text{v}}^{\text{g}} H_{\text{m}}$ (both values referring to $T = 298$ K) $= 8.6 \pm 0.7$ $\text{kJ} \cdot \text{mol}^{-1}$ compares to the value measured experimentally, $\Delta_{\text{cr}}^1 H_{\text{m}}(298 \text{ K}) = 9.2 \pm 0.4$ $\text{kJ} \cdot \text{mol}^{-1}$ (see section 3.4). The enthalpy of fusion $\Delta_{\text{cr}}^1 H_{\text{m}}$ calculated as the difference between $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}$ and $\Delta_{\text{v}}^{\text{g}} H_{\text{m}}$ is in excellent agreement with the value measured directly by calorimetry. Thus, our new results for vaporization and sublimation enthalpies of indole have been shown to be consistent.

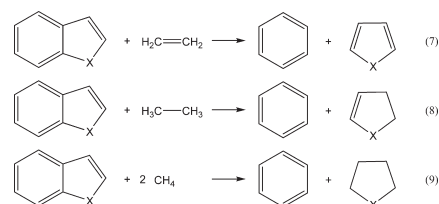
3.6. Calculation of the Gas Phase Enthalpies of Formation. Quantum Chemical Calculations. Values of sublimation and vaporization enthalpies of compounds under study selected in Table 2 can now be used together with the results from combustion experiments (Table 3) for further calculation of the gas standard enthalpies of formation, $\Delta_{\text{f}} H_{\text{m}}^{\circ}(\text{g})$ at 298 K. The resulting experimental values of $\Delta_{\text{f}} H_{\text{m}}^{\circ}(\text{g})$ are given in the last column in Table 3, and they can be now compared with the theoretical results from quantum chemical calculations.

We have calculated using G3(MP2) total energies E_0 at $T = 0$ K and enthalpies H_{298} at $T = 298$ K (Table S3, Supporting Information). In standard Gaussian- n theories, theoretical standard enthalpies of formation, $\Delta_{\text{f}} H_{\text{m}}^{\circ}(\text{g})$, are calculated through atomization reactions and bond separation reactions.³¹ In this work we have applied the atomization procedure (AT) and the following reactions for calculation enthalpies of five-membered ring heterocycles.

Table 4. Results of G3MP2 Calculation of the Standard Enthalpy of Formation $\Delta_{\text{f}} H_{\text{m}}^{\circ}(\text{g})$ for the Molecules Studied in This Work in the Gaseous Phase at 298.15 K, $\text{kJ} \cdot \text{mol}^{-1}$

compounds	AT	AT(corr)	(7)	(8)	(9)	exp	Δ^a
indene	152.5	161.6	156.7	158.5	154.6	160.7 ± 1.3	−0.9
2,3-benzofuran	6.4	16.6	8.1	14.4	6.9	13.5 ± 1.2	−3.1
indole	158.8	167.8	158.5		157.4	160.5 ± 1.2	−7.3
N-methylindole	149.1	158.2	149.7			157.9 ± 2.3	−0.3
2-methylindole	118.9	128.2				126.4 ± 3.6	−1.8
3-methylindole	125.3	134.6				137.8 ± 3.0	3.2
2,3-dimethylindole	86.2	95.8				91.0 ± 1.1	−4.8

^a Difference between column experimental value (column 7) and AT-(corr) (column 3) of this table.



Results of the calculations are given in Table 4. Results calculated from the standard atomization procedure (Table 4, column 2) are systematically less positive than those from the bond separation reactions for all compounds under study. At the same time, the selected bond separation are generally in good agreement with the experimental values (Table 4). However, on one hand, not all the species involved in reactions 7–9 were supported with reliable enthalpies of formation. On the other hand, it is well established that the enthalpies of formation obtained from the first-principle calculations are very sensitive to the choice of the bond separation or isodesmic reactions used for this purpose.³¹ The different quality of the experimental data, involved in estimation, as well as a unbalance of electronic energies calculated for the reaction participants is a possible explanation. In contrast to the bond separation reactions, atomization reactions suggests the quality of the data on the right side (the constituted atoms) is the same for all compounds under study.³¹ However, as mentioned above, the enthalpies of formation from the atomization procedure deviate systematically from the experimental values. In our recent work we have established the following good linear correlation between experimental values and values calculated by atomization enthalpies of formation:²

$$\Delta_{\text{f}} H_{\text{m}}^{\circ}(\text{g})(\text{exp}) / \text{kJ} \cdot \text{mol}^{-1} = 0.992 \times \Delta_{\text{f}} H_{\text{m}}^{\circ}(\text{g})(\text{AT}) + 10.3 \quad (10)$$

Using this correlation, we calculated the “corrected” enthalpies of formation of the compounds under study (Table 4, column 3) and these values are now in good agreement (generally within their boundaries of the experimental uncertainties of 2–3 $\text{kJ} \cdot \text{mol}^{-1}$) with the experimental results. Having established this “modified atomization procedure”, we can now use the eq 10 for estimating enthalpies of the parent compounds from the G3-(MP2) energies without requiring any “suitable” bond separation or isodesmic reactions. Surprisingly, even the “corrected” result from atomization procedure for indole itself deviates by about 7 $\text{kJ} \cdot \text{mol}^{-1}$ from the experimental data. Considerable experimental

Table 5. Strain-Free Increments Γ_i for Estimation of $\Delta_f H_m^\circ(g)$ at $T = 298$ K of Hydrocarbons, Nitrogen, and Oxygen Containing Compounds, $\text{kJ} \cdot \text{mol}^{-1}$ ^a

Γ_i	value	Γ_i	value	Γ_i	value
$\text{CH}_3[\text{C}]$	−42.05 ³²	$\text{CH}_3[\text{N}]$	−42.05 ³⁶	$\text{C}_B\text{H}[2\text{C}_B]$	13.72 ³⁵
$\text{CH}_2[2\text{C}]$	−21.46 ³²	$\text{CH}_2[\text{N}, \text{C}]$	−26.9 ³⁶	$\text{C}_B[\text{C}, 2\text{C}_B]$	23.51 ³⁵
$\text{CH}[3\text{C}]$	−9.04 ³²	$\text{CH}[\text{N}, 2\text{C}]$	−20.0 ³⁶	$\text{C}_B[3\text{C}_B]$	23.51 ³⁵
$\text{C}[4\text{C}]$	−1.26 ³²	$\text{C}[\text{N}, 3\text{C}]$	−16.1 ³⁶	$\text{CH}_2[\text{C}_d]$	26.4 ³⁴
$\text{CH}_2[\text{C}_d, \text{C}]$	−21.46 ^b	$\text{NH}_2[\text{C}]$	19.4 ³⁶	$\text{C}_d\text{H}[\text{C}_d, \text{C}]$	36.0 ³⁴
$\text{CH}[\text{C}_d, 2\text{C}]$	−9.04 ^b	$\text{NH}[2\text{C}]$	64.1 ³⁶	$\text{C}_d[\text{C}_d, 2\text{C}]$	42.7 ³⁴
$\text{C}[\text{C}_d, 3\text{C}]$	−1.26 ^b	$\text{N}[3\text{C}]$	103.2 ³⁶	$\text{C}_d\text{H}[\text{C}_d, \text{C}_B]$	28.5 ³⁴
$\text{CH}_2[\text{O}, \text{C}]$	−33.06 ³⁷	$\text{C}_B[\text{N}, 2\text{C}_B]$	2.1 ³⁶	$\text{C}_d\text{H}[\text{N}, \text{C}_d]$	14.7 ³⁸
$\text{O}[2\text{C}]$	−99.24 ³⁷	$\text{NH}_2[\text{C}_B]$	16.6 ³⁶	$\text{C}_d[\text{N}, \text{C}_d]$	17.0 ³⁸
$\text{C}_B[\text{O}, 2\text{C}_B]$	3.42 ³⁷	$\text{NH}[\text{C}_B, \text{C}]$	65.4 ³⁶	$\text{C}_d\text{H}[\text{O}, \text{C}_d]$	7.7 ³⁹
		$\text{N}[\text{C}_B, 2\text{C}]$	115.2 ³⁶	$\text{C}_d[\text{O}, \text{C}_d, \text{C}]$	8.5 ³⁹

^a C_d represents a double-bonded C atom; C_B , the C atom in a benzene ring. ^b Strain free increments were adopted to be equal of those in alkanes ³⁴

effort has been performed in this work to establish the reliability of the enthalpy of formation of indole. Taking into account that the G3(MP2) is claimed¹⁶ to reproduce experimental data within 3–5 $\text{kJ} \cdot \text{mol}^{-1}$, we would consider such a disagreement as still acceptable. Thus, the results from first principles calculations have helped to establish thermodynamic consistency of the experimental results from transpiration and combustion calorimetry. The G3(MP2) method combined with the modified atomization procedure can be recommended for reliable calculations of $\Delta_f H_m^\circ(\text{gas}, 298 \text{ K})$ of the heterocyclic compounds similar to those studied in this work.

3.7. Strain Effects in the Five-Membered Heterocycles.

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,³² calculated from group contributions (increments):

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

A group is defined like by Benson^{33,34} as a polyvalent atom in a molecule together with all of its ligands. The system of strain-free increments³² 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^{33,34} increments is the possibility of the determining strain enthalpies. Schleyer et al.³² established the values of “strain-free” increments only for hydrocarbons (Table 5). We have extended this system with increments for O- and N-containing organic molecules^{36–39} (Table 5). These increments have been used in this work to derive strains, H_S , of five-membered cyclic compounds (Figures 2 and 3).

Cyclopentane is conventionally strained by 30.9 $\text{kJ} \cdot \text{mol}^{-1}$ (Figure 2). 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. In the case of a five-membered ring the replacement of a methylene group by an oxygen (tetrahydrofuran, $H_S = 24.1 \text{ kJ} \cdot \text{mol}^{-1}$) or a nitrogen atom (pyrrolidine $H_S = 29.2 \text{ kJ} \cdot \text{mol}^{-1}$ and *N*-Me-pyrrolidine $H_S = 23.4 \text{ kJ} \cdot \text{mol}^{-1}$) 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*-pyrrol-1-yl are somewhat more strained in comparison to tetrahydrofuran and pyrrolidine (Figure 2). It is somewhat suspicious, however, that strain in the unsaturated *N*-methylated cycle (2,3-dihydro-1-methyl-1*H*-pyrrole $H_S = 9.2 \text{ kJ} \cdot \text{mol}^{-1}$) is 14 $\text{kJ} \cdot \text{mol}^{-1}$ lower than in the saturated analogue (*N*-Me-pyrrolidine $H_S = 23.4 \text{ kJ} \cdot \text{mol}^{-1}$).

In heterocyclic compounds containing fused benzene rings there is also the similar additional possibility of torsional strain or twisting of the olefin link compared to that of the unsaturated five-membered ring. Is there any quantitative difference between strain caused in the ring by a double bond and by a fused benzene ring? Data on 2,3-dihydrobenzofuran ($H_S = 25.4 \text{ kJ} \cdot \text{mol}^{-1}$) and indolidine ($H_S = 24.2 \text{ kJ} \cdot \text{mol}^{-1}$) have indicated the sizable stabilization of about 7 $\text{kJ} \cdot \text{mol}^{-1}$ in these compounds compared to that of five-membered rings without the fused benzene ring. Taking into account that indan ($H_S = 23.2 \text{ kJ} \cdot \text{mol}^{-1}$) is destabilized to a similar extent as cyclopentene ($H_S = 26.3 \text{ kJ} \cdot \text{mol}^{-1}$), the reason for the additional stabilization of 2,3-dihydrobenzofuran and indolidine is suggested to be the conjugation of the benzene ring with a lone pair of electrons of the heteroatom.

The five-membered rings fused with the benzene ring (indan, 2,3-dihydrobenzofuran, and indolidine) are destabilized approximately at the same level as the *unsaturated* aliphatic five-membered rings (cyclopentene, 2,3-dihydrofuran, 2,3-dihydro-1*H*-pyrrol-1-yl, and 2,3-dihydro-1-methyl-1*H*-pyrrole). What happens to the strain by introduction of the double bond into the five-membered rings fused with the benzene ring (indene, benzofuran, indole, and 1-methylindole)? From Figure 2 general stabilization is apparent: indene is 14.6 $\text{kJ} \cdot \text{mol}^{-1}$ more stable than indan. A substantially more profound stabilization by 56–58 $\text{kJ} \cdot \text{mol}^{-1}$ has been observed (Figure 2) for the conjugation between double bond, heteroatom, and a single benzene ring.

The fusion of the five-membered ring with a second benzene ring increase the amount of stabilization. The results for fluorene ($H_S = -6.3 \text{ kJ} \cdot \text{mol}^{-1}$) showed its stabilization of 30 $\text{kJ} \cdot \text{mol}^{-1}$ in comparison to that for indan ($H_S = 23.2 \text{ kJ} \cdot \text{mol}^{-1}$). Dibenzofuran ($H_S = -11.5 \text{ kJ} \cdot \text{mol}^{-1}$) is only 37 $\text{kJ} \cdot \text{mol}^{-1}$ more stabilized than 2,3-dihydrobenzofuran ($H_S = 25.4 \text{ kJ} \cdot \text{mol}^{-1}$). 9-*H*-Carbazole ($H_S = -20.7 \text{ kJ} \cdot \text{mol}^{-1}$) and 9-methylcarbazole ($H_S = -34.3 \text{ kJ} \cdot \text{mol}^{-1}$) are 43–45 $\text{kJ} \cdot \text{mol}^{-1}$ more stable in comparison to indolidine and *N*-methylindolidine (Figure 2). The general stabilization of these molecules is caused by the conjugation of both benzene rings with the heteroatom, which has entirely overcome the original strain of the cyclopentane ring ($H_S = 30.9 \text{ kJ} \cdot \text{mol}^{-1}$).

It is also interesting to track the evolution of strain in the methylated indols, where experimental data are available (Figure 3).^{5,6,23} It has been already apparent from Figure 2 that all *N*-methylated nitrogen containing five-membered rings (e.g., *N*-methylindole) are about 15 $\text{kJ} \cdot \text{mol}^{-1}$ more stable than parent *N*–H species (e.g., indole itself) due to the different energetic contributions of $\text{NH}[\text{C}_B, \text{C}]$ and $\text{N}[\text{C}_B, 2\text{C}]$ (Table 5). Methylation of the five-membered ring in indole (2-methylindole, 3-methylindole, and 2,3-dimethylindole) has hardly any impact on the strain except for 3-methylindole where a destabilization of about 10 $\text{kJ} \cdot \text{mol}^{-1}$ (in comparison to that for indole) has been observed (Figure 3). However, taking into account the experimental

uncertainty ($\pm 3.0 \text{ kJ} \cdot \text{mol}^{-1}$) of the enthalpy of formation of 3-methylindole, a possible impact on the strain due to the inductive effect of the methyl groups in the 3-position, seems to be questionable.

The investigation of the compounds (Figure 1) covered a broad range of structures of heteroatom derivatives of indene. Discussion of strains of these compounds given in Figures 2 and 3 have shown internal consistency of the data chosen for the thermodynamic analysis. These experimental data can be recommended for validation of the modern first-principles calculations.

■ ASSOCIATED CONTENT

S Supporting Information. TABLE S1. Results from typical combustion experiments for 2,3-benzofuran at $T = 298.15$. TABLE S2. Results from typical combustion experiments for indole at $T = 298.15 \text{ K}$. TABLE S3. G3MP2 Total energies at 0 K and enthalpies at 298 K of the molecules studied in this work. TABLE S4. Correction of the enthalpies of formation calculated with the G3MP2. Figure S1. Plot of vapor pressure against reciprocal temperature for indene. Figure S2. Plot of vapor pressure against reciprocal temperature for indole. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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