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Enthalpy of Formation of Five-Membered Nitrogen-Containing Aromatic Heterocycles

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Abstract—The correlation between experimental and computed (PM3) values of heat of formation of five-membered and fused nitrogen-containing aromatic heterocycles has been revealed. The corresponding linear regression equation has been applied to compute enthalpies of formation of 37 compounds.

Keywords: five-membered nitrogen-containing aromatic heterocycle, heat of formation, semi-empirical quantum chemistry method, PM3

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Direct acquisition of thermochemical data for organic and organoelemental compounds is associated with serious experimental complications, being even impossible in certain cases. In view of this, the simulation methods (including the semi-empirical quantum-chemical ones) have become incredibly important, allowing for computation of enthalpy of formation of various compounds utilizing many available software implementations with moderate system requirements. The semi-empirical methods can be used to reveal the anomalies in determination of enthalpy of formation of organic compounds [1]. Fairly good correlation between the simulated and the experimental values of enthalpy of formation in the cases of adamantane derivatives [2–4], polycyclic aromatic hydrocarbons [5] as well as sulfur- [6, 7], oxygen- [8], and nitrogen-containing [9] heterocycles has allowed application of the quantum-chemical methods to predict enthalpy of formation of such compounds.

In this work we have considered the five-membered and fused nitrogen-containing aromatic heterocycles exhibiting a range of practically important properties. In particular, the phenylpyrrole derivatives have been recognized for valuable therapeutic and pharmacological properties; they have been used to prepare the BODIPY fluorescent azaindene dyes and electroconductive composite pigments as well as to modify the electroconductive properties of the polymers applied in medical studies [10]. Due to the easy processing and a set of chemical, thermal, optical, and electrical properties, polypyrroles have been utilized in photoelectrochemical solar cells (as the photocorrosion inhibitors), in electrochemical capacitors and other energy accumulators, and as catalysts. Polypyrrole has been considered as promising material for artificial neural tissue fabrication [11].

Imidazole and benzimidazole derivatives exhibit a range of pharmacological activity, including antiviral, immunotropic, antitumor, anti-inflammatory, fungicidal, analgesic, and hypotensive action [12–14]. These compounds have been widely used for protection of metal surfaces, as steel corrosion inhibitors, and in cosmetology.

Derivatives of pyrazoles have been used in medicinal chemistry as antibacterial, anti-inflammatory, antiviral, anti-convulsive, and antidepressant agents [15].

Monocyclic tri- and tetrazoles have been widely used in the industrial production of drugs, pesticides, and dyes [15, 16]. Tetrazoles have been successfully applied in medicine, biochemistry, technology, agriculture, analytical chemistry, information recording systems, and fine organic synthesis. *N*-Substitution of tetrazoles allows modification of their biological activity and complex forming properties [17]. The tetrazoles class contains highly efficient corrosion inhibitors, components of pyrotechnical and gas-

Table 1. Simulated enthalpies of formation of five-membered aromatic nitrogen-containing heterocycles (kJ/mol)

Comp. no.	Compound name	Enthalpy of formation[a]			Absolute deviation[b]	
		$\Delta_f H^0_{exp}$	$\Delta_f H^0_{calc}$	$\Delta_f H^{0*}_{calc}$	Δ	Δ*
1	Pyrrole, C_4H_5N	143.2 [23] **108.3±0.50** [24]	113.43	104.7	29.77 5.13	3.6
2	1-Methylpyrrole, C_5H_7N	103.1±0.5 [25]	108.21	100.0	5.11	3.1
3	1,2-Dimethylpyrrole, C_6H_9N	39.8±0.8 [25]	28.98	29.1	10.82	10.7
4	1,2.5-Trimethylpyrrole, $C_7H_{11}N$	4.6 ± 2.6 [26]	27.36	27.7	7.24	6.9
5	1-Phenylpyrrole, $C_{10}H_9N$	226.4±2.4 [27]	231.73	210.6	5.33	15.8
6	1-(*p*-Tolyl)pyrrole, $C_{11}H_{11}N$	187.7±2.7 [27]	192.27	175.3	4.57	12.4
7	2,5-Dimethyl-1-phenylpyrrole, $C_{12}H_{13}N$	157.0±2.9 [28]	157.40	144.1	0.4	12.9
8	Indole, C_8H_7N	156.30±1.25 [27] **164.3±1.3** [29] 181.6 [25]	177.56	162.1	21.26 13.26 4.04	2.2
9	2-Phenylindole, $C_{14}H_{11}N$	254.5±3.6 [30]	275.14	249.4	20.64	5.1
10	1-Methyl-2-phenylindole, $C_{15}H_{13}N$	242.1±3.2 [30]	274.65	249.0	32.55	6.9
11	2-Phenyl-1-ethylindole, $C_{16}H_{15}N$	218.3±3.2 [30]	249,26	226.3	30.96	8.0
12	1*H*-Indoline, C_8H_9N	120.0±2.9 [29]	87.8	81.8	32.2	38.2
13	9*H*-Carbazole, $C_{12}H_9N$	205±3.0 [31] **209.6±3.5** [32] 222.9 [33]	225.60	205.1	20.6 16.0 2.7	4.5
14	9-Methyl-9*H*-carbazole, $C_{13}H_{11}N$	**201.0±4.1** [25] 199.2±2.4 [31]	221.27	201.2	20.27 22.07	0.2
15	9-Ethyl-9*H*-carbazole, $C_{13}H_{11}N$	169.7±2.6 [31]	196.70	179.2	27.0	9.5
16	9-Methyl-2,3,4,9-tetrahydro-1*H*-carbazole, $C_{13}H_{15}N$	93.1 [34]	96.3	89.4	3.2	3.7
17	Imidazole, $C_3H_4N_2$	129.5 [23] 139.3±1.9 [35] **128.0±7.5** [36] 132.9±0.6 [37]	131.02	120.4	1.52 8.28 3.02 1.88	7.6
18	1-Methylimidazole, $C_4H_6N_2$	137.8±4.0 [38]	124.91	115.0	12.89	22.8
19	2-Methylimidazole, $C_4H_6N_2$	**89.1** [39] 89.8±1.1 [40]	88.98	82.8	0.12 0.82	6.3
20	1-Ethylimidazole, $C_5H_8N_2$	110.8±4.3 [38]	99.19	92.0	11.61	18.8
21	2-Ethylimidazole, $C_5H_8N_2$	68.3±4.3 [39]	68.94	64.9	0.64	3.4
22	1-Propylimidazole, $C_6H_{10}N_2$	88.9 [39]	76.56	71.7	12.34	17.2
23	2-Propylimidazole, $C_6H_{10}N_2$	53.0 [39]	46.31	44.6	6.69	8.4
24	1-Isopropylimidazole, $C_6H_{10}N_2$	84.6 [39]	74.33	69.7	10.27	14.9
25	2-Isopropylimidazole, $C_6H_{10}N_2$	53.2 [39]	47.23	45.5	5.97	7.7
26	1-Butylimidazole, $C_7H_{12}N_2$	52.3±4.0 [41]	54.02	51.5	1.72	0.8
27	1-*tert*-Butylimidazole, $C_7H_{12}N_2$	68.3 [39]	53.28	50.9	15.02	17.4

Table 1. (Contd.)

Comp. no.	Compound name	Enthalpy of formation[a]			Absolute deviation[b]	
		$\Delta_f H^0_{exp}$	$\Delta_f H^0_{calc}$	$\Delta_f H^{0*}_{calc}$	Δ	Δ*
28	2-*tert*-Butylimidazole, $C_7H_{12}N_2$	37.6 [39]	30.09	30.1	7.51	7.5
29	1-Pentylimidazole, $C_8H_{14}N_2$	39.0±3.0 [41]	31.36	31.3	7.64	7.7
30	1-Hexylimidazole, $C_9H_{16}N_2$	9.1±4.0 [41]	8.72	11.0	0.38	1.9
31	1-Heptylimidazole, $C_{10}H_{18}N_2$	–12.4±4.0 [41]	–13.95	–9.3	1.55	3.1
32	1-Octylimidazole, $C_{11}H_{20}N_2$	–33.8±4.0 [41]	–36.62	–29.6	2.82	4.2
33	1-Nonylimidazole, $C_{12}H_{22}N_2$	–55.4±4.0 [41]	–59.25	–49.8	3.85	5.6
34	1-Decylimidazole, $C_{13}H_{24}N_2$	–76.9±4.0 [41]	–81.96	–70.2	5.06	6.7
35	1-Undecylimidazole, $C_{14}H_{26}N_2$	–98.4±4.0 [41]	–104.64	–90.5	6.24	7.9
36	1-Dodecylimidazole, $C_{15}H_{28}N_2$	–119.9±4.0 [41]	–127.32	–110.8	7.42	9.1
37	1-Phenylimidazole, $C_9H_8N_2$	264.7±4.3 [46]	250.98	227.8	13.72	36.9
38	2-Phenylimidazole, $C_9H_8N_2$	223.2±1.9 [39]	229.98	209.0	6.78	14.2
39	1-Benzylimidazole, $C_{10}H_{10}N_2$	244.1±3.4 [38]	238.61	216.7	5.49	27.4
40	Benzimidazole, $C_7H_6N_2$	181.7±1.4 [37]	199.78	182.0	18.08	0.3
41	2-Methylbenzimidazole, $C_8H_8N_2$	129.5±2.3 [42]	157.27	143.9	27.80	14.4
42	2-Ethylbenzimidazole, $C_9H_{10}N_2$	114.0±3.0 [42]	137.39	126.2	23.39	12.2
43	2-Propylbenzimidazole, $C_{10}H_{12}N_2$	63.2±1.4 [43]	114.79	105.9	51.59	42.7
44	2-Isopropylbenzimidazole, $C_{10}H_{12}N_2$	78.3±4.2 [43]	116.27	107.2	37.97	28.9
45	2-*tert*-Butylbenzimidazole, $C_{11}H_{14}N_2$	43.3±3.3 [39]	99.23	92.0	55.93	48.7
46	2-Phenylbenzimidazole, $C_{13}H_{10}N_2$	**258.0±2.5** [44] 223.2±1.9 [39]	299.73	271.4	41.73 76.53	13.4
47	2-Benzylbenzimidazole, $C_{14}H_{12}N_2$	239.2±4.4 [44]	303.55	274.9	64.35	35.7
48	Pyrazole, $C_3H_4N_2$	177.4 [23] 181.0±8.8 [36] **179.4±0.8** [37]	204.30	186.0	26.90 23.30 24.90	6.6
49	1-Methylpyrazole, $C_4H_6N_2$	156.5±2.1 [38]	198.96	181.3	41.15	24.8
50	3-Methylpyrazole, $C_4H_6N_2$	140.1±2.6 [45]	165.53	151.3	25.42	11.2
51	1-Ethylpyrazole, $C_5H_8N_2$	132.6±3.3 [38]	173.75	158.7	41.15	26.1
52	1-Propylpyrazole, $C_6H_{10}N_2$	97.6 [39]	153.02	140.1	55.42	42.5
53	1-Isopropylpyrazole, $C_6H_{10}N_2$	104.3 [39]	148.62	136.2	44.32	31.9
54	1,3,5-Trimethylpyrazole, $C_6H_{10}N_2$	81.6±2.6 [45]	118.81	109.5	37.21	27.9
55	1-*tert*-Butylpyrazole, $C_7H_{12}N_2$	90.0 [39]	130.00	119.5	40.00	29.5
56	1-Phenylpyrazole, $C_9H_8N_2$	291.4±4.5 [46]	325.96	294.9	34.56	3.5
57	1-Benzylpyrazole, $C_{10}H_{10}N_2$	276.6±2.9 [38]	312.34	282.7	35.74	6.1
58	Indazole, $C_7H_6N_2$	243.0±1.3 [37] **254.2±4.6** [47]	273.05	247.6	30.05 18.85	6.6

Table 1. (Contd.)

Comp. no.	Compound name	Enthalpy of formation[a]			Absolute deviation[b]	
		$\Delta_f H^0_{exp}$	$\Delta_f H^0_{calc}$	$\Delta_f H^{0*}_{calc}$	Δ	Δ^*
59	1,2,4-Triazole, $C_2H_3N_3$	192.7±0.8 [48] **193.7±1.9** [47] 188.5 [49] 189.8 [50]	216.85	197.3	24.15 23.15 28.35 27.05	3.6
60	1,2,4-Triazolo[1,5-*b*]pyrimidine, $C_5H_4N_4$	351.8±13.2 [51]	372.90	336.9	21.10	14.9
61	Benzotriazole, $C_6H_5N_3$	335.5±1.3 [48]	357.53	323.2	22.03	12.3
62	1*H*-Tetrazole, CH_2N_4	320.0±3.0 [52] **321.1** [53]	360.88	326.2	40.88 39.78	5.1
63	2*H*-Tetrazole, CH_2N_4	334.3[54]	369.9	334.3	35.60	0.0
64	1,5-Dimethyltetrazole, $C_3H_6N_4$	273.2±2.9 [55]	309.58	280.3	36.38	7.1
65	2,5-Dimethyltetrazole, $C_3H_6N_4$	251.2±2.9 [55]	320.71	290.2	69.51	39.0
66	1-Phenyltetrazole, $C_7H_6N_4$	**448.0±3.0** [52] 465.8 [53]	481.95	434.5	33.95 16.15	13.5
67	5-Phenyltetrazole, $C_7H_6N_4$	**413.0±5.9** [52] 407.5 [53]	462.96	417.5	49.96 55.46	4.5
68	1,5-Diphenyltetrazole, $C_{13}H_{10}N_4$	**527.0±4.0** [52] 535.6 [53]	589.83	531.1	62.83 54.23	4.1
69	2,5-Diphenyl-*2H*-tetrazole, $C_{13}H_{10}N_4$	515.1±4.6 [53]	594.58	535.3	79.48	20.2
	Mean absolute deviation	With compounds **12**, **37**, **39**, **43**, **45**, **47**, **52**, **53**, **55**, and **65**			22.80	13.6
		Without compounds **12**, **37**, **39**, **43**, **45**, **47**, **52**, **53**, **55**, and **65**			19.30	9.6

[a] The data used in derivation of the linear regression are given in bold. [b] $\Delta = |\Delta_f H^0_{calc} - \Delta_f H^0_{exp}|$; $\Delta^* = |\Delta_f H^{0*}_{calc} - \Delta_f H^0_{exp}|$.

generating compositions, and explosives. Tetrazoles are used in preparation of pyrazoles, imidazoles, 1,2,4-triazoles, 1,3,4-oxadiazoles, and otherwise inaccessible 3*H*-1,3,4-benotriazepines [18–20]. They have been recognized for extraordinary thermochemical properties and have been used in power-consuming processes [21].

Certain fused 1,2,3-triazoles are efficient against hepatitis C virus and inhibit benzodiazepine and adenosine receptors [22]. Unsubstituted benzotriazole is an efficient corrosion inhibitor. 2-Substituted benzotriazoles and indazoles have been used as optical bleaches and photostabilizers of plastics. Some of the simplest 1-substituted benzotriazoles are important organic reagents [15].

Application of semi-empirical quantum-chemical methods to predict enthalpies of formation of five-membered and fused nitrogen-containing aromatic heterocycles was tested using a set of 69 compounds with the known experimental values of the gas-phase heat of formation (Table 1) [23–55]: monocycles with a single nitrogen atom, pyrrole (**1**) as well as its alkyl (**2**–**4**) and aryl (**5**–**7**) derivatives; monocycles with two nitrogen atoms, imidazole (**17**) as well as its alkyl (**18**–**36**) and aryl (**37**–**39**) derivatives; pyrazole (**48**) as well as its alkyl (**49**–**55**) and aryl (**56**, **57**) derivatives; monocycles with three (**59**) and four (**62**, **63**) nitrogen atoms as well as their alkyl (**64**, **65**) and aryl (**66**–**69**) derivatives; benzo-fused mono- (**8**–**12**), di- (**40**–**47**, **58**), and triazoles (**60**, **61**); dibenzo-fused azoles (**13**–**16**).

The error in the experimental determination of the formation enthalpy of the mentioned compounds did not exceed 6 kJ/mol, except that for 1,2,4-triazolo[1,5-*a*]-

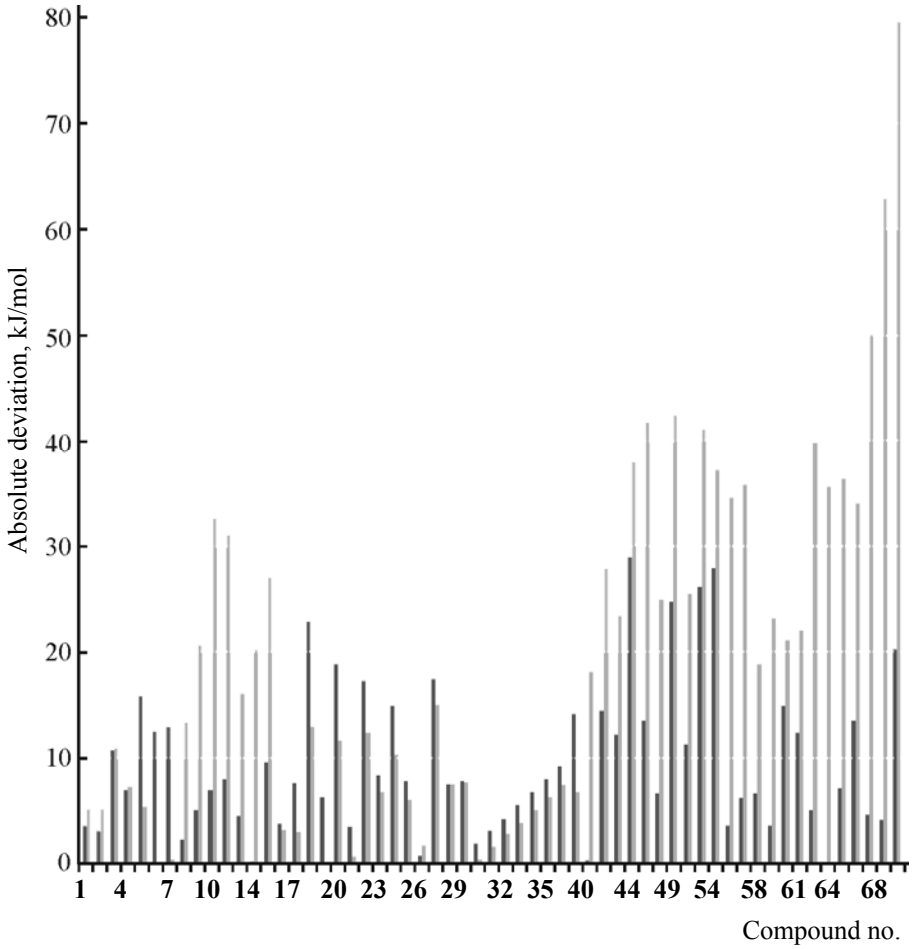

Fig. 1. Absolute deviation of the simulated and experimental values of enthalpy of formation (compounds **1**–**69**; compounds **12**, **37**, **39**, **43**, **45**, **47**, **52**, **53**, **55**, and **65** excluded) before (gray) and after (black) correction.

pyrimidine (**60**) (13.2 kJ/mol), imidazole **17**, and pyrazole **48**. However, the experimental error referenced in the latter two cases (7.5 and 8.8 kJ/mol, respectively [36]) was later improved (0.6 and 0.8 kJ/mol, respectively [37]).

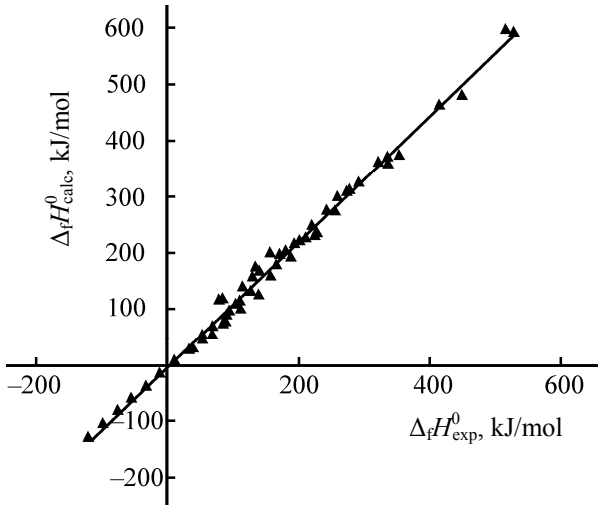

Fig. 2. Relationship between the $\Delta_f H^0_{calc}$ and $\Delta_f H^0_{exp}$ values.

We have applied the PM3, MINDO, AM1, and MNDO semi-empirical quantum-chemical methods implemented in MOPAC software package to optimize geometry and simulate the formation enthalpy for all the above-listed compounds.

In the cases of indoline (**12**), 2-benzyl- (**47**), 2-*tert*-butyl- (**45**), and 2-propylbenzimidazole (**43**), 1-propyl- (**52**), 1-isopropyl- (**53**), and 1-*tert*-butylpyrazole (**55**), and 2,5-dimethyltetrazole (**65**), the simulated $\Delta_f H^0_{calc}$ values differed from the experimental $\Delta_f H^0_{exp}$ ones by 30–70 kJ/mol. In the cases of 1-phenyl- and 1-benzylimidazole (**37**, **39**) the difference was smaller (13.72 and 5.49 kJ/mol, respectively) but resulted in significant deviation from the linear dependence. In the cases of 5-phenyltetrazole (**67**), 1,5-diphenyl-1*H*-tetrazole (**68**), and 2,5-diphenyl-2*H*-tetrazole (**69**), the difference between the experimental and the simulated

Table 2. Absolute deviations of the experimental enthalpies of formation from those simulated via the PM3, PM6, and PM7 methods (kJ/mol)

Comp. no.	$\Delta_f H^0_{exp}$	PM7	PM6	PM3		Comp. no.	$\Delta_f H^0_{exp}$	PM7	PM6	PM3	
				before correction	after correction					before correction	after correction
1	25.90	2.34	0.63	5.1	3.6	**19**	21.50	9.46	8.16	0.1	6.3
2	24.60	4.77	1.55	5.1	3.1	**21**	16.30	10.50	11.00	0.6	3.4
3	9.50	8.20	16.82	10.8	10.7	**40**	43.43	33.77	32.13	18.1	0.3
13	50.10	24.98	13.51	16.0	4.5	**48**	42.90	7.91	0.29	24.9	6.6
14	47.60	34.02	26.15	20.3	0.2	**58**	58.08	20.88	8.37	18.9	6.6
15	40.56	30.63	22.47	27.0	9.5	**62**	76.60	6.49	15.82	39.8	5.1
16	22.30	14.52	0.84	3.2	3.7	**63**	79.95	15.06	0.17	35.6	0.0
17	31.76	6.11	9.50	3.0	7.6	Mean absolute deviation		15.31	11.16	15.23	4.75

Table 3. Simulated enthalpies of formation, kJ/mol

Comp. no.	Compound name	$\Delta_f H^0_{calc}$	$\Delta_f H^{0*}_{calc}$	Comp. no.	Compound name	$\Delta_f H^0_{calc}$	$\Delta_f H^{0*}_{calc}$
69	2,4-Dimethylpyrrole, C_6H_9N	31.84	31.7	**82**	3,5-Diethyl-4-methyl-1*H*-pyrazole, $C_8H_{14}N_2$	43.08	41.7
70	2,4-Dimethyl-3-ethyl-1*H*-pyrrole, $C_8H_{13}N$	–25.59	–19.7	**83**	3,5-Diisopropyl-4-methyl-1*H*-pyrazole, $C_{10}H_{18}N_2$	3.95	6.7
71	2,5-Dimethyl-3-ethyl-1*H*-pyrrole, $C_8H_{13}N$	–29.74	–23.4	**84**	1-Methyl-3,5-di-*tert*-butylpyrazole, $C_{12}H_{22}N_2$	3.17	6.0
72	2,5-Dimethyl-1-ethylpyrrole, $C_8H_{13}N$	0.85	3.9	**85**	1,4-Dimethyl-3,5-di-*tert*-butylpyrazole, $C_{13}H_{24}N_2$	–11.43	–7.0
73	1-Butylpyrrole, $C_8H_{13}N$	39.76	38.8	**86**	3,5-Diethyl-4-methylpyrazole, $C_8H_{14}N_2$	44.09	42.6
74	2,5-Diethyl-1*H*-pyrrole, $C_8H_{13}N$	–11.31	–6.9	87	1-Methyl-5-*tert*-butylpyrazole, $C_8H_{14}N_2$	97.66	90.6
75	1-Butyl-2-methyl-1*H*-imidazole, $C_8H_{14}N_2$	13.13	14.9	**88**	2,3-Dimethylindole, $C_{10}H_{11}N$	96.55	89.6
76	1-Butyl-4-methyl-1*H*-imidazole, $C_8H_{14}N_2$	14.38	16.1	**89**	9*H*-Purine, $C_5H_4N_4$	260.47	236.3
77	1-Butyl-5-methyl-1*H*-imidazole, $C_8H_{14}N_2$	13.13	14.9	**90**	5-Ethyl-2*H*-tetrazole, $C_3H_6N_4$	297.43	269.4
78	2-Methyl-1-pentyl-1*H*-imidazole, $C_9H_{16}N_2$	–9.52	–5.3	**91**	2-Ethyl-2*H*-tetrazole, $C_3H_6N_4$	336.09	304.0
79	5-Methyl-1-pentyl-1*H*-imidazole, $C_9H_{16}N_2$	–7.55	–3.6	**92**	1-Ethyl-5-methyl-1*H*-tetrazole, $C_4H_8N_4$	283.09	256.6
80	4-Methyl-1-pentyl-1*H*-imidazole, $C_9H_{16}N_2$	–8.29	–4.2	**93**	5-Ethyl-1-methyl-1*H*-tetrazole, $C_4H_8N_4$	286.85	259.9
81	1-Methyl-3-*tert*-butylpyrazole, $C_8H_{14}N_2$	103.36	95.7	**94**	5-Isopropyl-2*H*-tetrazole, $C_4H_8N_4$	290.22	262.9

Table 3. (Contd.)

Comp. no.	Compound name	$\Delta_f H^0_{calc}$	$\Delta_f H^{0*}_{calc}$	Comp. no.	Compound name	$\Delta_f H^0_{calc}$	$\Delta_f H^{0*}_{calc}$
95	1-Isopropyl-1*H*-tetrazole, $C_4H_8N_4$	300.46	272.1	**101**	1,3-Dimethylindole, $C_{10}H_{11}N$	133.11	122.3
96	1-Phenyl-5-methyl-1*H*-tetrazole, $C_8H_8N_4$	443.10	399.8	**102**	1,2-Dimethylindole, $C_{10}H_{11}N$	131.56	120.9
97	1-Methyl-5-phenyl-1*H*-tetrazole, $C_8H_8N_4$	589.82	531.1	**103**	1-Ethylindole, $C_{10}H_{11}N$	148.84	136.4
98	2-Phenyl-5-methyl-2*H*-tetrazole, $C_8H_8N_4$	451.57	407.3	**104**	3-Ethylindole, $C_{10}H_{11}N$	118.16	108.9
99	5,5'-Bitetrazole, $C_2H_2N_8$	714.67	642.8	**105**	4-Ethylindole, $C_{10}H_{11}N$	124.12	114.3
100	2-(3,5-Dimethylpyrazol-1-yl) benzimidazole, $C_{12}H_{12}N_4$	470.90	424.6				

values was significant (49.96, 62.83, and 79.48 kJ/mol, respectively), but the linearity of the $\Delta_f H^0_{calc} = f(\Delta_f H^0_{exp})$ dependence was preserved; therefore, the data for those compounds were used in the further regression analysis, whereas the data for the ten above-mentioned compounds **12**, **37**, **39**, **43**, **45**, **47**, **52**, **53**, **55**, and **65** were excluded from the analysis in view of the insufficient consistency between the experimental and the simulated values.

The histogram in Fig. 1 displays the increasing absolute deviation Δ between the $\Delta_f H^0_{calc}$ and $\Delta_f H^0_{exp}$ values in the pyrroles → imidazoles → pyrazoles → triazoles → tetrazoles and alkylazoles → arylazoles → benzoazoles → dibenzoazoles series. Increasing of the number of nitrogen atoms in the cycle and replacment of an alkyl substituent with an aryl one resulted in a higher deviation between the experimentally determined values and the corresponding simulated data for five-membered nitrogen-containing heterocycles.

The correlation coefficients between the experimental enthalpy of formation and the values simulated using the PM3, AM1, MNDO, and MINDO methods were 0.9963, 0.9916, 0.9625, and 0.3725, respectively, for the set of 59 considered compounds. It is to be seen that the correlation was fairly good in the cases of the PM3 and AM1 methods, the MNDO provided for the moderately good correlation, and the MINDO method gave poor results. The correlation coefficients were close in the cases of the PM3 and AM1 methods; however, the mean absolute deviation of the values was much lower in the first case (19.3 and 103.2 kJ/mol, respectively). In view of that, the PM3 method was used in further study and could be recommended for prediction of gas-phase enthalpy of formation of five-membered nitrogen-containing heterocycles.

The relationship between the $\Delta_f H^0_{calc}$ and $\Delta_f H^0_{exp}$ values was linear (Fig. 2) and could be expressed in the form of the following regression equation.

$$\Delta_f H^0_{calc} = 1.1173\ \Delta_f H^0_{exp} - 3.5581.$$

The regression equation was used for recalculation of the PM3-simulated heat of formation in order to match them to the experimental data (Table 1). That procedure transformed the simulated $\Delta_f H^0_{calc}$ values into the corrected values $\Delta_f H^{0*}_{calc}$ the mean absolute deviation of the corrected values from the experimental ones (Δ*) reduced twofold, from 19.3 to 9.6 kJ/mol.

Comparison of the enthalpies of formation determined using the PM3 method followed by the correction and those determined using the PM6 and PM7 methods applying the Parameter Model [56] (Table 2) revealed that the deviations attained in this work (4.75 kJ/mol) were about three times lower than those in the case of the PM7 method.

To summarize, the gas-phase enthalpies of formation of five-membered nitrogen-containing heterocyclic compounds as simulated via the PM3 method were in good correlation with the experimentally determined ones. The derived linear regression equation allowed for correction of the quantum-chemical simulation results making them closer to the experimental data. The described method was further applied to determine the gas-phase enthalpy of formation of 37 five-membered nitrogen-containing heterocyclic compounds (Table 3).

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