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Enthalpies of Formation of Polycyclic Aromatic Hydrocarbons

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Abstract—Comparison of the experimental enthalpies of formation of 77 polycyclic aromatic hydrocarbons with those calculated by semiempirical quantum-chemical methods showed that the AM1 approximation ensures the best agreement between the experimental and calculated values. The enthalpies of formation of 60 compounds of this series were calculated using the AM1 method and the corresponding linear regression equation.

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Good correlations were found previously between the experimental enthalpies of formation of thiophene derivatives [1] and oxygen [2], alkyl [3], nitro, nitroxy, and nitroso [4] derivatives of adamantane and the corresponding values calculated by semiempirical quantum-chemical methods; these correlations were represented by linear regression equations which were used to predict enthalpies of formation of compounds belonging to the above series.

The present article deals with polycyclic aromatic hydrocarbons [5] that are known to be key structural fragments in structural organic chemistry. Polycyclic aromatic hydrocarbons attract interest from the viewpoints of both organic chemistry and materials science. Specific electronic properties of these compounds make their use in electronics and optoelectronics (primarily, in the design of electroluminescent devices, field transistors, and solar batteries) quite promising.

Experimental determination of the enthalpies of formation of polycyclic aromatic compounds involves difficulties related to their synthesis, purification (contamination with isomers), and poor solubility; incomplete combustion of these compounds gives rise to large experimental errors in the determination of their enthalpies of formation by combustion calorimetry [6]. Therefore, calculation procedures, including quantum-chemical methods such as AM1, PM3, MNDO, and MINDO, are widely used for this purpose. The choice of the calculation method is dictated by the necessity of obtaining the best correlation between the calculated and experimental enthalpies of formation. In the present work, compounds **I**–**LXXVII** with known experimental heats of formation in the gas phase [6–40] were selected. Complete optimization of geometric parameters of their molecules was performed, and their enthalpies of formation were calculated in terms of the PM3, MINDO, AM1, and MNDO approximations included into MOPAC software package (Table 1). The data for compounds **XXVIII**, **LIX**, **LXI**, **LXIX**, **LXXIV**, and **LXXVII** were excluded, for they deviated most strongly from linear correlation. The correlation coefficients for the remaining compounds were 0.9922 (AM1), 0.9914 (PM3), 0.9540 (MINDO), and 0.9793 (MNDO). According to [41], the correlations obtained for the enthalpies of formation calculated by the AM1 and PM3 methods may be regarded as excellent, whereas MNDO and MINDO calculations ensure only satisfactory correlations.

The best correlation between $\Delta_f H^0_{calc}$ and $\Delta_f H^0_{exp}$ for the gas phase was obtained with the use of the AM1 method; it is represented by the following linear regression equation:

$$\Delta_f H^0_{calc} = 1.1454;\ \Delta_f H^0_{exp} + 10.044. \quad (1)$$

The AM1 enthalpies of formation of compounds **I**–**LXXVII** were then recalculated using Eq. (1). In going from the former ($\Delta_f H^0_{calc}$) to the recalculated values ($\Delta_f H^{0*}_{calc}$) (Table 2), deviations from the experimental enthalpies of formation (Δ and Δ*, respectively) considerably decreased. The average absolute deviation was 13.19 kJ/mol against 41.08 kJ/mol. The largest deviations from the experimental values were

Table 1. Calculated and experimental enthalpies of formation of polycyclic aromatic hydrocarbons

Comp. no.	Compound, formula	Enthalpy of formation $\Delta_f H°$, kJ/mol								
		PM3	Δ	MINDO	Δ	AM1	Δ	MNDO	Δ	experimental[a]
I	Indene, C_9H_8	170.12	8.92	228.95	67.75	191.47	30.27	160.13	1.07	161.2±2.3 [6]
II	Indan, C_9H_{10}	47.08	13.82	85.14	24.24	48.12	12.78	27.10	33.80	**60.9±2.1** [6]
			13.62		24.44		12.58		33.60	60.7±1.5 [36]
			11.99		25.44		11.58		32.60	59.7±2.0 [37]
III	Naphthalene, $C_{10}H_8$	170.18	19.89	231.88	81.59	169.79	19.50	160.37	10.08	**150.3** [7]
			19.58		81.28		19.19		9.77	150.6±1.5 [6]
IV	Azulene, $C_{10}H_8$	340.35	60.35	358.32	78.32	353.17	73.17	301.78	21.78	**280.0** [8]
			51.25		69.22		64.07		12.68	289.1 [7]
			32.35		50.32		45.17		6.22	308 [40]
V	1-Methylnaphthalene, $C_{11}H_{10}$	136.37	23.37	219.88	106.88	142.03	29.03	139.37	26.37	**113.0** [7]
			19.47		102.98		25.13		22.47	116.9±2.7 [9]
VI	2-Methylnaphthalene, $C_{11}H_{10}$	131.53	24.83	206.45	99.75	138.34	31.64	128.61	21.91	**106.7** [7]
			15.43		90.35		22.24		12.51	116.1±2.6 [9]
VII	Acenaphthylene, $C_{12}H_8$	305.96	42.76	388.37	125.17	337.81	74.61	280.95	17.75	**263.2±3.7** [6]
			47.96		130.37		79.81		22.95	258±5.9 [10]
VIII	Biphenylene, $C_{12}H_8$	459.54	42.14	447.29	29.89	503.59	86.19	396.48	20.92	**417.4±1.9** [6]
			39.14		26.89		83.19		23.92	420.4±1.9 [33]
IX	Biphenyl, $C_{12}H_{10}$	201.09	20.79	272.61	92.31	199.17	18.87	192.78	12.48	180.3±3.3 [6]
X	Acenaphthene, $C_{12}H_{10}$	162.51	5.71	237.10	80.30	178.21	22.41	138.70	18.10	156.8±3.1 [6]
			6.51		81.10		22.21		17.30	**156.0±4** [10]
XI	1,2-Dimethylnaphthalene, $C_{12}H_{12}$	104.89	21.34	213.92	130.37	116.18	32.63	124.20	40.65	83.55 [11]
XII	1,4-Dimethylnaphthalene, $C_{12}H_{12}$	101.04	18.53	208.33	125.82	114.54	32.03	119.47	36.96	82.51 [11]
XIII	1,3-Dimethylnaphthalene, $C_{12}H_{12}$	94.81	13.01	194.13	112.33	109.96	28.16	107.48	25.68	81.80 [11]
XIV	1,5-Dimethylnaphthalene, $C_{12}H_{12}$	103.29	21.49	209.56	127.76	114.69	32.89	120.03	38.23	81.80 [11]
XV	1,6-Dimethylnaphthalene, $C_{12}H_{12}$	97.67	15.16	193.87	111.36	110.55	28.04	107.27	24.76	82.51 [11]
XVI	1,7-Dimethylnaphthalene, $C_{12}H_{12}$	96.95	15.15	194.23	112.43	109.91	28.11	107.61	25.81	81.80 [11]
XVII	1,8-Dimethylnaphthalene, $C_{12}H_{12}$	116.45	7.75	231.49	122.79	134.20	25.5	147.71	39.01	**108.7** [7, 11, 12]
			7.65		122.69		25.4		38.91	108.8±3.0 [11, 13]
XVIII	2,6-Dimethylnaphthalene, $C_{12}H_{12}$	91.25	8.74	180.47	97.96	106.52	24.01	96.63	14.12	82.51 [11]
XIX	2,7-Dimethylnaphthalene, $C_{12}H_{12}$	91.55	9.04	180.27	97.76	105.76	23.25	96.24	13.73	**82.51** [11]
			12.05		100.77		26.26		16.74	79.5±0.6 [34]
XX	2,3-Dimethylnaphthalene, $C_{12}H_{12}$	95.31	9.76	194.41	108.86	108.91	23.36	107.29	21.74	**85.55** [11]
			19.21		118.31		32.81		31.19	76.1±2.0 [14]

Table 1. (Contd.)

Comp. no.	Compound, formula	Enthalpy of formation ($\Delta_f H°$), kJ/mol								
		PM3	Δ	MINDO	Δ	AM1	Δ	MNDO	Δ	experimental[a]
XXI	Fluorene, $C_{13}H_{10}$	205.11	28.41 30.11 38.21	292.11	115.41 117.11 125.21	227.44	50.74 52.44 60.54	188.19	11.49 13.19 21.29	**176.7±3.1** [6] 175.0±1.5 [15] 166.9±4.1 [16]
XXII	Diphenylmethane, $C_{13}H_{12}$	180.87	15.87 18.57 23.67	252.51	87.51 90.21 95.31	176.34	11.34 14.04 19.14	180.01	15.01 17.71 22.81	**165.0±2.2** [6] 162.3±2.3 [6] 157.2 [7]
XXIII	4-Methyl-1,1'-biphenyl, $C_{13}H_{12}$	161.90	23.70	246.04	107.84	167.11	28.91	160.14	21.94	138.2±2.9 [17]
XXIV	2-Methyl-1,1'-biphenyl, $C_{13}H_{12}$	168.93	16.13 2.57	263.13	110.33 91.63	176.45	23.654.95	169.61	16.8 11.89	**152.8±1.5** [18] 171.5 [7]
XXV	2-Ethyl-6-methylnaphthalene, $C_{13}H_{14}$	72.56	11.26	156.65	95.35	81.68	20.38	76.45	15.15	61.30 [11]
XXVI	2-Ethyl-3-methylnaphthalene, $C_{13}H_{14}$	75.80	10.03	174.40	108.63	86.81	21.04	91.43	25.66	65.77 [11]
XXVII	1-Ethyl-8-methylnaphthalene, $C_{13}H_{14}$	98.67	0.57	218.12	120.02	119.0	20.90	138.49	40.39	98.1±1.5 [19]
XXVIII	Pyracyclene, $C_{14}H_8$	501.12	92.52	594.79	186.19	567.30	158.70	460.55	54.45	408.6 [6]
XXIX	Anthracene, $C_{14}H_{10}$	258.00	27.1027.20	360.05	129.15 129.25	263.26	32.36 32.46	246.25	15.35 15.45	**230.9** [7] 230.8±4.6 [20]
XXX	Phenanthrene, $C_{14}H_{10}$	230.23	28.9329.0323.33	357.79	156.49 156.59 150.89	240.33	39.03 39.13 33.43	232.96	31.66 31.76 26.06	**201.3** [7] 201.2±4.7 [21] 206.9±4.6 [20]
XXXI	Pyracene, $C_{14}H_{12}$	190.63	16.33	274.72	100.42	225.28	50.98	153.95	20.35	174.3±5.3 [6]
XXXII	4,4'-Dimethylbiphenyl, $C_{14}H_{14}$	122.63	11.33	219.32	108.02	135.01	23.71	127.51	16.21	111.3±3.6 [17]
XXXIII	2-Butylnaphthalene, $C_{14}H_{16}$	70.22	17.92	137.61	85.31	62.63	10.33	75.22	22.92	52.30 [11]
XXXIV	1-Butylnaphthalene, $C_{14}H_{16}$	74.01	20.96	155.94	102.89	68.77	15.72	91.24	38.19	53.05 [11]
XXXV	1,4,5,8-Tetramethylnaphthalene, $C_{14}H_{16}$	71.62	9.98	245.79	164.19	109.89	28.29	131.61	50.01	81.6±3.6 [7, 13]
XXXVI	1-Pentylnaphthalene, $C_{15}H_{18}$	55.25	22.82	133.21	100.78	43.14	10.71	74.96	42.53	32.43 [11]
XXXVII	2-Pentylnaphthalene, $C_{15}H_{18}$	47.76	16.09	114.87	83.20	43.14	11.47	58.93	27.26	31.67 [11]
XXXVIII	Pyrene, $C_{16}H_{10}$	289.93	64.43 64.23 75.03	406.30	180.80 180.60 191.40	281.78	56.28 56.08 66.88	253.97	28.47 28.27 39.07	225.5±2.5 [6] **225.7±1.3** [22] 214.9 [23, 39]
XXXIX	Fluoranthene, $C_{16}H_{10}$	334.78	43.38 44.98 45.78 42.78	474.13	182.73 184.33 185.13 182.13	367.88	76.48 78.08 78.88 75.88	304.53	13.13 14.73 15.53 12.53	291.4±4.0 [6] **289.8** [23] 289 [7] 292.0±2.2 [10]
XL	4,5,9,10-Tetrahydropyrene, $C_{16}H_{14}$	120.06	29.86	234.08	143.88	122.08	31.88	113.42	23.22	90.2±1.4 [24]

Table 1. (Contd.)

Comp. no.	Compound, formula	Enthalpy of formation ($\Delta_f H°$), kJ/mol								
		PM3	Δ	MINDO	Δ	AM1	Δ	MNDO	Δ	experimental[a]
XLI	2,7-Dimethylphenanthrene, $C_{16}H_{14}$	151.76	8.66 8.76	292.37	149.27 149.37	176.16	33.06 33.16	157.95	14.85 14.95	**143.1** [7] 143±3 [25]
XLII	4,5-Dimethylphenanthrene, $C_{16}H_{14}$	217.08	23.48	385.88	192.28	235.34	41.74	242.57	48.97	193.6 [7]
XLIII	9,10-Dimethylphenanthrene, $C_{16}H_{14}$	165.48	1.62 1.52	354.31	187.21 187.31	199.98	32.88 32.98	221.45	54.35 54.45	**167.1** [7] 167 [26]
XLIV	Triphenylene, $C_{18}H_{12}$	285.67	15.57 11.47	472.43	202.33 198.23	316.08	45.98 41.88	321.37	51.27 47.17	**270.1±4.4** [6] 274.2 [7]
XLV	Benzo[*c*]phenanthrene, $C_{18}H_{12}$	352.19	60.99	492.87	201.67	383.71	92.51	343.02	51.82	291.2 [6, 7]
XLVI	Chrysene, $C_{18}H_{12}$	296.47	26.67 27.77	466.23	196.43 197.53	318.93	49.13 50.23	313.47	43.67 44.77	269.8 [7] **268.7±4.7** [6]
XLVII	Naphthacene, $C_{18}H_{12}$	352.87	69.57 10.27 21.27	494.79	211.49 152.19 163.19	363.77	80.47 21.17 32.17	338.50	55.20 4.10 6.90	**283.3** [7] 342.6±5.9 [6] 331.6±4.4 [27]
XLVIII	Benzo[*a*]anthracene, $C_{18}H_{12}$	311.56	18.56 21.26	466.73	173.73 176.43	327.38	34.3837. 08	313.29	20.2922 .99	**293.0** [7] 290.3±6.0 [6]
XLIX	1,4-Diphenylbenzene, $C_{18}H_{14}$	301.78	17.38 17.38 22.78	425.37	140.97 140.97 146.37	305.91	21.51 21.51 26.91	313.8	29.40 29.40 34.80	284.4±3.8 [6] 284.4±3.5 [35] **279±6.3** [28]
L	1,2-Diphenylbenzene, $C_{18}H_{14}$	316.35	33.55 30.85	447.01	164.21 161.51	322.17	39.37 36.67	305.50	22.70 20.00	**282.8±3.2** [6] 285.5±3.6 [35]
LI	1,3-Diphenylbenzene, $C_{18}H_{14}$	304.14	24.24 24.14	426.85	146.95 146.85	306.39	26.49 26.39	296.71	16.8116 .71	279.9±3.9 [35] **280.0±3.9** [6]
LII	6,6-Diphenylfulvene, $C_{18}H_{14}$	448.40	46.40	592.88	190.88	482.22	80.22	438.19	36.19	402 [7]
LIII	5,12-Dihydronaphthacene, $C_{18}H_{14}$	230.82.	5.92 8.52	363.69	138.79 141.39	239.32	14.42 17.02	227.29	2.39 4.99	**224.9** [6] 222.3 [7]
LIV	2,5-Diphenyl-1,5-hexadiene, $C_{18}H_{18}$	302.16	17.16	423.32	138.32	299.34	14.34	304.38	19.38	285 [29]
LV	3,4,5,6-Tetramethylphenanthrene, $C_{18}H_{18}$	147.02	9.88 12.98	375.53	218.63 215.53	182.14	25.24 22.14	205.89	48.99 45.89	156.9 [7] **160±4.6** [25]
LVI	2,4,5,7-Tetramethylphenanthrene, $C_{18}H_{18}$	138.58	12.18 8.58	332.37	205.97 202.37	171.57	45.17 41.57	177.92	51.52 47.92	126.4 [7] **130±4** [25]
LVII	Triphenylmethane, $C_{19}H_{16}$	313.69	37.59 42.49	471.96	195.86 200.76	313.49	37.39 42.29	338.42	62.32 67.22	**276.1±5.0** [6] 271.2 [7]
LVIII	2,6-Diphenyl-1,6-heptadiene, $C_{19}H_{20}$	280.56	21.56	405.23	146.23	276.33	17.33	293.54	34.54	259 [29]
LIX	Dibenzo[*ghi*,*mno*] fluoranthene (corannulene), $C_{20}H_{10}$	609.08	150.58 148.48	778.07	319.57 317.47	655.06	196.56 194.46	561.82	103.321 01.22	458.5±9.2 [6] 460.6±6.5 [32]
LX	Perylene, $C_{20}H_{12}$	343.18	24.88 23.78 33.58	548.96	230.66 229.56 239.36	373.66	55.36 54.26 64.06	353.52	35.22 34.12 43.92	**318.3±3.7** [6] 319.4±2.2 [32] 309.6 [7]

Table 1. (Contd.)

Comp. no.	Compound, formula	Enthalpy of formation ($\Delta_f H°$), kJ/mol								
		PM3	Δ	MINDO	Δ	AM1	Δ	MNDO	Δ	exsperimental[a]
LXI	Benzo(*k*)fluoranthene (8,9-benzofluoranthene), $C_{20}H_{12}$	436.67	130.47 140.07	614.58	308.38	441.36	135.16 144.76	482.22	176.021 85.62	306.2±6.2 [6] 296.6±6.4 [38]
LXII	Tripticene, $C_{20}H_{14}$	355.96	33.96 34.26	581.82	259.82 260.12	388.13	66.13 66.43	378.42	56.42 56.72	**322±13** [30] 321.7 [7]
LXIII	3,9-Dimethylbenzo[*a*-] anthracene, $C_{20}H_{16}$	233.44	44.74 44.44	414.97	226.27 225.97	264.02	75.32 75.02	249.13	60.43 60.13	188.7 [7] **189±3** [25]
LXIV	1,12-Dimethylbenzo[*a*]-anthracene, $C_{20}H_{16}$	301.26	49.76	523.23	271.73	325.52	74.02	333.83	82.33	251.5 [7]
LXV	7,12-Dimethylbenzo[*a*]-anthracene, $C_{20}H_{16}$	278.19	0.49 1.19	516.74	239.04 239.74	314.79	37.09 37.79	334.14	56.44 57.14	277.7 [7] **277** [26]
LXVI	5,6-Dimethylchrysene, $C_{20}H_{16}$	267.15	4.75 5.15	502.77	240.37 240.77	298.58	36.18 36.58	320.06	57.66 58.06	**262.4** [7] 262 [26]
LXVII	Dibenzo[*a*,*c*]anthracene, $C_{22}H_{14}$	363.65	32.65	590.98	259.98	399.85	68.85	399.39	16.71	331±11 [6]
LXVIII	Dibenzo[*a*,*h*]anthracene, $C_{22}H_{14}$	371.05	43.05	576.04	248.04	394.13	66.13	382.45	54.45	328±11 [6]
LXIX	Coronene, $C_{24}H_{12}$	457.98	162.98 150.48 155.98	621.90	326.90 245.60 319.90	484.67	189.67 177.17 182.67	518.07	223.072 10.5721 6.07	295±11 [6] 307.5±9.8 [32] 302.0±8.0 [31]
LXX	1,3,5-Triphenylbenzene, $C_{24}H_{18}$	405.80	38.30 34.00	581.66	214.16 209.86	414.65	47.15 42.85	401.02	33.52 29.22	**367.5** [7] 371.8±3.8 [6]
LXXI	4,4'-Diphenylbiphenyl, $C_{24}H_{18}$	404.57	4.57 22.57	578.15	178.15 196.15	412.66	12.66 30.66	399.98	0.02 17.98	400±11 [6] **382±7.5** [28]
LXXII	Tetraphenylmethane, $C_{25}H_{20}$	480.93	93.73 83.13	806.04	418.84 408.24	492.41	105.21 94.61	566.56	179.361 68.76	387.2±4.9 [6] **397.8** [7]
LXXIII	Dibenzo[*g*,*p*]chrysene (tetrabenzonaphthalene), $C_{26}H_{16}$	497.51	5.49	818.55	315.55	591.19	88.19	539.35	36.35	503 [6]
LXXIV	9,9'-Bi-9*H*-Fluorene (bifluorenyl), $C_{26}H_{18}$	461.09.	130.99 130.99	701.53	371.43	513.54	183.44	457.25	127.15	330.1±4.2 [6] 330.1±2.3 [15]
LXXV	9,10-Diphenylanthracene, $C_{26}H_{18}$	491.19	25.59 12.89	744.29	278.69 265.99	508.99	43.39 30.69	499.36	33.76 21.06	**465.6** [7] 478.3±7.4 [6]
LXXVI	9,9'-Bianthracene, $C_{28}H_{18}$	546.26	71.26 91.96	833.88	358.88 379.58	570.13	95.13 115.83	560.91	85.91 106.61	**475** [6] 454.3 [7]
LXXVII	9,9'-Biphenanthrene, $C_{28}H_{18}$	479.20	115.2	817.62	453.62	513.63	149.63	526.83	162.83	364 [6]
Average absolute deviation, kJ/mol	With account taken of **XXVIII**, **LIX**, **LXI**, **LXIX**, **LXXIV**, and **LXXVII**	35.46		171.13		51.52		43.06		
	Excluding **XXVIII**, **LIX**, **LXI**, **LXIX**, **LXXIV**, and **LXXVII**	25.64		159.73		41.08		33.15		

[a] Boldface values were used to calculate the correlation coefficients.

observed for compounds **II**, **VII**, **XXXIX**, **XLV**, **XLVII**, **XLIX**, **LIII**, **LXIII**, **LXIV**, **LXXI**, **LXXII**, and **LXXV**.

The average absolute deviations obtained in the present work using Eq. (1) and by the Benson group additivity method (Table 3) were fairly similar, 12.79 and 10.02 kJ/mol, respectively. Table 4 contains the enthalpies of formation of compounds **LXXVIII**–**CXXXVIX** calculated by the AM1 method and using Eq. (1).

Thus, a good correlation was found between the experimental gas-phase enthalpies of formation of poly-

Table 2. Experimental enthalpies of formation of polycyclic aromatic compounds and those calculated by the AM1 method

Comp. no.	Enthalpy of formation, kJ/mol				Comp. no.	Enthalpy of formation, kJ/mol			
	$\Delta_f H^0_{calc}$	$\Delta_f H^{0*}_{calc}$	$\Delta_f H^0_{exp}$	Δ* [a]		$\Delta_f H^0_{calc}$	$\Delta_f H^{0*}_{calc}$	$\Delta_f H^0_{exp}$	Δ* [a]
I	191.47	158.40	161.2 [6]	2.80	**XXIII**	167.11	137.13	138.2 [17]	1.07
II	48.12	33.24	60.9 [6] 60.7 [36] 59.7 [37]	27.66 27.46 26.46	**XXIV**	176.45	145.28	152.8 [18] 171.5 [7]	7.52 26.22
III	169.79	139.47	150.29 [7] 150.6 [6]	10.82 11.13	**XXV**	81.68	62.54	61.3 [11]	1.24
IV	353.17	299.57	280.0 [8] 289.1 [7] 308 [40]	19.57 10.47 8.43	**XXVI**	86.81	67.02	65.77 [11]	1.25
V	142.03	115.23	113.0 [7] 116.1 [9]	2.23 0.87	**XXVII**	119.00	95.12	98.1 [19]	2.98
VI	138.34	112.01	106.7 [7] 116.1 [9]	5.31 4.09	**XXVIII**	567.30	486.51	408.6 [6]	77.91
VII	337.81	286.16	263.2 [6] 258 [10]	22.96 28.16	**XXIX**	263.26	221.07	230.9 [7] 230.8 [20]	9.83 9.73
VIII	503.59	430.89	417.4 [6] 420.4 [33]	13.49 10.49	**XXX**	240.33	201.05	201.3 [7] 201.2 [21] 206.9 [20]	0.25 0.15 5.4
IX	199.17	165.12	180.3 [6]	15.18	**XXXI**	225.28	187.91	174.3 [6]	13.61
X	178.21	146.82	156.0 [10] 156.8 [6]	9.18 9.98	**XXXII**	135.01	109.10	111.3 [17]	2.20
XI	116.18	92.46	83.55 [11]	8.91	**XXXIII**	62.63	45.91	52.3 [11]	6.39
XII	114.54	91.03	82.51 [11]	8.52	**XXXIV**	68.77	51.27	53.05 [11]	1.78
XIII	109.96	87.23	81.8 [11]	5.43	**XXXV**	109.89	87.17	81.6 [7, 13]	5.57
XIV	114.69	91.36	81.8 [11]	9.56	**XXXVI**	43.14	28.89	32.43 [11]	3.54
XV	110.55	87.75	82.51 [11]	5.24	**XXXVII**	43.14	28.89	31.67 [11]	2.78
XVI	109.91	87.19	81.8 [11]	5.39	**XXXVIII**	281.78	237.24	225.7 [22] 225.5 [6] 214.9 [23, 39]	11.54 11.74 22.34
XVII	134.20	108.40	108.66 [12] 108.8 [11, 13]	0.26 0.4	**XXXIX**	367.88	312.41	289.8 [23] 291.4 [6] 289 [7] 292.0 [10]	22.61 21.01 23.41 20.41
XVIII	106.52	84.23	82.51 [11]	1.72	**XL**	122.08	97.81	90.2 [24]	7.61
XIX	105.76	83.57	82.51 [11] 79.5 [34]	1.06 4.07	**XLI**	176.16	145.03	143.1 [7] 143 [25]	1.93 2.03
XX	108.91	86.32	85.55 [11] 76.1 [14]	0.77 10.22	**XLII**	235.34	196.70	193.6 [7]	3.09
XXI	227.44	189.80	176.7 [6] 175.0 [15] 166.9 [16]	13.10 14.80 22.90	**XLIII**	199.98	165.83	167.1 [7] 167 [26]	1.27 1.17
XXII	176.34	145.19	165.0 [6] 162.3 [6] 157.2 [7]	19.81 17.11 12.01	**XLIV**	316.08	267.19	270.1 [6] 274.2 [7]	2.91 7.01

Table 2. (Contd.)

Comp. no.	Enthalpy of formation, kJ/mol				Comp. no.	Enthalpy of formation, kJ/mol			
	$\Delta_f H^0_{calc}$	$\Delta_f H^{0*}_{calc}$	$\Delta_f H^0_{exp}$	Δ^* [a]		$\Delta_f H^0_{calc}$	$\Delta_f H^{0*}_{calc}$	$\Delta_f H^0_{exp}$	Δ^* [a]
XLIX	305.91	258.31	279.0 [28]	20.69	**LXIV**	325.52	275.43	251.5 [7]	23.93
			284.4 [6]	26.09					
			284.4 [35]	26.09					
L	322.17	272.50	282.8 [6]	10.30	**LXV**	314.79	266.06	277.0 [7]	10.94
			285.5 [35]	13.00				277.7 [26]	11.64
LI	306.39	258.72	280.0 [6]	21.27	**LXVI**	298.58	251.91	262.4 [7]	10.49
			279.9 [35]	21.18				262 [26]	10.09
LII	482.22	412.24	402.0 [7]	10.24	**LXVII**	399.85	340.32	331.0 [6]	9.32
LIII	239.32	200.17	224.9 [6]	24.73	**LXVIII**	394.13	335.33	328.0 [6]	7.33
			222.3 [7]	22.13					
LIV	299.34	253.57	285.0 [29]	32.43	**LXIX**	484.67	414.38	295 [6]	119.38
								307.5 [32]	106.88
								302 [31]	112.38
LV	182.14	150.25	160.0 [25]	9.75	**LXX**	414.65	353.24	367.5 [7]	14.26
			156.9 [7]	6.65				371.8 [6]	18.29
LVI	171.57	141.02	130.0 [25]	11.02	**LXXI**	412.66	351.51	382.0 [28]	30.49
			126.4 [7]	14.62				400 [6]	48.49
LVII	313.49	264.93	276.1 [6]	11.17	**LXXII**	492.41	421.13	397.8 [7]	23.33
			271.2 [7]	6.27				387.2 [6]	33.93
LVIII	276.33	232.48	259 [29]	26.51	**LXXIII**	591.19	507.37	503.0 [6]	4.37
LIX	655.06	563.14	458.5 [6]	104.64	**LXXIV**	513.54	439.58	330.1 [6,	109.48
			460.6 [32]	102.54				15]	
LX	373.66	317.46	318.3 [6]	0.84	**LXXV**	508.99	435.61	465.6 [7]	29.99
			319.4 [32]	1.94				478.3 [6]	42.69
			309.6 [7]	7.86					
LXI	441.36	376.56	306.2 [[6]	70.36	**LXXVI**	570.13	488.99	475.0 [6]	13.99
			296.6 [38]	79.96				454.3 [7]	34.69
LXII	388.13	330.09	322.0 [30]	8.09	**LXXVII**	513.63	439.66	364 [6]	75.66
			321.7 [7]	8.39					
LXIII	264.02	221.74	189.0 [25]	32.74	Average absolute deviation (excluding **XXVIII**, **LIX**, **LXI**, **LXIX**, **LXXIV**, and **LXXVII**)				13.19
			188.7 [7]	33.04					

[a] $\Delta^* = |\Delta_f H^{0*}_{calc} - \Delta_f H^0_{exp}|$.

cyclic aromatic hydrocarbons and those calculated by the AM1 semiempirical quantum-chemical method, so that the latter may be recommended for use in thermochemical calculations of such compounds. The linear regression equation describing the above correlation makes it possible to correct the calculated values for achievement of maximal proximity to the experimental data. The gas-phase enthalpies of formation of 62 polycyclic aromatic hydrocarbons calculated by the AM1 method and using the linear regression equation may be useful for studying mechanisms of chemical reactions and searching for methods to control them.

Table 3. Absolute deviations of the calculated enthalpies of formation of organic compounds (Δ) from the experimental data

Comp. no.	$\Delta_f H^0_{exp}$, kJ/mol	|Δ|, kJ/mol			Comp. no.	$\Delta_f H^0_{exp}$, kJ/mol	|Δ|, kJ/mol		
		additivitymethod [7]	AM1				additivitymethod [7]	AM1	
			without correction	with correction				without correction	with correction
III	150.3 [7]	0.5	19.5	10.83	**XLVII**	283.3 [7]	0.4	80.47	25.52
IV	289.1 [7]	0.4	64.07	10.47	**XLVIII**	293.0 [7]	11.8	34.38	15.95
V	113.0 [7]	4.2	29.03	2.23	**LII**	402 [7]	15.1	80.22	10.24
VI	106.7 [7]	10.5	31.64	5.31	**LIII**	222.3 [7]	3.6	17.02	22.13
VIII	417.9 [7]	0.3	86.19	12.99	**LV**	156.9 [7]	24.3	22.14	6.65
X	156.0 [10]	0.9	22.21	9.18	**LVI**	126.4 [7]	1.2	41.57	14.62
XVII	108.7 [7, 11, 12]	2.0	25.5	0.30	**LVII**	271.2 [7]	0.8	42.29	6.27
XXII	157.2 [7]	0.5	19.14	12.01	**LX**	309.6 [7]	10.9	64.06	7.86
XXIX	230.9 [7]	14.2	32.36	9.87	**LXII**	321.7 [7]	0	66.43	8.39
XXX	201.3 [7]	13.0	39.03	0.25	**LXIII**	188.7 [7]	27.2	75.02	33.04
XXXV	81.6 [7, 13]	18.01	28.29	5.57	**LXIV**	251.5 [7]	8.3	74.02	23.93
XXXVIII	225.7 [22]	11.1	56.08	11.12	**LXV**	277.7 [7]	39.8	37.79	11.64
XXXIX	289.0 [7]	0.5	78.88	22.08	**LXVI**	262.4 [7]	22.0	36.18	11.3
XLI	143.1 [7]	5.9	33.06	1.93	**LXX**	367.5 [7]	11.6	47.15	14.26
XLII	193.6 [7]	0.7	41.74	3.09	**LXXII**	397.8 [7]	0.9	94.61	23.33
XLIII	167.1 [7]	15.6	32.88	1.28	**LXXV**	465.6 [7]	51.4	43.39	29.99
XLIV	274.2 [7]	1.9	41.88	7.01	**LXXVI**	454.3 [7]	4.9	115.83	34.69
XLV	291.2 [6]	11.3	92.51	35.03					
XLVI	269.8 [7]	8.9	50.23	0.12	Average absolute deviation		10.02	51.34	12.79

Table 4. Enthalpies of formation (kJ/mol) of polycyclic aromatic hydrocarbons calculated by the AM1 method and using Eq. (1); $\Delta_f H^0_{calc} = 1.1454\ \Delta_f H^0_{exp} + 10.044$

Comp. no.	Compound, formula	$\Delta_f H^0_{calc}$	$\Delta_f H^{0*}_{calc}$	Comp. no.	Compound, formula	$\Delta_f H^0_{calc}$	$\Delta_f H^{0*}_{calc}$
LXXVIII	1-Ethylnaphthalene, $C_{12}H_{12}$	120.17	96.15	**LXXIX**	2-Ethylnaphthalene, $C_{12}H_{12}$	114.06	90.81
LXXX	Phenalene, $C_{13}H_{10}$	215.17	179.09	**LXXXI**	1-Propilnaphthalene, $C_{13}H_{14}$	94.94	74.12
LXXXII	1-Isopropylnaphthalene, $C_{13}H_{14}$	107.26	84.88	**LXXXIII**	2-Ethyl-7-methylnaphthalene, $C_{13}H_{14}$	81.88	62.72
LXXXIV	2-Isopropylnaphthalene, $C_{13}H_{14}$	97.17	76.07	**LXXXV**	1,4-Dimethyl-7-ethylazulene, $C_{14}H_{16}$	266.94	224.29
LXXXVI	1-Isopropyl-8-methyl-naphthalene, $C_{14}H_{16}$	111.47	88.55	**LXXXVII**	2-*tert*-Butylnaphthalene, $C_{14}H_{16}$	93.78	73.11
LXXXVIII	1-(1-Methylpropyl)-naphthalene, $C_{14}H_{16}$	84.83	65.29	**LXXXIX**	4-Methylphenanthrene, $C_{15}H_{12}$	235.83	197.12
XC	4-Isopropyl-1,6-dimethylnaphthalene, $C_{15}H_{18}$	48.24	33.35	**XCI**	5-Isopropyl-1,6-dimethylnaphthalene, $C_{15}H_{18}$	68.57	51.10
XCII	1-Phenylnaphthalene, $C_{16}H_{12}$	286.64	241.48	**XCIII**	Benzo[*a*]fluorene, $C_{17}H_{12}$	310.36	262.19
XCIV	Benzo[*b*]fluorene, 2,3-Benzofluorene, $C_{17}H_{12}$	301.30	254.28	**XCV**	Benzo[*ghi*]fluoranthene, $C_{18}H_{10}$	489.91	418.95

Table 4. (Contd.)

Comp. no.	Compound, formula	$\Delta_f H^0_{calc}$	$\Delta_f H^{0*}_{calc}$	Comp. no.	Compound, formula	$\Delta_f H^0_{calc}$	$\Delta_f H^{0*}_{calc}$
XCVI	7-Isopropyl-1-methyl-phenanthrene, $C_{18}H_{18}$	140.83	114.18	**XCVII**	Benzo[*a*]pyrene, $C_{20}H_{12}$	366.16	310.91
XCVIII	Benzo[*b*]fluoranthene (benzo[*e*]acephenanthrene), $C_{20}H_{12}$	452.44	386.24	**XCIX**	Benzo[*j*]fluoranthene, $C_{20}H_{12}$	456.37	389.67
C	Benzo[*e*]pyrene, $C_{20}H_{12}$	351.43	298.05	**CI**	Phenylanthracene, $C_{20}H_{14}$	386.37	328.38
CII	Cholanthrene, $C_{20}H_{14}$	338.51	286.77	**CIII**	5,8-Dimethylbenzo[*c*]-phenanthrene, $C_{20}H_{16}$	315.06	266.30
CIV	1,12-Dimethylbenzo[*c*]-phenanthrene, $C_{20}H_{16}$	433.49	369.69	**CV**	3-Methylcholanthrene, $C_{21}H_{16}$	307.08	259.33
CVI	1,2'-Dinaphthylmethane, $C_{21}H_{16}$	338.0	286.32	**CVII**	2,2'-Dinaphthylmethane, $C_{21}H_{16}$	331.55	280.69
CVIII	Anthanthrene, $C_{22}H_{12}$	415.98	354.41	**CIX**	Benzo[*b*]chrysene, $C_{22}H_{14}$	408.73	348.08
CX	Benzo[*a*]chrysene (picene), $C_{22}H_{14}$	401.30	341.59	**CXI**	Benzo[*b*]naphthacene (pentacene), $C_{22}H_{14}$	471.39	402.78
CXII	Dibenzo[*aj*]anthracene, $C_{22}H_{14}$	394.92	336.02	**CXIII**	Pentaphene, $C_{22}H_{14}$	411.53	350.52
CXIV	Benzo[*a*]naphthacene, $C_{22}H_{14}$	424.66	361.98	**CXV**	Dibenzo[*b*,*g*]phenanthrene (naphtho[1,2-*a*]anthracene), $C_{22}H_{14}$	428.84	365.63
CXVI	Benzo[*c*]chrysene, $C_{22}H_{14}$	415.13	353.66	**CXVII**	Benzo[*g*]chrysene, $C_{22}H_{14}$	416.45	354.82
CXVIII	Pentahelicene, ([5]helicene), $C_{22}H_{14}$	570.86	489.62	**CXIX**	Indeno[5,6,7,1-*pqra*]-perylene, $C_{24}H_{12}$	579.62	497.27
CXX	Benzo[*ghi*]cyclopenta[*cd*]-perylene, $C_{24}H_{12}$	553.38	474.36	**CXXI**	Benz[*mno*]indeno[1,7,6,5-*cdef*]chrysene, $C_{24}H_{12}$	529.79	453.77
CXXII	5,6,7,1-Benzo[*j*]indeno-[5,4,3,2,1-*nopqr*]tetraphene, $C_{24}H_{12}$	678.50	583.60	**CXXIII**	Benzo[*mno*]indeno[5,6,7,1-*defg*]chrysene, $C_{24}H_{12}$	590.38	506.67
CXXIV	Tetrabenzocyclooctatetraene (tetraphenylene), $C_{24}H_{16}$	467.11	399.04	**CXXV**	3,3'-Diphenylbiphenyl, $C_{24}H_{18}$	414.02	352.69
CXXVI	[6]Helicene, $C_{26}H_{16}$	804.27	693.40	**CXXVII**	Hexacene, $C_{26}H_{16}$	574.33	492.65
CXXVIII	Dibenzo[*b*,*p*]chrysene, $C_{26}H_{16}$	503.61	430.91	**CXXIX**	8b,16b-Dihydrodibenzo[*g*,*p*]-chrysene, $C_{26}H_{18}$	488.70	417.89
CXXX	[7]Circulene, $C_{28}H_{14}$	1045.60	904.10	**CXXXI**	Phenanthro[1,10,9,8-*opqra*]-perylene (*meso*-naphthodianthracene), $C_{28}H_{14}$	591.39	507.55
CXXXII	Benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene, $C_{28}H_{14}$	491.04	419.94	**CXXXIII**	Pyranthrene, $C_{30}H_{16}$	577.31	495.26
CXXXIV	Benzo(*c*)naphtho[2,1-*p*]-chrysene, $C_{30}H_{18}$	682.19	586.82	**CXXXV**	Tetrabenzo[*a*,*c*,*h*]anthracene, $C_{30}H_{18}$	543.75	465.96
CXXXVI	Heptacene, $C_{30}H_{18}$	802.11	691.52	**CXXXVII**	Dibenzo[*a*,*l*]pentacene	611.83	525.39
CXXXVIII	5,6-Diphenylnaphthacene, $C_{30}H_{20}$	609.20	523.10	**CXXXIX**	Ovalene, $C_{32}H_{14}$	879.54	759.12

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