

- (44) Seybold, P. G. *Int. J. Quantum Chem.: Quantum Biol. Symp.* **1983**, 10, 95 and 103.
 (45) Balaban, A. T.; Quintas, L. V. *Math. Chem. (Mülheim/Ruhr)* **1983**, 14, 213.
 (46) Müller, W. R.; Szymanski, K.; Knop, J. V.; Trinajstić, N. J. *J. Chem. Inf. Comput. Sci.* **1990**, 30, 160.
 (47) Knop, J. V.; Müller, W. R.; Szymanski, K.; Trinajstić, N. J. *J. Chem. Inf. Comput. Sci.* **1991**, 31, 83.
 (48) Graham, R. L.; Pollak, H. O. *Bell Syst. Tech. J.* **1971**, 50, 2495.
 (49) Burkert, K.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, 1982.
 (50) Saunders, M. J. *Am. Chem. Soc.* **1987**, 109, 3150.
 (51) Balasubramanian, K. *Chem. Phys. Lett.* **1990**, 169, 224.
 (52) Nikolić, S.; Trinajstić, N.; Mihalić, Z.; Carter, S. *Chem. Phys. Lett.* **1991**, 179, 21.
 (53) Mihalić, Z.; Trinajstić, N. J. *Mol. Struct. (Theochem)* **1991**, 232, 65.
 (54) Nikolić, S.; Trinajstić, N.; Mihalić, Z. *J. Math. Chem.*, submitted.
 (55) Balaban, A. T.; Motoc, I. *Math. Chem. (Mülheim/Ruhr)* **1979**, 5, 197.
 (56) Motoc, I.; Balaban, A. T. *Rev. Roum. Chim.* **1981**, 26, 593.
 (57) Motoc, I.; Balaban, A. T.; Mekenyan, O.; Bonchev, D., *Math. Chem. (Mülheim/Ruhr)* **1982**, 13, 369.
 (58) Kovačević, K.; Plavšić, D.; Trinajstić, N.; Horvat, D. *MATH/CHEM/COMP 1988*; Graovac, A., Ed.; Elsevier: Amsterdam, 1989; p 213.
 (59) Razinger, M.; Chrétien, J. R.; Dubois, J. E. *J. Chem. Inf. Comput. Sci.* **1985**, 25, 23.
 (60) Seybold, P. G.; May, M.; Bagal, U. A. *J. Chem. Educ.* **1987**, 64, 575.
 (61) Needham, D. E.; Wei, I.-C.; Seybold, P. G. *J. Am. Chem. Soc.* **1988**, 110, 4186.
 (62) Hansen, P. J.; Jurs, P. C. *J. Chem. Educ.* **1988**, 65, 574.

Optimum Graph-Theoretical Models for Enthalpic Properties of Alkanes

MANUEL GARBALENA and WILLIAM C. HERNDON*

Department of Chemistry, University of Texas at El Paso, El Paso, Texas 79968

Received August 27, 1991

Simple additive schemes based on graph-theoretical properties of molecular graphs are evaluated for correlating thermodynamic properties of alkanes. The properties considered in this work are $\Delta H_f^\circ(\text{g})$, $\Delta H_f^\circ(\text{l})$, $\Delta H(\text{atomization})$, heats of vaporization, and heat capacities of vaporization. The original sources for thermochemical data were checked since some of the past attempts to correlate alkane properties, e.g., $\Delta H_f^\circ(\text{g})$, have made use of calculated or interpolated values rather than restricting the analysis to experimental data. The evaluation is conducted using stepwise multilinear regression methodology. The statistical qualities of the final correlative equations are excellent (in all cases but one, squared multiple correlation coefficients > 0.995). In each case, the most successful model equation involves the use of labeled paths of length zero, one, and two as the independent variables. Therefore, each parameter has a simple molecular structure interpretation and can be obtained from the molecular graph by inspection.

1. INTRODUCTION

In general, there are causal relationships between the molecular structures of organic compounds and their chemical, physical, and biological properties.¹⁻¹⁴ Many of these relationships have been investigated using graph-theoretical descriptors of molecular structures. This is particularly true for the alkanes, which constitute the prototypical organic compounds presupposed to have graph-like character. In fact, explicitly or implicitly, nearly all additive procedures that have been proposed to systematize thermodynamic properties of alkanes use graph-theoretical topological indices or counts of particular graph features as the independent parameters to correlate the dependent enthalpic variables.^{3,15-36}

In this paper we attempt to ascertain the optimum graph-theoretical models to correlate thermodynamic enthalpic properties of alkanes. The properties treated are $\Delta H_f^\circ(\text{g})$, $\Delta H_f^\circ(\text{l})$, $\Delta H(\text{atomization})$, heats of vaporization [$\Delta H(\text{vapor})$], and heat capacities of vaporization [$C_p(\text{vapor})$]. The format of the report is as follows. Definitions and an outline of our procedures are described in section 2. Correlations of gas- and liquid-phase heats of formation and heats of atomization are discussed in section 3, while heats of vaporization and heat capacities of vaporization are treated and discussed in section 4. Finally, some summarizing remarks are presented in the last section.

2. PROCEDURES

In addition to various graph-theoretical molecular descriptors, the database consists of a list of abbreviations for alkanes (based on systematic nomenclature^{17,26}) and experimental values for $\Delta H_f^\circ(\text{g})$, $\Delta H_f^\circ(\text{l})$, $\Delta H(\text{atomization})$, $\Delta H(\text{vapor})$, and $C_p(\text{vapor})$. The compilations of thermodynamic values

due to Cox and Pilcher³⁸ and to Pedley, Naylor, and Kirby³⁹ served as the primary sources for ΔH_f° data. The original references were consulted if a cited value was not clearly identified as derived from an experiment. In some previous ΔH_f° /structure studies,^{2,30} a large number of the quoted $\Delta H_f^\circ(\text{g})$ are actually calculated values, typically estimated using an experimentally determined $\Delta H_f^\circ(\text{l})$ and an interpolated or theoretical value for $\Delta H(\text{vapor})$.

The global molecular descriptors for each molecule consisted of the total number of carbon atoms, the Wiener numbers,^{8,16} and the Kier/Hall χ indices,² order 1-6. Descriptors based on the hydrogen-suppressed graph included counts of the vertices sorted by degrees and counts of all unlabeled paths of length 1-10. The paths were also sorted and counted based on the degrees of the vertices included in the path, which corresponds to enumeration of labeled paths in the molecular graph. Finally, the number of *gauche*-*n*-butane interactions, steric parameters for locked 1,2-interactions and 1,3-steric interactions were included according to the criteria of Kalb et al.²⁶ Of course, these latter parameters are not strictly graph-theoretical since they are derived from an examination of the (putative) most stable conformation of each individual alkane.

Many of the parameters in the data set have a dual interpretation; for example, the vertex degrees of the hydrogen-suppressed graph are linearly related to the numbers of C-H bonds according to types (primary, secondary, and tertiary). Anticipating the results of the present study, we would like to draw the readers attention to the labeled paths of length zero, one, and two; P_0 , P_1 , and P_2 , respectively. The labeled P_0 's coincide with the types of carbon atoms or single-carbon groups (CH_3 , CH_2 , CH , C). The labeled P_1 's naturally represent specific types of carbon-carbon bonds, and labeled P_2 's

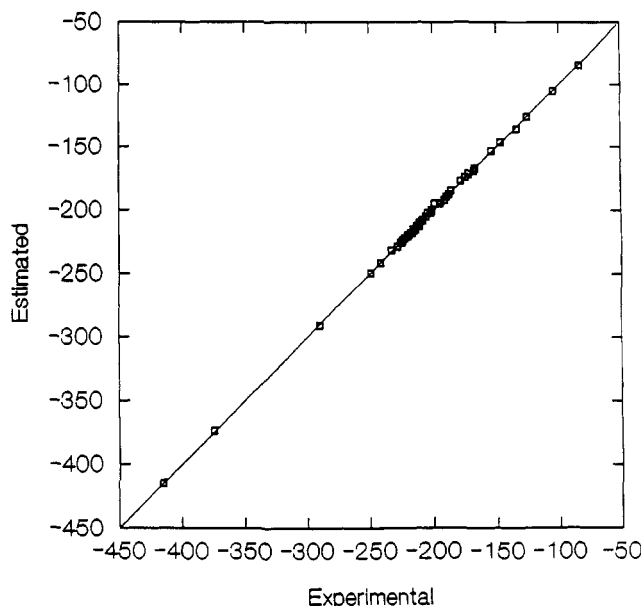


Figure 1. Correlation of experimental and calculated $\Delta H_f^\circ(\text{g})$ for alkanes (kJ/mol). Parameters in Table II.

could correspond to various 1,3-nonbonded interaction terms.

The relationship between experimental thermodynamic properties and the numerical molecular descriptors is assumed to have the following multilinear form:

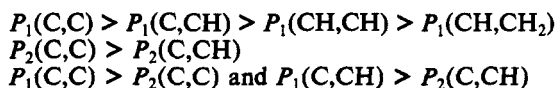
$$\Delta H = a_1 D_1 + a_2 D_2 + \dots + a_n D_n \quad (1)$$

where n is the total number of descriptors (D), and several of the a_i coefficients of the independent D_i variables are expected to have statistically insignificant values. All descriptors were entered into a potential model correlation equation (eq 1), and the individual terms were screened for inclusion in a final regression equation using a standard stepwise multivariate linear regression analysis. The forward entry method was used, coupled with backward elimination procedures. The values of the options controlling the statistical criteria for inclusion of independent variables were those recommended on the basis of Monte Carlo studies of regression models.⁴⁰

3. HEATS OF FORMATION AND ATOMIZATION

Experimental ΔH_f° gas-phase values are available for 46 acyclic alkanes, listed in Table I.^{38,39} The parameters of the optimum model equation to correlate this data are given in Table II, and Figure 1 is a plot of estimated values versus the experimental $\Delta H_f^\circ(\text{g})$. The statistical parameters, $R^2 = 1.000$ and the large F -ratio (1.02×10^4), also listed in Table II, indicate the excellent quality of the correlation. Figure 2 is a plot of the results for octanes, which allows a more informative examination of the correlation.

The parameters selected by the stepwise analysis each correspond to an easily perceived structural subgraph in the general class of alkane molecular graphs. Additive stabilizing terms for carbon atom types (P_0 's) are ameliorated by destabilizing 1,2- and 1,3-interactions, the P_1 's and P_2 's, respectively. One notes that the regression coefficients of the interaction terms increase in a regular manner depending on the degree of substitution and also exhibit a decrease with increasing intervening distances between path terminal vertices, e.g.



One sensible structural interpretation is that the P_1 's and P_2 's correspond to destabilizing steric terms that arise from crowding of alkyl groups. The P_0 's must then incorporate the

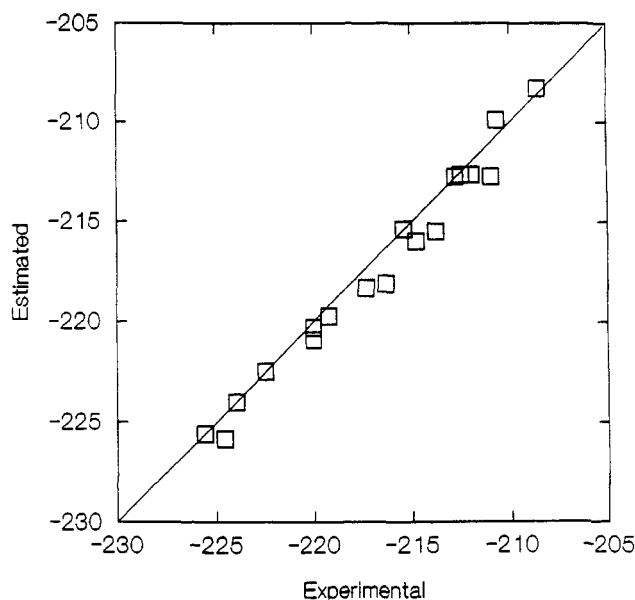


Figure 2. Correlation of experimental and calculated $\Delta H_f^\circ(\text{g})$ for octanes (kJ/mol).

stabilizing C-H and C-C bond-energy contributions. The absence of an $P_0(\text{C})$ term for the quaternary carbon atom is a disturbing aspect of this simplistic explication. However, the analysis given below for $\Delta H(\text{atomization})$ of the alkanes provides the explanation for this omission.

The heat of atomization is the enthalpy change on dissociation of a molecule into its component atoms. Heats of atomization for the 46 alkanes with known $\Delta H_f^\circ(\text{g})$ were calculated from the equation:

$$\Delta H(\text{atomization}, \text{C}_n\text{H}_m) = n\Delta H_f^\circ[\text{C}(\text{g})] + m\Delta H_f^\circ[\text{H}(\text{g})] - \Delta H_f^\circ(\text{g}, \text{C}_n\text{H}_m) \quad (2)$$

where $\Delta H_f^\circ[\text{C}(\text{g})] = 715.05$ kJ/mol and $\Delta H_f^\circ[\text{H}(\text{g})] = 217.99$ kJ/mol.³⁸ The parameters and regression coefficients of the optimum additive equation for $\Delta H(\text{atomization})$ are listed in Table II. The derived and estimated $\Delta H(\text{atomization})$'s are not listed in Table I because of the simple algebraic relationship to the $\Delta H_f^\circ(\text{g})$ values.

The $\Delta H(\text{atomization})$ equation incorporates a statistically significant $P_0(\text{C})$ term in addition to containing all terms of the $\Delta H_f^\circ(\text{g})$ equation. The destabilizing interaction terms retain their exact numerical values from the $\Delta H_f^\circ(\text{g})$ analysis, while an examination of the regression coefficients shows that each P_0 parameter on the $\Delta H_f^\circ(\text{g})$ scale is related to its magnitude on the $\Delta H(\text{atomization})$ scale as follows:

$$P_0[\Delta H_f^\circ(\text{g}, \text{CH}_k)] = \Delta H_f^\circ[\text{C}(\text{g})] + k\Delta H_f^\circ[\text{H}(\text{g})] - P_0[\Delta H(\text{atomization}, \text{CH}_k)] \quad (3)$$

The optimized regression coefficient for the $P_0(\text{C})$ parameter is 715.03 kJ/mol, corresponding almost exactly to the 715.05 kJ/mol heat for sublimation of carbon (graphite). The calculated value for the $P_0(\text{C})$ parameter is therefore 0.02 kJ/mol on the $\Delta H_f^\circ(\text{g})$ energy scale. Thus, the reason that $P_0(\text{C})$ does not appear in the $\Delta H_f^\circ(\text{g})$ model equation is due to the fact that its value is statistically insignificant when compared to the fluctuations in the fit of the $\Delta H_f^\circ(\text{g})$ data, as indicated by the 1.2 kJ/mol standard deviation in the estimated values (Table II).

The optimum model equation to correlate alkane liquid-phase heats of formation (Table II) requires the same parameters as the gas-phase ΔH_f° correlation. The results are illustrated in Figure 3, and it is evident that the parameterized equation is a very good rectification of the experimental data. Each P_0 term is of the order of 4–6 kJ more negative than the

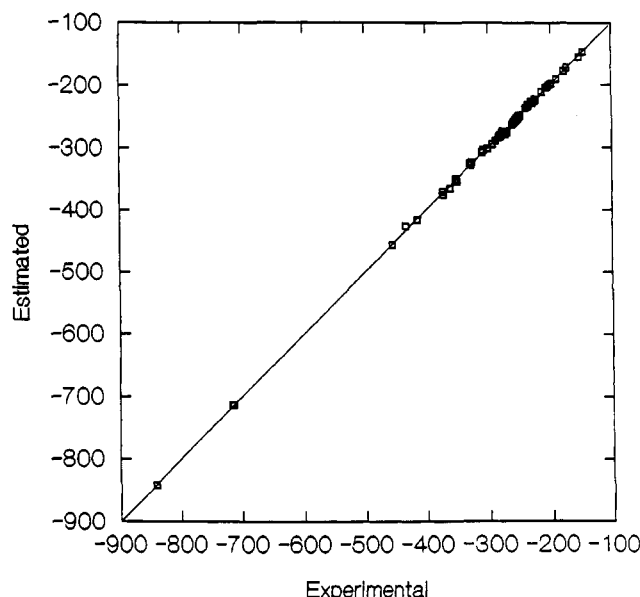


Figure 3. Correlation of experimental and calculated $\Delta H_f^\circ(l)$ for alkanes (kJ/mol). Parameters in Table II.

corresponding gas-phase parameter, stabilizing the liquid-phase, and the relative magnitudes and orders of the P_1 and P_2 terms are comparable for the two phases. The fact that the same parameters appear for both gas and liquid ΔH_f° 's allows one to obtain the algebraic expression for the $\Delta H(\text{vapor})$ given in eq 4. The coefficients of this equation should be compared with the optimized values determined as described in the next section.

$$\begin{aligned} \Delta H(\text{vapor}) = & 5.63P_0(\text{CH}_3) + 5.14P_0(\text{CH}_2) + \\ & 3.81P_0(\text{CH}) - 0.66P_1(\text{CH}, \text{CH}_2) - 0.10P_1(\text{C}, \text{CH}_2) - \\ & 2.10P_1(\text{CH}, \text{CH}) + 0.17P_1(\text{C}, \text{CH}) - 1.87P_1(\text{C}, \text{C}) + \\ & 0.33P_2(\text{C}, \text{CH}) + 1.79P_2(\text{C}, \text{C}) \quad (4) \end{aligned}$$

4. HEATS OF VAPORIZATION

Experimental heats of vaporization (liquid > gas) for 42 alkanes, available from our primary sources,^{38,39} are listed in Table I. These experimental values, of course, were used to calculate 42 of the 46 (experimental) $\Delta H_f^\circ(g)$ in Table I. The four remaining known $\Delta H_f^\circ(g)$'s pertain to compounds which are either gases or solids under ambient conditions. The parameter coefficients of the optimum correlative equation are given in Table II, and a plot of estimated versus experimental values is depicted in Figure 4.

The model equation for $\Delta H(\text{vapor})$ has only five parameters. In this case, the stepwise regression procedures do not allow the inclusion of any P_1 terms, or any parameters other than P_0 's and P_2 's to correlate the data. Our reaction to this result was initial surprise that such a parsimonious set of parameters would be sufficient to give the very good correlation of the data exemplified by the very low standard deviation (0.772 kJ/mol) and the plot in Figure 4.

However, an examination of eq 4 (see above) shows that several of the independent parameters in a $\Delta H(\text{vapor})$ equation are actually expected to be smaller than the standard error in the estimated values of the dependent variable. Then the precise identities of the included terms in the optimum regression equation are controlled by the stepwise regression protocol, in this case giving the tabulated equation in Table II. It is probable that the absence of the P_1 terms in the correlating equation does not have a basic structure/enthalpy significance. Addition of compounds containing P_1 's and P_2 's to the database would, of course, alter the numerical values of the parameter coefficients and could very well also alter the mix of terms in a final regression equation.

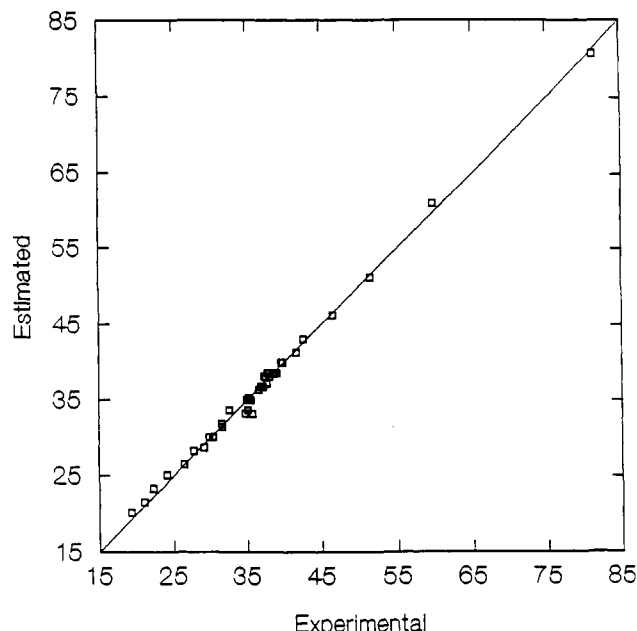


Figure 4. Correlation of experimental and calculated $\Delta H(\text{vaporization})$ for alkanes (kJ/mol). Parameters in Table II.

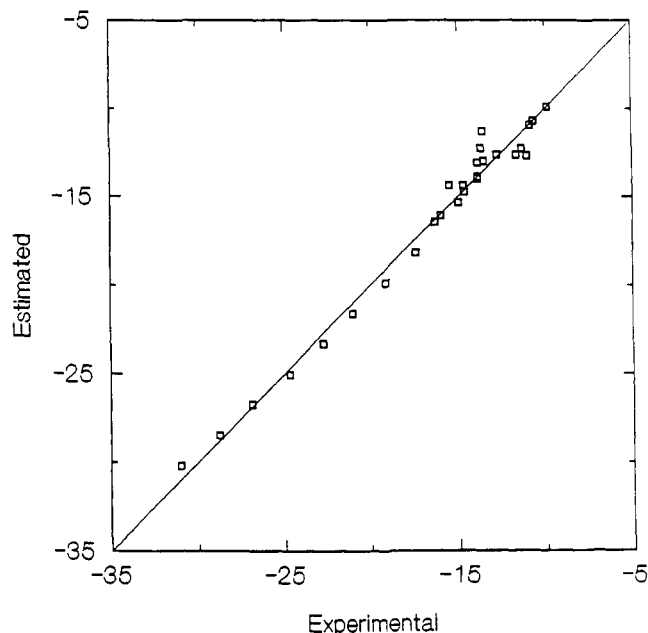


Figure 5. Correlation of experimental and calculated $C_p(\text{vapor})$ for alkanes ($\text{cal deg}^{-1} \text{mol}^{-1}$). Parameters in Table II.

Heat capacities of vaporization for 28 liquid alkanes comprise the last set of experimental entries in Table I.³⁵ The stepwise regression again makes exclusive use of the labeled path parameters to correlate the data. This data set is rather small but a good correlation is still obtained judging from the plot in Figure 5 based on the model equation in Table II. The standard error of the estimates is very small (0.876 kJ/mol), and the F -ratio can be characterized as sufficient.

The reason for the absence of a $P_2(\text{C}, \text{C})$ term in the $C_p(\text{vapor})$ regression equation is due to the absence of that structural feature in any of the compounds comprising the data set. Based on the results for the $\Delta H(\text{vapor})$, an additional diminution in the number of parameters in the model C_p equation is also expected. Likewise, as discussed above, the precise identity of the terms included in the regression equation might be expected to be immaterial, as long as all consequential structural features are, in some way, taken into account. For example, $P_0(\text{CH}_3)$'s and $P_0(\text{CH}_2)$'s (primary and

Table I. Comparison of Experimental and Estimated Enthalpic Properties^a

compd	$\Delta H_f^\circ(\text{g})$	est.	$\Delta H_f^\circ(\text{l})$	est.	$\Delta H(\text{vapor})$	est.	$C_p(\text{vapor})$	est.
2	-83.8	-84.42		-95.68		11.65		-6.14
3	-104.7	-105.06		-121.47		16.59		-7.86
4	-125.6	-125.71	-146.6	-147.26	21.0	21.52		-9.58
2m3	-134.2	-135.54	-153.5	-156.26	19.3	20.16		-9.21
5	-147.1	-146.36	-173.5	-173.05	26.4	26.46	-13.6	-11.29
2m4	-154.1	-153.45	-178.2	-178.64	24.1	25.10	-10.9	-10.93
22mm3	-167.9	-168.83	-190.1	-191.37	22.2	23.30	-13.7	-12.28
6	-167.1	-167.00	-198.7	-198.83	31.6	31.40	-13.5	-13.01
2m5	-174.8	-174.09	-204.6	-204.43	29.8	30.04	-11.7	-12.64
3m5	-172.1	-171.35	-202.4	-201.03	30.3	30.04	-12.8	-12.64
23mm4	-178.3	-176.93	-207.4	-204.96	29.1	28.67	-11.4	-12.28
22mm4	-186.1	-184.55	-213.8	-212.13	27.7	28.24	-11.1	-12.69
7	-187.7	-187.65	-224.3	-224.62	36.6	36.34	-14.6	-14.73
2m6	-194.6	-194.74	-229.5	-230.22	34.9	34.97	-15.5	-14.36
3m6	-191.3	-192.00	-226.4	-226.82	35.1	34.97	-14.7	-14.36
3e5	-189.6	-189.26	-225.1	-223.42	35.5	34.97		-14.36
22mm5	-205.9	-205.20	-240.6	-237.92	34.7	33.18		-14.41
23mm5	-198.9	-194.84	-231.4	-227.37	32.5	33.61	-13.9	-13.99
24mm5	-201.7	-201.83	-236.8	-235.82	35.1	33.61		-13.99
33mm5	-201.2	-200.27	-236.9	-232.89	35.7	33.18	-13.9	-13.11
223-3m4	-204.5	-202.39	-236.0	-234.54	31.5	31.81	-10.7	-10.70
8	-208.6	-208.30	-250.2	-250.41	41.6	41.27	-16.3	-16.45
2m7	215.4	215.39	-255.0	256.01	39.6	39.91	-16.0	-16.08
3e6	-210.7	-209.91	-250.4	-249.21	39.7	39.91		-16.08
22mm6	-224.6	-225.84	-261.9	-263.70	37.3	38.11		-16.13
23mm6	-213.8	-215.49	-252.6	-253.16	38.8	38.55		-15.71
24mm6	-219.2	-219.74	-257.0	-258.21	37.8	38.55		-15.71
25mm6	-222.5	-222.48	-260.4	-261.61	37.9	38.55		-15.71
33mm6	-220.0	-220.92	-257.5	-258.68	37.5	38.11		-14.82
34mm6	-212.8	-212.75	-251.8	-249.76	39.0	38.55		-15.71
3e2m5	-211.0	-212.75	-249.6	-249.76	38.6	38.55		-15.71
3e3m5	-214.8	-215.99	-252.8	-253.65	38.0	38.11		-13.52
223-3m5	-220.0	-220.30	-256.9	-256.93	36.9	36.75		-12.42
224-3m5	-224.0	-224.00	-259.2	-260.70	35.2	35.20	-13.9	-13.90
233-3m5	-216.3	-218.11	-253.5	-255.30	37.2	36.75		-11.12
234-3m5	-217.3	-218.33	-255.0	-253.72	37.7	37.18	-15.0	-15.34
2233-4m4	-225.6	-225.60		-257.54		34.95	-9.9	-9.90
9	-228.2	-228.94	-274.7	-276.20	46.5	46.21	-17.4	-18.17
33ee5	-232.8	-231.71	-275.4	-274.42	42.6	43.05		-13.94
2233-4m5		-241.32	-278.3	-278.30		39.89		-10.32
2234-4m5		-234.85	-277.7	-274.66		38.77		-11.91
2244-4m5	-241.5	-241.50	-280.0	-282.03	38.5	38.50		-17.52
2334-4m5		-235.95	-277.9	-277.72		40.32		-9.13
10	-249.5	-249.59	-301.0	-301.99	51.5	51.15	-19.1	-19.89
2m9		-256.68	-309.8	-307.58		49.78		-19.52
5m9		-253.94	-307.9	-304.19		49.78		-19.52
11		-270.23	-327.2	-327.77		56.08	-21.0	-21.61
2255-4m7		-300.41	-351.2	-349.34		49.76		-19.66
3355-4m7		-272.94	-325.7	-323.56		48.37		-18.35
22445-5m6		-275.06	-329.0	-325.21		47.01		-15.95
12	-289.6	-290.88	-349.3	-353.56	59.7	61.02	-22.7	-23.32
3366-4m8		-316.13	-372.8	-370.10		54.70		-20.07
4466-4m9		-314.23	-371.0	-375.14		58.25		-21.79
35mm35ee7		-304.38	-360.5	-365.09		58.25		-19.18
5577-4m11		-355.53	-433.5	-426.71		68.12		-25.23
46ee46mm9		-345.67	-414.7	-416.66		68.12		-22.62
16	-374.8	-373.47	-456.1	-456.71	81.3	80.77	-31.0	-30.20
5but22		-581.54	-713.5	-713.39		128.77		-47.02
11but22		-581.54	-713.5	-713.39		128.77		-47.02
11dec21		-684.78	-842.1	-842.33		153.45		-55.61
18	-414.8	-414.76		-508.29		90.64		-33.64
32		-703.81		-869.32		159.75		-57.70
334-3m6		-236.02	-277.5	-277.69		41.69		-12.83
223-3m6		-240.94	-282.7	-282.72		41.69		-14.14
225-3m6		-253.58	-293.3	-295.09		41.69		-17.48
224-3m6		-241.91	-282.8	-283.08		40.14		-15.62
22mm7		-246.49	-288.2	-289.49		43.05		-17.85
244-3m6		-239.72	-280.2	-281.46		40.14		-14.32
235-3m6		-243.23	-284.0	-284.55		42.12		-17.06
233-3m6		-238.76	-281.1	-281.09		41.69		-12.83
3e-22mm5		-238.20	-272.7	-279.32		41.69		-14.14
3e-24mm5		-236.23	-269.7	-276.11		42.12		-17.06
13		-311.53		-379.35		65.96	-24.7	-25.04
14		-332.17		-405.14		70.89	-26.9	-26.76
15		-352.82		-430.92		75.83	-28.8	-28.48

^aUnits are kJ/mol except for $C_p(\text{vapor})$ which is cal deg⁻¹ mol⁻¹.

Table II. Correlation Equations for Enthalpic Properties^{a,b}

parameter	parameter coefficients				
	$\Delta H_f^\circ(\text{g})$	$\Delta H(\text{atomization})$	$\Delta H_f^\circ(\text{l})$	$\Delta H(\text{vapor})$	$C_p(\text{vapor})$
$P_0(\text{CH}_3)$	-42.21 (0.16)	1411.22 (0.27)	-47.84 (0.23)	5.83 (0.07)	-3.07 (0.08)
$P_0(\text{CH}_2)$	-20.65 (0.06)	1171.66 (0.07)	-25.79 (0.07)	4.94 (0.04)	-1.72 (0.03)
$P_0(\text{CH})$	-8.92 (0.62)	941.95 (0.79)	-12.73 (1.01)	2.69 (0.17)	
$P_0(\text{C})$		715.03 (1.28)			
$P_1(\text{CH}, \text{CH}_2)$	2.74 (0.32)	-2.74 (0.33)	3.40 (0.55)		
$P_1(\text{C}, \text{CH}_2)$	4.93 (0.29)	-4.92 (0.36)	5.03 (0.40)		1.30 (0.43)
$P_1(\text{CH}, \text{CH})$	9.74 (0.85)	-9.73 (0.88)	11.84 (1.39)		
$P_1(\text{C}, \text{CH})$	17.57 (0.90)	-17.56 (1.11)	17.40 (1.02)		4.64 (0.96)
$P_1(\text{C}, \text{C})$	27.65 (1.54)	-27.63 (2.00)	29.51 (2.72)		8.51 (1.00)
$P_2(\text{C}, \text{CH})$	8.94 (1.28)	-8.93 (1.40)	8.61 (1.34)	-1.55 (0.80)	1.86 (0.98)
$P_2(\text{C}, \text{C})$	22.54 (1.38)	-22.53 (1.66)	20.75 (1.44)	-1.39 (0.87)	
no. of cases	46	46	69	42	28
multiple R	1.000	1.000	1.000	0.997	0.990
multiple R ²	1.000	1.000	1.000	0.995	0.980
std error	1.215	1.233	2.476	0.772	0.876
F-ratio	1.02×10^4	2.96×10^7	1.68×10^4	1.78×10^3	2.19×10^2

^a Parameter units are kJ/mol except for $C_p(\text{vapor})$ which is in cal deg⁻¹ mol⁻¹. ^b Standard error in parentheses.

secondary carbon atoms) are the only significant paths of length zero present in the correlating equation. However, the P_1 and P_2 interaction parameters that do appear in the correlation also enumerate tertiary [$P_0(\text{CH})$] and quaternary [$P_0(\text{C})$] carbons, albeit, in a less direct manner.

5. DISCUSSION AND SUMMARY

The low standard errors, high correlation coefficients, and large F -ratios indicate that the parametric equations presented in this paper are very good representations of the experimental enthalpic data summarized in Table I. We infer that the correlation equations listed in Table II can be used for accurate predictions, and the estimated values for each property are also presented in Table I. The caveats expressed in section 4 regarding the structural interpretations of the correlation parameters do not weaken the predictive capabilities of these equations.

A referee has suggested that the branched alkanes may exhibit systematic, larger residuals than those displayed by the unbranched alkanes. An examination of the results for the two groups demonstrates that indeed the means of the residuals are somewhat different for the unbranched and branched systems, respectively, as follows: 0.48 and 0.97 kJ for the $\Delta H_f^\circ(\text{g})$, 0.87 and 1.78 kJ for the $\Delta H_f^\circ(\text{l})$. However, there are no particular groups of compounds nor specific structural parameters that can be identified as the cause of the small (less than 1 kJ) differences. An absence of systematic errors and an internal congruency between the separate groups of unbranched and branched compounds is further verified by two completely independent analyses of the $\Delta H_f^\circ(\text{g})$ data which gives $P_0(\text{CH}_3) = -42.08$ (unbranched), $P_0(\text{CH}_3) = -42.31$ (branched), $P_0(\text{CH}_2) = -20.68$ (unbranched), and $P_0(\text{CH}_2) = -20.43$ kJ (branched) for the two common parameters.

There are major differences in some of our estimates, e.g., for $\Delta H_f^\circ(\text{g})$, compared with nonexperimental values for 18 alkanes compiled in Pedley et al.,³⁹ 21 alkanes listed in Kier and Hall,² and 38 alkanes tabulated in Somayajulu and Zwolinski.³⁰ A similar comment applies for the estimates of the other enthalpic properties given in Table I. It is, of course, difficult to state that the present estimates are more accurate or more useful in the absence of relevant experimental data. However, the ease of application and the consistency of the overall results that are reported here may be construed to support the use of the model equations given in Table II.

The topological, graph-theoretical approach to correlating properties is the simplest approximation which articulates the molecular structure-property cognition, and this approximation is sufficient to account for the variations in enthalpic data listed

in Table I. The general fact that each alkane is a mixture of conformational isomers, and that the observed enthalpic property must be averaged over the population of conformers, seems to have no bearing on the applicability of the model equations summarized in Table II.

In the case of molar volumes, we have previously shown⁴¹ that there are algebraic equivalencies between topological indices, counts of structural features, and the average number of *gauche*-*n*-butane interactions for normal alkanes. These equivalencies demonstrate that there is an analytical correspondence of graph-theoretical descriptors to actual conformational properties in these substances. Edward has considered the same problem from a more qualitative viewpoint which includes branched alkanes as part of the analysis.³⁴ The extension of this analysis to elucidate the relationships that are summarized in Table II is under investigation.

ACKNOWLEDGMENT

The financial support of the Welch Foundation (Houston, TX) and of the University of Texas at El Paso Materials Research Center of Excellence (a component of the National Science Foundation Minority Research Centers of Excellence) is gratefully acknowledged.

REFERENCES AND NOTES

- (1) Valkenburg, W. V., Ed. *Biological Correlations—The Hansch Approach*; American Chemical Society: Washington, DC, 1972.
- (2) Balaban, A. T., Ed. *Chemical Applications of Graph Theory*; Academic: London, 1976.
- (3) Kier, L. B.; Hall, L. H. *Molecular Connectivity in Chemistry and Drug Research*; Academic: New York, 1976.
- (4) Hansch, C.; Leo, A. *Substituent Constants for Correlation Analysis in Chemistry and Biology*; Wiley: New York, 1979.
- (5) Stuper, A. J.; Brugger, W. E.; Jurs, P. C. *Computer Assisted Studies of Chemical Structure and Biological Function*; Wiley: New York, 1979.
- (6) Randić, M.; Krais, G. A.; Deonauv-Jerman-Blazic, B. In *Chemical Applications of Topology and Graph Theory*; King, R. B., Ed.; Elsevier: Amsterdam, 1983; pp 192–205.
- (7) Golander, V. E.; Rozenblit, A. B. *Logical and Combinatorial Algorithms for Drug Design*; Research Studies Press, Ltd.: Letchworth, England, 1983.
- (8) Trinajstić, N. *Chemical Graph Theory*; CRC Press: Boca Raton, FL, 1983; Vol. I and II.
- (9) Klopman, G. *J. Am. Chem. Soc.* **1984**, *106*, 7315.
- (10) Balaban, A. T. *J. Chem. Inf. Comput. Sci.* **1985**, *25*, 334.
- (11) Jurs, P. C.; Stouch, T. S.; Czerwinski, M.; Narvaez, J. N. *J. Chem. Inf. Comput. Sci.* **1985**, *25*, 296.
- (12) Kier, L. B.; Hall, L. H. *Molecular Connectivity in Structure-Activity Analysis*; Research Studies Press, Ltd.: Letchworth, England, 1986.
- (13) Jerman-Blazic, B.; Fabic, I.; Randić, M. *J. Comput. Chem.* **1986**, *7*, 176.
- (14) Klopman, G.; Namboodiri, K.; Kalos, A. N. In *Molecular Basis of Cancer, Part A: Macromolecular Structure, Carcinogens, and Oncogens*; Rein, R., Ed.; Alan R. Liss: New York, 1985; pp 287–298.

- (15) Fajans, K. *Chem. Ber.* **1920**, *53*, 643.
- (16) (a) Wiener, H. *J. Am. Chem. Soc.* **1947**, *69*, 17. (b) Wiener, H. *J. Am. Chem. Soc.* **1947**, *69*, 2636. (c) Wiener, H. *J. Phys. Chem.* **1948**, *52*, 425. (d) Wiener, H. *J. Phys. Chem.* **1948**, *52*, 1082.
- (17) (a) Platt, J. R. *J. Chem. Phys.* **1947**, *15*, 419. (b) Platt, J. R. *J. Phys. Chem.* **1952**, *56*, 328.
- (18) Franklin, J. F. *Ind. Eng. Chem.* **1949**, *41*, 1070.
- (19) Laidler, K. J. *Can. J. Chem.* **1956**, *34*, 626.
- (20) Benson, S. W.; Buss, J. H. *J. Chem. Phys.* **1958**, *29*, 546.
- (21) Allen, T. L. *J. Chem. Phys.* **1959**, *31*, 1039.
- (22) Skinner, H. A. *J. Chem. Soc.* **1962**, 4396.
- (23) Skinner, H. A.; Pilcher, G. *Q. Rev. Chem. Soc.* **1963**, *17*, 264.
- (24) Gordon, M.; Scatlebury, G. R. *Trans. Faraday Soc.* **1964**, *60*, 604.
- (25) Smolenskii, E. E. *Zh. Fiz. Khim.* **1964**, *38*, 1288.
- (26) Kalb, A. J.; Chung, A. L. H.; Allen, T. L. *J. Am. Chem. Soc.* **1966**, *88*, 13.
- (27) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.
- (28) Good, W. D. *J. Chem. Eng. Data* **1969**, *14*, 231.
- (29) Hosoya, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2332.
- (30) (a) Somayajulu, G. R.; Zwolinski, B. J. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1971. (b) *Ibid.* **1974**, *70*, 967. (c) *Ibid.* **1974**, *70*, 973.
- (31) Gordon, M.; Kennedy, J. W. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 484.
- (32) Kao, J. W. H.; Chung-Phillips, A. *J. Chem. Phys.* **1975**, *63*, 4143.
- (33) Gasteiger, J.; Jacob, P.; Strauss, U. *Tetrahedron* **1979**, *35*, 139.
- (34) (a) Edward, J. T. *Can. J. Chem.* **1980**, *58*, 1897. (b) *Ibid.* **1981**, *59*, 3192.
- (35) Guthrie, J. P.; Taylor, K. F. *Can. J. Chem.* **1984**, *62*, 363.
- (36) Needham, D. E.; Wei, I.-C.; Seybold, P. G. *J. Am. Chem. Soc.* **1988**, *110*, 4186.
- (37) McHughes, M. C.; Poshuta, R. D. *J. Math. Chem.* **1990**, *4*, 227.
- (38) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.
- (39) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed., Chapman and Hall: New York, 1986.
- (40) Bendel, R. B.; Afifi, A. A. *J. Am. Stat. Assoc.* **1977**, *72*, 46.
- (41) Radhakrishnan, T. P.; Herndon, W. C. *J. Math. Chem.* **1988**, *2*, 391. Also see ref 34.

Applications of Graph Theory and Topology for the Study of Aromaticity in Inorganic Compounds¹

R. B. KING

Department of Chemistry, University of Georgia, Athens, Georgia 30602

Received August 27, 1991

The topology of overlap of the atomic orbitals participating in the requisite delocalization for an aromatic system can be described by a graph, the eigenvalue spectrum of which can be related to molecular orbital energy parameters as determined by Hückel theory. Such aromatic systems can be classified according to the nodality of the overlapping atomic orbitals. Thus, the three-dimensional deltahedral boranes $B_nH_n^{2-}$ and carboranes $B_{n-2}C_2H_n$ ($6 \leq n \leq 12$) are examples of anodal orbital aromatic systems since the delocalization in their bonding arises from overlap of anodal radial boron or carbon sp hybrids. Two-dimensional planar polygonal hydrocarbons such as cyclopentadienide, benzene, and tropylium are examples of uninodal orbital aromatic systems since the delocalization in their bonding arises from overlap of uninodal *p* orbitals at each of the carbon vertices. Similarly, three-dimensional polyoxometallates such as octahedral $M_6O_{19}^{n-}$ and cuboctahedral $XM_{12}O_{40}^{n-}$ are examples of binodal orbital aromatic systems since the delocalization in their bonding arises from overlap of the binodal d_{xy} orbitals at each of the metal vertices. The delocalization in these binodal aromatic systems is much weaker than that in the uninodal and anodal aromatic systems since the relevant orbital overlap in the binodal aromatic systems must occur through indirect M-O-M bonds rather than direct vertex-vertex bonds.

INTRODUCTION

Important ideas arising from molecular orbital theory²⁻⁴ include the concepts of resonance energy and aromaticity. Graph-theory derived methods have subsequently been used to refine these ideas,⁵⁻⁷ which were initially applied to two-dimensional planar hydrocarbons [e.g., cyclopentadienide ($C_5H_5^-$), benzene (C_6H_6), and tropylium ($C_7H_7^+$)] and corresponding heterocycles [e.g., pyridine (C_5H_5N) and thiophene (C_4H_4S)]. More recently the concepts of resonance energy and aromaticity have been extended to the three-dimensional deltahedral boranes $B_nH_n^{2-}$ and carboranes $C_2B_{n-2}H_n$ ($6 \leq n \leq 12$) in which the boron and/or carbon atoms form the deltahedra depicted in Figure 1. In this context a *deltahedron* is defined as a polyhedron in which all faces are triangles like the Greek letter *delta*, Δ . The Wade analogy⁸⁻¹¹ [e.g., between $Fe(CO)_5$ and BH vertices or $Co(CO)_3$ and CH vertices] makes similar ideas applicable to transition-metal clusters consisting of metal deltahedra [e.g., the octahedral $Rh_6(CO)_{16}$ or the icosahedral¹² $Ni_{12}E(CO)_{22}^{2-}$ where $E = Ge, Sn$]. Related ideas recently¹³ have been shown to be applicable to electron delocalization in the readily reducible early-transition-metal po-

lyoxometallates, which may be regarded as three-dimensional aromatic systems based on a large octahedron or cuboctahedron (Figure 2) of transition-metal atoms.

Previous considerations of aromaticity in polygonal or polyhedral clusters have focused on the dimensionality of the structure.¹⁴ Thus the planar polygonal hydrocarbons $C_3H_3^-$, C_6H_6 , and $C_7H_7^+$ are two-dimensional aromatic systems whereas the deltahedral boranes ($B_nH_n^{2-}$) and carboranes ($C_2B_{n-2}H_n$) as well as the polyoxometallates are three-dimensional aromatic systems. This paper focuses on another aspect of the aromaticity in these systems, namely, the nodality of the valence orbitals of the vertex atoms participating in the delocalization. An outline of the graph-theoretical approach to aromaticity is first presented.

BACKGROUND

A graph G is defined¹⁵ as a finite nonempty set V (the *vertices*) together with a (possibly empty) set E (the *edges*)—disjoint from V of two-element subsets of (distinct) elements of V . In the graph-theoretical bonding models discussed in this paper, the set V or vertices represent skeletal atoms or