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Group Vector Space Method for Estimating the Normal Boiling Temperature and Enthalpy of Vaporization of Organic Compounds

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The specific position of a group in the molecule has been considered, and a group vector space method has been developed to estimate the normal boiling temperature and enthalpy of vaporization of organic compounds. Expressions for the boiling temperature T_b and enthalpy of vaporization $\Delta_{vap}H(T_b)$ have been established, and numeric values of relative group parameters have been obtained. The average percent deviations of the estimation of T_b and$\Delta_{vap}H(T_b)$ are 1.5 and 1.0, respectively, which show that the present method demonstrates significant improvement in the ability to predict the above properties, compared to that of conventional group methods.

Introduction

For physical properties of organic compounds, the normal boiling temperature and enthalpy of vaporization are required in many calculations and process simulations and for product design. It is not always possible, however, to find reliable experimental literature values of the above properties for the compounds of interest, nor is it practical to measure the properties as the need arises. Therefore, the estimation methods are profusely employed.

For the estimation of boiling temperatures of pure organic compounds, the simple group method developed by Joback and Reid[1] is useful. The method provides the important advantage of quick estimates without requiring substantial computational resources. However, it is of questionable accuracy and utility. To overcome this limitation, the two-level group contribution method proposed by Constantinou and Gani[2] and the group-interaction contribution method by Marrero-Morejon and Pardillo-Fontdevila[3] were used to estimate the boiling temperatures. For these two methods, the number of compounds involved in the parameter regression is less than 507, which is not very different from the number of parameters in the property correlation. Model parameters in the group method are obtained by fitting the property data of a great many substances. Only if the number of substances in the linear regression is much greater than that of parameters in the model does the group method show good extrapolation. Compared with the number of substances in the regression, the higher the parameter number in the model, the poorer the predicting function of the model. In addition to the above methods, Rowley et al.[4] developed a new group-contribution method (GCM) based on Domalske-Hearing (DH) groups and other molecular descriptors already tabulated in the DIPPR database.

Numerous techniques for estimating the enthalpy of vaporization have been proposed.[5] Two representatives of the group contribution methods developed in recent years are the methods by Hoshino et al.[6] and Ma.[7] The accuracy of estimating the enthalpies of vaporization with these two methods is not high, and their percent average deviations are 1.5 and 1.45, respectively.

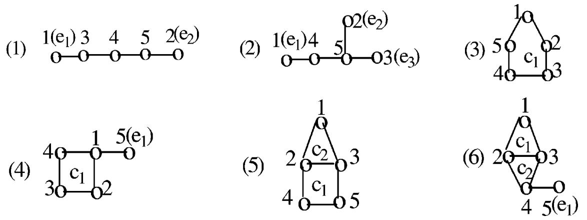

Figure 1. Six topological structures of organic compounds.

In our early work,[8] a group vector space method for estimating the boiling and melting temperature of hydrocarbons was proposed. This article extends the method from hydrocarbons to organic compounds in general. The group vector space method for estimating the boiling temperature and enthalpy of vaporization of organic compounds with lower deviations is proposed here.

Group Vector Space for Organic Compounds

In this work, we select 40 simple groups to describe organic compounds. These groups are the same as those used by Joback and Reid.[1] The molecule is considered to be in a given space, and every group in the molecule is only a point in the space. To write this conveniently, graphs with different numbers of points are all expressed as graphs with five points. Thus, the organic molecules can be expressed as the six topologic graphs in Figure 1.

The topologic structure of a molecule can be described by the distance matrix of the molecule. The distance matrix is a square symmetric matrix. n^2 elements for the n-order square matrix must be input. The input quantity for the large molecule is too large; furthermore, the distance matrix is unable to describe molecular structure characteristics such as chains, rings, and branches sufficiently. To overcome the above limitation, the following group vector space method has been proposed.

Considering the chain graph first, the dimension number of the space is equal to the number of end points (e_i) on

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the chain, and one end point determines the dimension of the space. The coordinate of an end point in the dimension is determined by its zero, and the coordinate of another point in this dimension is the distance from that point to the end point. (The distance between two adjacent groups is defined as 1.) For example, the no. 1 molecule in Figure 1 has three end points, so the dimension of its space is 3, namely, e_1, e_2, e_3. The distances of group 1 to every dimension e_1, e_2, and e_3 are 0, 3, and 3, respectively, and the coordinates of this group in the space are (0, 3, 3). For the cyclic graph, one ring (c_i) represents a dimension. In that dimension, the coordinate of the ring point equals the number of points on the ring, and the coordinate of a nonring point equals the sum of the distance from the point to the ring and the number of points on the ring. If the route from the ring point to the end point is nonunique, then the shortest route should be selected. Therefore, the dimension number m of the space for a graph is equal to the sum of the number k_e of end points (e_i) and the number k_c of rings (c_i) in the graph. Another example is the no. 6 molecule in Figure 1; it has two rings and one end point, so it has three dimensions c_1, c_2, and e_1. The distance of group 5 to the e_1 dimension is decided by its zero; the sum (5) of the distance (2) to ring 1 and the points (3) on ring 1 is its coordinate at the c_2 dimension; similarly, its coordinate at the c_1 dimension is 4. Therefore, the coordinates of group 5 in the space are (5, 4, 0). Every point in the graph has m coordinates in the m-dimensional space. The graph may be described by a space matrix: the number of rows in the matrix equals the number of points in the graph, and the number of columns equals the dimension number of the space. These space matrices of the above six topologic graphs are as follows:

$$(1)\quad \begin{array}{c|cc} & e_1 & e_2 \\ \hline 1 & 0 & 4 \\ 2 & 4 & 0 \\ 3 & 1 & 3 \\ 4 & 3 & 1 \\ 5 & 2 & 2 \end{array};\qquad (2)\quad \begin{array}{c|ccc} & e_1 & e_2 & e_3 \\ \hline 1 & 0 & 3 & 3 \\ 2 & 3 & 0 & 2 \\ 3 & 3 & 2 & 0 \\ 4 & 1 & 2 & 2 \\ 5 & 2 & 1 & 1 \end{array};\qquad (3)\quad \begin{array}{c|c} & c_1 \\ \hline 1 & 5 \\ 2 & 5 \\ 3 & 5 \\ 4 & 5 \\ 5 & 5 \end{array};$$

$$(4)\quad \begin{array}{c|cc} & c_1 & e_1 \\ \hline 1 & 4 & 1 \\ 2 & 4 & 2 \\ 3 & 4 & 3 \\ 4 & 4 & 2 \\ 5 & 5 & 0 \end{array};\qquad (5)\quad \begin{array}{c|cc} & c_1 & c_2 \\ \hline 1 & 3 & 5 \\ 2 & 3 & 4 \\ 3 & 3 & 4 \\ 4 & 4 & 4 \\ 5 & 4 & 4 \end{array};\qquad (6)\quad \begin{array}{c|ccc} & c_1 & c_2 & e_1 \\ \hline 1 & 3 & 4 & 3 \\ 2 & 3 & 3 & 2 \\ 3 & 3 & 3 & 2 \\ 4 & 4 & 3 & 1 \\ 5 & 5 & 4 & 0 \end{array}$$

These matrices show that the space position of point i in the graph can be represented by an m-dimensional vector ($b_{i1}\ b_{i2}\ ...\ b_{im}$). Then the module a_i of the point i vector is

$$a_i = (\sum_{j=1}^{m} b_{ij}^2)^{1/2} \qquad (i = 1, 2, 3, 4, 5)$$

The average square root of the module of some point i in the graph is defined as the module index v_i of this point vector. That is,

$$v_i = \frac{a_i}{(\sum_{j=1}^{5} a_j^2)^{1/2}} \qquad (i = 1, 2, 3, 4, 5)$$

The quantity v_i is used to describe the point i position in the space. By analogy, the module index v_i of group i in the molecule is taken to characterize the position of that group in the molecular space. Thus, every simple group, except halogen groups, has its own independent module and module index. For the four halogen groups, their module indexes were determined to be the same as those of the hydrocarbon groups with which they were connected.

Correlation and Group Parameters

The expression of physical property f for the simple group method is

$$f = a + \sum_i n_i \Delta f_i \tag{1}$$

where subscript i represents the group type, Δf_i is the contribution value of the i-type group, n_i is the number of i-type groups in the molecule, and a is the correlation constant.

The group has an individual contribution because different groups have different effects on the physical properties; for two identical groups, whose positions in the molecule are different, they have different contributions, so the position contribution is induced to express the different position of groups in the molecule. To improve the estimation accuracy, the correction position contribution is added to the correlation equation. Therefore, in this study, the group contribution was divided into three parts: the independent contribution of the group, the position contribution of the group, and the correction position contribution of the group. The physical property f is expressed as follows:

$$f = a + \sum_i [\Delta f_{0i} + (\sum_{j=1}^{n_i} \nu_k)\Delta f_{Ii} + (\sum_{j=1}^{n_i} e^{-\nu_k})\Delta f_{pi}] \tag{2}$$

The subscript k is calculated by the following equation:

$$k = j + \sum_{m=1}^{i-1} n_m \tag{3}$$

where Δf_{0i}, Δf_{Ii}, and Δf_{Pi} are the independent contributions of the i-type group, the position contribution, and the correction position contribution of the i-type group, respectively, and V_k is the module index of the k group; $\sum_{j=1}^{n_i} \nu_k$ is the sum of the module index of i-type groups.

Accordingly, the expressions of the normal boiling temperature and the enthalpy of vaporization are written as follows:

$$T_b/K = -25.141 + \sum_i [\Delta T_{b0i} + (\sum_{j=1}^{n_i} \nu_k)\Delta T_{bIi} + (\sum_{j=1}^{n_i} e^{-\nu_k})\Delta T_{bpi}] \tag{4}$$

$$\Delta_{vap}H(T_b)/T_b/\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 0.0885 + \sum_i [\Delta_{vap}S_{0i} + (\sum_{j=1}^{n_i} \nu_k)\Delta_{vap}S_{Ii} + (\sum_{j=1}^{n_i} e^{-\nu_k})\Delta_{vap}S_{pi}] \tag{5}$$

where T_b and $\Delta_{vap}H(T_b)$ are boiling temperature and enthalpy of vaporization at normal boiling temperature,

Table 1. Values of Group Parameters

no.	group[a]	ΔT_{b0i}	ΔT_{bli}	ΔT_{bpi}	$\Delta_{vap}S_{0i} \times 10^3$	$\Delta_{vap}S_{li} \times 10^3$	$\Delta_{vap}S_{pi} \times 10^3$
1	$-CH_3$	17.204	157.289	7.050	0.7809	−2.3257	−0.2533
2	$>CH_2$	−5.551	168.174	−2.086	1.1926	−2.0674	0.1992
3	$>CH-$	9.777	154.616	−2.848	0.7131	0.68248	−0.8774
4	$>C<$	47.850	64.051	−2.463	2.1991	−8.1705	0.3504
5	$=CH_2$	−21.039	165.789	−0.947	−0.0205	−2.1364	0.2022
6	$=CH-$	10.916	137.059	−0.710	0.8167	−0.6424	0.2813
7	$=C<$	64.953	36.384	−1.486	8.3551	−12.5474	−1.4965
8	$=C=$	40.422	187.714	−29.034	9.0890	7.2966	−6.8995
9	$\equiv CH$	17.386	163.085	−34.784	7.2549	17.2635	−14.4769
10	$=CH-$	−27.596	237.383	1.858	11.4486	−18.6035	4.2197
11	$(>CH_2)_R$	1.572	156.722	−11.716	1.3508	−3.3825	2.4645
12	$(>CH-)_R$	−11.744	189.690	0.272	−4.8422	10.0514	−1.4581
13	$(>C<)_R$	36.615	92.634	−7.617	−2.4003	15.8098	−4.9915
14	$=(CH-)_R$	−9.654	178.977	−2.069	1.6066	−0.8898	−1.9277
15	$(=C<)_R$	5.988	181.093	−6.438	−2.5411	9.3671	−1.1434
16	-F	−41.337	376.922	−18.463	−30.0469	36.9465	24.5450
17	-Cl	−130.494	526.307	−15.066	−0.7583	−64.6456	−12.0404
18	-Br	−36.090	233.133	3.224	0.7457	8.3119	−0.8901
19	-I	−76.850	320.208	−6.112	−5.0923	17.6022	−2.3949
20	-OH	−53.747	339.450	30.583	−3.3326	0.7783	7.2503
21	$(-OH)_{AC}$	−45.030	378.060	15.913	23.4767	−50.0589	12.9895
22	-O-	−121.466	264.092	81.773	0.0315	90.347	−2.4586
23	$(-O-)_R$	−120.115	397.438	86.024	0.1512	−518.941	319.3753
24	$>C=O$	−11.995	277.080	19.579	36.9541	30.2199	−30.2268
25	$(>C=O)_R$	786.315	0.256	−237.018	0.0000	0.0000	0.0000
26	$O=CH-$	38.961	273.065	−30.960	28.5313	3.0790	−30.2274
27	-COOH	−33.066	324.327	15.719	−2.0325	7.3828	1.6847
28	-COO-	−63.031	377.931	14.640	−0.3541	13.3769	−3.4691
29	$=C=O$	25.670	236.986	−10.956	−24.5151	10.6684	16.2582
30	$-NH_2$	−72.900	358.159	12.363	−15.4216	36.8143	3.5348
31	$>NH$	−23.181	261.971	15.469	−63.9732	0.0096	62.637
32	$(>NH)_R$	−60.604	402.411	−1.147	−0.0172	66.4685	−16.500
33	$>N-$	15835.96	10863.52	−14924.8	−0.0031	0.0000	0.0000
34	$-N=$	−56.263	250.725	23.107	9.8280	−11.2348	0.9858
35	$(-N=)_R$	10.221	385.776	−27.518	2.5718	12.8358	−5.3181
36	-CN	−190.577	382.201	109.878	−0.0110	11.7701	15.3251
37	$-NO_2$	−25.833	106.701	−3.647	0.1099	−0.6758	1.0704
38	-SH	−39.395	244.162	12.655	−1.8541	4.1144	1.5563
39	-S-	−46.892	317.864	5.215	−3.2532	3.6496	2.4600
40	$(-S-)_R$	−3.485	334.473	3.184	3.5692	4.1663	−2.9128

[a] Subscript R represents a ring group; AC represents a connection to the aromatic ring.

Table 2. Comparison of Accuracy between Widely Used Methods and the One Proposed for T_b Estimation

method	Joback and Reid[1]	Marrero-Morejon and Pardillo-Fontdevila[3]	Constantinou and Gani[2]	Rowley et al.[4]	proposed method
no. of data points	438	507	392	1141	1162
AAE[a]/K	12.9	6.48	5.35	7.75	6.33
APE[b]	3.6	1.73	1.42	1.9	1.5

[a] AAE = average absolute error. [b] APE = average percent error.

respectively. The units employed are Kelvin and kJ·mol^{-1}. $\Delta_{vap}S(T_b)$ is the entropy of vaporization at normal boiling temperature.

A great deal of experimental data in the literature[9−13] has been used to optimize the values of group parameters in eqs 4 and 5. The simple method of least squares is used for optimization with the following objective function:

$$OF = \sum_j^n \left| \frac{Q_j^{exp} - Q_j^{cal}}{Q_j^{exp}} \right| \qquad (6)$$

where Q_j^{exp} and Q_j^{cal} are the experimental value and the calculation value of the two properties. n is the number of compounds used in the regression. The group parameters obtained by correlating data are listed in Table 1.

Method Comparison and Estimation Results

The normal boiling temperature T_b predictions by the new method (eq 4) is compared with that obtained from the Joback and Reid[1] method, the Marrero-Morejon and Pardillo-Fontdevila[3] method, the Constantinou and Gani[2] method ,and the Rowley et al.[4] method. The results are listed in Table 2.

Table 3. Comparison of Accuracy between the Widely Used Methods and the One Proposed for $\Delta_{vap}H(T_b)$ Estimation

method	Hoshino[6]	Ma[7]	proposed method
no. of data points	411	483	503
APE[a]	1.5	1.45	1.0

[a] APE = average percent error.

Extensive comparisons are made between eq 5, the Hoshino method,[6] and the Ma[7] method. The results are listed in Table 3.

The normal boiling temperatures and the enthalpies of vaporization are given for 1166 and 503 compounds, respectively, which are divided into 6 groups. The average

Table 4. Correlation Accuracy and the Error Distribution of T_b and $\Delta_{vap}H(T_b)$ for Six Groups of Organic Compounds

	T_b/K			$\Delta_{vap}H(T_b)$/kJ·mol^{-1}		
compound	no. of data points	absolute deviation	percent deviation	no. of data points	absolute deviation	percent deviation
aliphatic hydrocarbon	222	4.06	1.15	124	0.26	0.81
naphthenic hydrocarbon	111	4.04	1.08	32	0.23	0.71
aromatic hydrocarbon	111	7.89	1.58	18	0.52	1.26
O,S compounds	390	6.13	1.45	176	0.35	1.00
N compounds	114	8.61	2.1	66	0.32	0.92
halogenated compounds	218	7.91	1.95	87	0.40	1.23
total	1166	6.28	1.53	503	0.33	1.00

Table 5. Estimation Results of T_b and $\Delta_{vap}H(T_b)$ for 32 Kinds of Compounds Using This Proposed Method

	$\Delta_{vap}H(T_b)$/kJ·mol^{-1}						T_b/K				
		proposed method		Ma[7] method				proposed method		Constantinou -Gani[2]	
compound	exp data[10]	est data	percent error	est data	percent error	compound	exp data[12]	est data	percent error	est data	percent error
2,2-dimethylpentane	29.23	29.44	0.73	29.33	0.34	2,3-dimethylbutane	331.12	327.72	−1.03	314.02	−5.16
2,2,4-trimethylpentane	30.79	31.03	0.79	30.87	0.27	octane	398.82	395.79	−0.76	406.63	1.96
3-methylnonane	38.26	37.82	−1.15	37.49	−2.02	3,4-dimethylhexane	390.88	381.73	−2.34	385.92	−1.27
2- methyl-1-butene	25.50	25.40	−0.41	25.60	−0.41	hexadecane	559.98	554.60	−0.96	549.20	−1.93
propyl cyclopentane	34.70	34.14	−1.63	34.06	−1.84	1-pentene	303.11	307.92	1.59	301.68	−0.47
cyclooctane	35.90	36.35	1.26	35.39	−1.42	2-methyl-2-butene	311.70	302.57	−2.93	304.94	−2.17
methyl isopropanone	32.35	32.36	0.04	32.08	−0.83	cyclopentane	322.38	318.61	−1.17	320.75	−0.51
1,4-diethylbezene	39.40	39.82	1.08	32.59	−17.3	cyclopentene	317.35	322.09	1.49	306.01	−3.57
1-propanol	41.44	41.74	0.72	39.47	−4.75	1,4-dimethylbenzene	411.53	419.30	1.89	415.88	1.06
3,5-dimethylphenol	49.70	48.63	−2.15	48.66	−2.09	1-ethyl-4-methylbenzene	435.13	438.38	0.75	437.89	0.63
isobutyl formate	33.60	33.97	−1.11	34.30	2.07	2-methylnaphthalene	514.20	511.02	−0.62	503.09	−2.16
2,6-dimethylpyridine	37.46	37.74	0.75	37.50	0.11	1-propanol	370.93	365.88	−1.36	364.44	−1.75
chloroethane	24.53	24.72	0.76	24.70	0.70	cyclohexanol	433.94	427.53	−1.48	427.19	1.55
propyl formate	33.61	32.61	−2.97	32.89	−2.14	propyl butanoate	416.50	418.68	0.52	423.46	1.67
2,5-dimethylpyridine	38.68	39.04	0.94	38.30	−0.98	2,6-dimethylpyridine	416.91	433.05	3.87	442.39	6.11
dipropylamine	33.47	33.77	0.89	33.89	1.27	1,2-dichloroethane	356.66	343.24	−3.76	363.67	1.97
average			1.09		2.41	average			1.66		2.12

Table 6. Results of T_b Estimation for Isopropyl Cyclohexane

no.	a_l	ν_l	no.	a_l	ν_l	group	n_i	$\sum_{j=1}^{n_i} \nu_k$	$\sum_{j=1}^{n_i} e^{-\nu_k}$	ΔT_{b0i}	ΔT_{bIi}	ΔT_{bpi}
1	8.246	0.348	6	9.274	0.392	$-CH_3$	2	0.696	1.412	17.204	157.289	7.050
2	8.246	0.348	7	8.246	0.348	$>CH-$	1	0.302	0.740	9.777	154.616	−2.848
3	7.141	0.302	8	7.348	0.310	$(>CH_2)_R$	5	1.708	3.555	1.572	156.722	−11.716
4	7.348	0.310	9	6.633	0.280	$(>CH-)_R$	1	0.280	0.756	−11.744	189.690	0.272
5	8.246	0.348										

deviations between the calculated values by this method and the experimental data are listed in Table 4.

To test the applicability and reliability of the new methods, estimations of the new method for 32 compounds not used in the parameter regression have been made. These results compare favorably with the Ma[7] method and the Constantinou and Gani[2] method in Table 5.

The proposed method gives, as shown in Tables 2, 3, and 5, more accurate predictions for T_b and $\Delta_{vap}H(T_b)$ than the compared methods. The accuracies for aromatic and halogenated compounds are lower, which results from the complex structure and group interaction of these compounds. The accuracy of the normal boiling temperature prediction by the new method is slightly lower than that by the Constantinou and Gani[2] method. This may be because of the lower accuracy of the T_b prediction by a linear expression. In the Constantinou and Gani[2] method, a logarithmic expression of the group contribution was used to estimate T_b. Moreover, for the present method, the number of model parameters and the number of compounds for the T_b estimation are 120 and 1166, and those for the Constantinou and Gani[2] method are 121 and 392, respectively.

Conclusions

The specific position of a group in the molecule has been considered, and a group vector space method for estimating boiling temperatures and enthalpies of vaporization of organic compounds has been developed. It is not identical to group contribution methods because in this method the group number in the molecule has not been used. Expression for boiling temperatures T_b and enthalpies of vaporization $\Delta_{vap}H(T_b)$ have been established, and the numeric values of relative group parameters have been obtained. The average percent deviations of the estimation of the above two properties arey 1.5 and 1.0, respectivel, which shows that the present method demonstrates significant improvements in predicting the above properties, compared to the predicition abilities of conventional group methods.

Appendix: Illustrative Examples of Estimation

The procedure for estimating the physical property of an organic compound can be readily performed. First, the structural formula and corresponding vector space matrix for the molecule were drawn. Then, module a_l of group l in the molecule and corresponding module index ν_l may be calculated by $a_l = (\sum_{j=1}^{m} b_{lj}^2)^{1/2}$ and $\nu_l = \{a_l\}/\{(\sum_{j=1}^{n} a_j^2)\}^{1/2}$, where n is the number of groups in the molecule. Finally, substituting each $\sum_{j=1}^{n} \nu_k$, $\sum_{j=1}^{n_i} e^{-\nu_k}$, and subscript $k = j + \sum_{m=1}^{i-1} n_m$ along with the values of the corresponding parameters found in Table 1 into the relative correlation, the estimation value of the physical property could be obtained. Three examples are shown as follows:

Table 7. Results of $\Delta_{vap}H(T_b)$ Estimation for *tert*-Butyl Methyl Thioether

no.	a_l	v_l	no.	a_l	v_l	group	n_i	$\sum_{j=1}^{n_i} \nu_k$	$\sum_{j=1}^{n_i} e^{-\nu_k}$	$\Delta_{vap}S_{0i} \times 10^3$	$\Delta_{vap}S_{Ii} \times 10^3$	$\Delta_{vap}S_{pi} \times 10^3$
1	4.123	0.416	4	5.196	0.525	$-CH_3$	4	1.774	2.570	0.7809	−2.3257	−0.2533
2	4.123	0.416	5	2.646	0.267	$>C<$	1	0.267	0.766	2.1991	−8.1705	0.3504
3	4.123	0.416	6	3.606	0.364	$-S-$	1	0.364	0.695	−3.2532	3.6496	2.4600

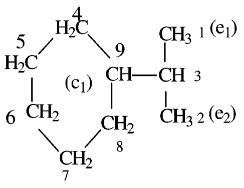
Table 8. Results of T_b Estimation for 1-Brom-2,4-dimethylbenzene

no.	a_l	v_l	no.	a_l	v_l	group	n_i	$\sum_{j=1}^{n_i}\nu_k$	$\sum_{j=1}^{n_i} e^{-\nu_k}$	ΔT_{b0i}	ΔT_{bIi}	ΔT_{bpi}
1	8.062	0.365	6	6.782	0.307	$-CH_3$	2	0.73	1.39	17.204	157.289	7.050
2	8.062	0.365	7	6.782	0.307	$(=CH-)_R$	3	0.97	1.54	−9.654	178.977	−2.069
3	7.348	0.333	8	7.483	0.339	$(=C<)_R$	4	0.95	2.18	5.988	181.093	−6.438
4	7.483	0.339	9	7.483	0.339	$-Br$	1	0.34	0.71	−36.09	233.133	3.224
5	6.633	0.300										

Example 1: Estimate T_b of Isopropyl Cyclohexane. Its experimental value is 427.7 K. The estimation data are listed in Table 6.

The estimated value of T_b/K is 435.07; the relative deviation is 1.7%.

Structural formula and corresponding vector space matrix:

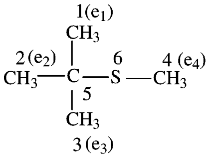


$$\begin{array}{c|ccc} & e_1 & e_2 & c_1 \\ \hline 1 & 0 & 2 & 8 \\ 2 & 2 & 0 & 8 \\ 3 & 1 & 1 & 7 \\ 4 & 3 & 3 & 6 \\ 5 & 4 & 4 & 6 \\ 6 & 5 & 5 & 6 \\ 7 & 4 & 4 & 6 \\ 8 & 3 & 3 & 6 \\ 9 & 2 & 2 & 6 \end{array}$$

Example 2: Estimate $\Delta_{vap}H(T_b)$ of tert-Butyl Methylthioether. Its experimental values of $\Delta_{vap}H(T_b)$/kJ·mol^{-1} and T_b/ K are 31.47 and 372.1, respectively. The estimation data are listed in Table 7.

The estimated value of $\Delta_{vap}H(T_b)$/kJ·mol^{-1} is 31.47; the relative deviation is 0%.

Structural formula and corresponding vector space matrix:

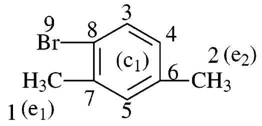


$$\begin{array}{c|cccc} & e_1 & e_2 & e_3 & e_4 \\ \hline 1 & 0 & 2 & 2 & 3 \\ 2 & 2 & 0 & 2 & 3 \\ 3 & 2 & 2 & 0 & 3 \\ 4 & 3 & 3 & 3 & 0 \\ 5 & 1 & 1 & 1 & 2 \\ 6 & 2 & 2 & 2 & 1 \end{array}$$

Example 3: Estimate T_b of 1-Brom-2,4-dimethylbenzene. Its experimental value is 478.15 K. The estimation data are listed in Table 8.

The estimated value of T_b/K is 486.91; the relative deviation is 0%.

Structural formula and corresponding vector space matrix:



$$\begin{array}{c|ccc} & e_1 & e_2 & c_1 \\ \hline 1 & 0 & 4 & 7 \\ 2 & 4 & 0 & 7 \\ 3 & 3 & 3 & 6 \\ 4 & 4 & 2 & 6 \\ 5 & 2 & 2 & 6 \\ 6 & 3 & 1 & 6 \\ 7 & 1 & 3 & 6 \\ 8 & 2 & 4 & 6 \\ 9 & 2 & 4 & 6 \end{array}$$

Supporting Information Available:

Group contributions and correlation equations in the Constantinou and Gani[2] method and the Ma[7] method and normal boiling temperatures and enthalpies of vaporization used in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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