Topological Index and Thermodynamic Properties. I. Empirical Rules on the Boiling Point of Saturated Hydrocarbons

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Empirical relations are proposed for the boiling point (bp) and the topological index (Z_G) of a saturated hydrocarbon as

$$bp = a \log Z_G + b$$

or $bp = (a \log Z_G + c)/\sqrt{N} + b,$

where N is the number of the carbon atoms. A number of compounds with or without ring(s) are plotted for these relations. Correlation is generally better for cyclic compounds than for chain compounds. Sterically hindered paraffins deviate appreciably. Several empirical rules on the isomeric lowering of the boiling point of saturated hydrocarbons are presented and most of them are shown to be consistent with the above relations. Several empirical formulae for the boiling point of normal paraffins are compared and discussed.

Topological index Z_G has been defined for a non-directed graph G, or the carbon atom sekeleton of a saturated hydrocarbon.[1-3] In relation to the mathematical treatment on Z_G many interesting properties were found. A graphical method for enumerating the coefficients of the characteristic or secular polynomial of the Hückel molecular orbital was proposed.[4] It was also pointed out that Z_G is correlated well with several of the thermodynamic quantities of molecules such as the boiling point.[1]

In this paper relations between the topological index and the boiling point of saturated hydrocarbons are analyzed in detail and several empirical rules on the boiling point are presented and discussed.

Topological Index

The definition and enumerating method of the topological index are summarized below.[1-4]

A non-adjacent number $p(G,k)$ for graph G is the number of ways in which such k bonds are so chosen from G that no two of them are connected, $p(G,0)$ being unity and $p(G,1)$ the number of bonds.

The topological index Z_G for G is defined as the sum of $p(G,k)$'s,

$$Z_G = \sum_{k=0}^{m} p(G, k). \tag{1}$$

For example Z_G's for the two graphs I and II are obtained as follows:[5]

$$Z_I = 1 + 6 + 8 + 2 = 17$$

$$Z_{II} = 1 + 6 + 5 = 12.$$

For larger graphs Z_G can be obtained using either

Chart 1

of the two composition principles, CPI and CPII. With the notations adopted in Fig. 1 we have

$$\text{CPI: } Z_G = Z_L Z_M + Z_A Z_B Z_C Z_D Z_E Z_F \tag{2}$$

$$\text{CPII: } Z_G = Z_A Z_B Z_C Z_M + Z_D Z_E Z_F Z_L$$
$$- Z_A Z_B Z_C Z_D Z_E Z_F \tag{3}$$

Application of CPI and CPII, respectively, to graphs I and II is illustrated in Fig. 2.

Tables of the $p(G,k)$ numbers and Z_G values for smaller tree graphs and non-tree graphs are respectively given in Refs. 2 and 3.
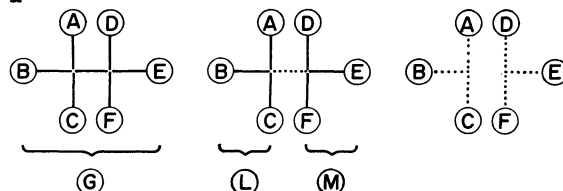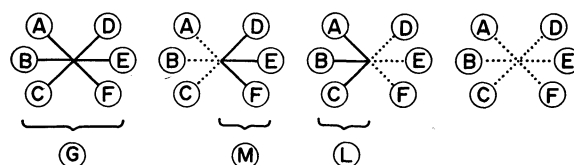
Fig. 1. Illustration for the two composition principles. A, B,⋯F, L, and M are subgraphs of graph G. Cutting of a bond is represented by a dotted line.

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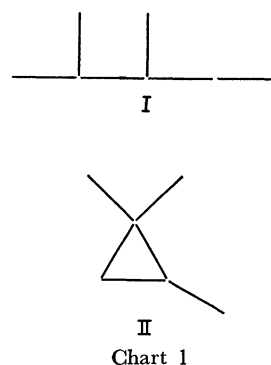
1) H. Hosoya, This Bulletin, 44, 2332 (1971).

2) K. Mizutani, K. Kawasaki, and H. Hosoya, *Natural Science Report of Ochanomizu Univ.*, 22, 39 (1971).

3) K. Kawasaki, K. Mizutani, and H. Hosoya, *ibid.*, 22, 181 (1971).

4) H. Hosoya, *Theor. Chim. Acta*, 25, 215 (1972).

5) I and II are, respectively, the carbon atom skeletons of 2,3-dimethylpentane and 1,1,2-trimethylcyclopropane.

Fig. 2. Application of the composition principles I and II, respectively, to graphs I and II.

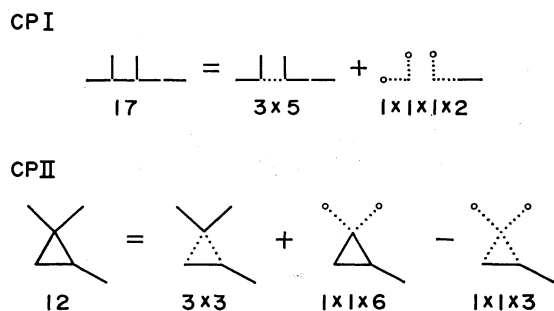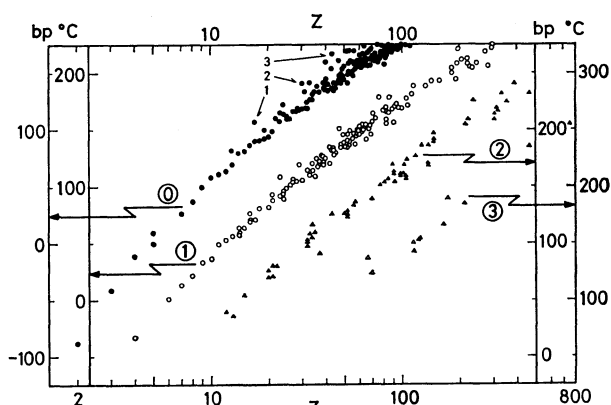Fig. 3. Boiling point-topological index plot of chain, mono-cyclic, bicyclic, and tricyclic saturated hydrocarbons. The point for methane is omitted ($bp=-161.5°C$, $Z=1$). Note the shift in the ordinate. The numbers in circles represent the numbers of rings. The small numbers 1, 2, and 3 are referred to the text.

General Aspects of Correlation

Figure 3 gives plots of the boiling points against log Z_G for chain, monocyclic, bicyclic, and tricyclic saturated hydrocarbons. The boiling point data were taken from the API report[6] and supplemented by the Beilstein Handbuch.[7] There exist serveral geometrical isomers which can not be discriminated by the topological index, e.g., 1,cis- and 1,trans-2-dimethylcyclopropanes. An averaged value is plotted for a group of such isomers.

Although there are observed several scattered points,[8] the boiling point for a series of compounds with similar structures rises roughly linear to log Z_G, namely,

$$bp = a \log Z_G + b. \tag{4}$$

For all the groups of compounds studied, the slope a is almost the same and the value b decreases with an increase in the number of rings. In other words, if two saturated hydrocarbons with the same Z_G value but with different numbers of rings are compared, the more the rings the lower the boiling point.

Strictly speaking, the slope a slowly decreases with log Z_G and the plots can be straightened up by taking $\log(Z_G-3)$ as the abscissa. However, it must be emphasized here that, contrary to the attempts by many authors,[10-13] our standpoint is not to find out the best-fit empirical formula but to understand the topological aspects of the boiling point with as few parameters as possible. Further, it may be noted that several thermodynamic quantities such as critical temperature, heat of vaporization, absolute entropy, vapor pressures at various temperatures are also correlated with the topology of a molecule,[14] and that the boiling point is chosen here as the most typical of them.

Let us see the relation (4) in more detail. The plot bp—log Z_G for the chain isomers C_7H_{16} and the plot
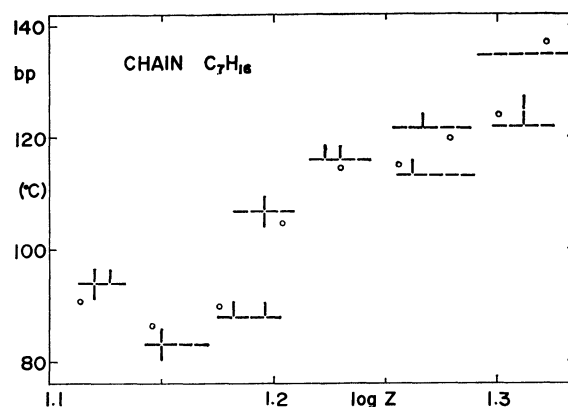
Fig. 4. Boiling point-topological index plot of the chain C_7H_{16} isomers.
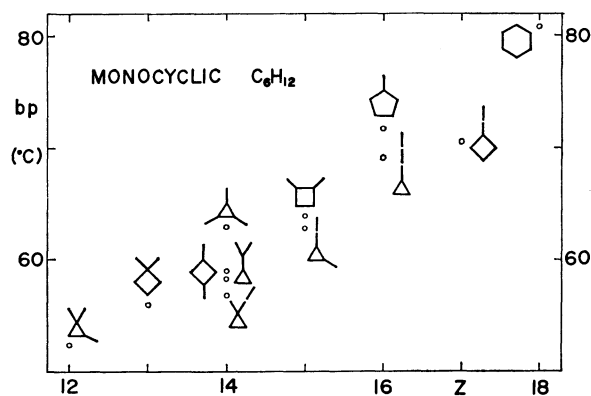
Fig. 5. Boiling point-topological index plot of the monocyclic C_6H_{12} isomer.

6) American Petroleum Institute Research Project 44, "Selected Values of Properties of Hydrocarbons and Related Compounds", Thermodynamics Research Center, Texas A & M Univ. (1971).

7) Deutschen Chemisches Gesellschaft, "Beilstein Handbuch der organischen Chemie".

8) The points for the following compounds deviate appreciably from other members of the series and are omitted from Fig. 3. They are 1,2,3-trimethyl-4-isopropylcyclopentane ($Z=125$, $bp=157$—$158°C$),[7] 1-methyl-2,3-diisopropylcyclopentane ($Z=194$, $bp=150$—$152°C$),[7] 1,1,3,3-tetramethyl-2,4-diethylcyclobutane ($Z=161$, $bp=124$—$125°C$)[7], and 1,4-dimethylbicyclo[2.1.1]hexane ($Z=37$, $bp=91°C$).[9] It is possible that these data are wrong.

9) A. Cairncross and E. P. Blanchard, Jr., J. Amer. Chem. Soc., 88, 496 (1966).

10) H. Wiener, ibid., 69, 17 (1947); J. Phys. Chem., 52, 425 (1948).

11) J. R. Platt, J. Phys. Chem., 56, 328 (1952).

12) W. J. Taylor, J. M. Pignocco, and F. D. Rossini, J. Res. Natl. Bur. Stand., 34, 413 (1945); K. Li, R. L. Arnett, M. B. Epstein, R. B. Ries, L. P. Bitler, J. M. Lynch, and F. D. Rossini, J. Phys. Chem., 60, 1400 (1956); J. B. Greenshields and F. D. Rossini, ibid., 62, 271 (1958).

13) K. Altenburg, Brenstoff-Chem., 47, 100, 331 (1966).

14) H. Hosoya, unpublished.

bp—Z_G for the monocyclic isomers C_6H_{12} are shown, respectively, in Figs. 4 and 5. The boiling points are fairly well correlated with Z_G or $\log Z_G$ both for chain and cyclic compounds. This is the case for other lower members of hydrocarbons. However, as molecules become larger the plots for chain compounds are getting scattered as seen in Fig. 3. Most points deviating appreciably are those of sterically crowded compounds such as 2,2,3,3-tetramethylbutane (marked with 1 in Fig. 3), 2,2,3,3-tetramethylpentane (2) and 2,2,3,3,4-pentamethylpentane (3).

On the other hand, for higher members of cyclic compounds the correlation is as good as the smaller molecules. Surprisingly, the plots for the known family of cyclenes ($C_{10}H_{16}$ and $C_{11}H_{18}$) with three fused rings are lined up as seen in Fig. 6. Thus let us consider the problem separately for chain and cyclic compounds.
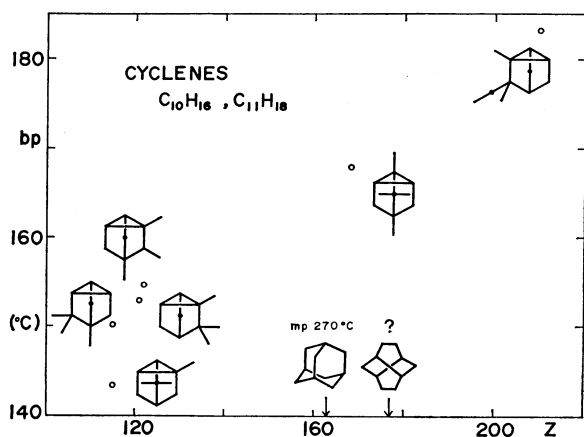

Fig. 6. Boiling point-topological index plot of the cyclene isomers $C_{10}H_{16}$ and $C_{11}H_{18}$.

Chain Paraffins

Since the effect of the branching of the topological index is analyzed elsewhere,[1] discussion will be given here of phenomenological point of view.

Empirical Formula.   During an attempt in straightening up of the relation (4) for normal paraffins it was found that the plot of $\sqrt{N}(bp-a)$ of branched
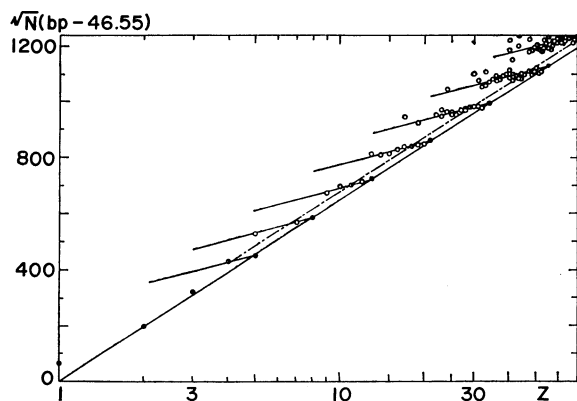

Fig. 7. Plots of $\sqrt{N}(bp-46.55)$ against $\log Z$ for chain saturated hydrocarbons. Boiling points are in °K.
●: normal paraffins, ◑: 2-methyl isomers and ○: other isomers.

chain paraffins with N carbon atoms against $\log Z_G$ gives an interesting pattern as shown in Fig. 7. The points for normal paraffins lie perfectly on a line passing the origin, while isomeric paraffins lie on "branches" stemming from the points of the corresponding normal paraffins. The slopes of the branches seem to be almost the same. Although many points still deviate in this plot, the points for a series of compounds with similar structures such as 2-methyl isomers are found to lie on a line parallel to that of the normal paraffins. Thus we get

$$bp = (a \log Z_G + c)/\sqrt{N} + b. \tag{5}$$

The values of a and b are constant for a series of compounds either with the same N or with similar structures and are given in Table 1. Accuracy of Eq. (5) for normal paraffins will be compared in Appendix with a variety of hitherto proposed empirical formulae.

TABLE 1. THE VALUES OF THE CONSTANTS IN THE BOILING POINT-TOPOLOGICAL INDEX RELATION[a]

Category	a	b	c
Normal paraffins	650.3	46.55	0
Compounds with similar structures[b]	650.3	46.55	Dependent on the type
Compounds with the same N[c]	310.0	46.55	Dependent on N

a) The boiling point (in °K) can be obtained from the relation $bp=(a \log Z_G+c)/\sqrt{N}+b$.

b) Obtained from the least squares calculation for the compounds with N from 2 to 10.

c) Obtained from the least squares calculation for the heptane isomers by omitting 3-ethylpentane and 2,2,3-trimethylbutane. N is the number of the carbon atoms.

Empirical Rules.   From Eq. (5) the boiling point lowering (Δbp) of an isomer is expected to be

$$\Delta bp = bp(\text{normal}) - bp(\text{isomer}) \tag{6}$$

$$= a \log (Z_{\text{normal}}/Z_{\text{isomer}})/\sqrt{N}. \tag{7}$$

In Tables 2 and 3 observed and calculated values are compared for six different series of paraffin isomers.

TABLE 2. OBSERVED AND CALCULATED BOILING POINT LOWERING OF PARAFFINS BY INTRODUCING A TERTIARY CARBON ATOM

N	Series A			Series B			Series C		
	Z_G	Δbp[a] (°C)		Z_G	Δbp (°C)		Z_G	Δbp (°C)	
		obsd	calcd		obsd	calcd		obsd	calcd
4	4	11.2	15.0						
5	7	8.2	8.1						
6	11	8.4	9.2	12	5.4	4.4			
7	18	8.3	7.9	19	6.5	5.1			
8	29	8.1	7.6	31	6.8	4.4	30	8.0	5.9
9	47	7.6	7.1	50	6.6	4.3	49	8.4	5.2
10	76	7.1	6.7	81	6.3	4.0	79	8.4	5.1
11	123	6.7	6.4	131	5.9	3.9	128	8.0	4.8
12	199	6.3	6.2	212	5.5	3.6	207	7.3	4.7

a) $\Delta bp(\text{obsd})=bp$ (normal)$-bp$(isomer). $\Delta bp(\text{calcd})=310 \log(Z_{\text{normal}}/Z_{\text{isomer}})/\sqrt{N}$.

TABLE 3. Observed and calculated boiling point lowering of paraffins by
introducing a quarternary carbon atom[a]

N	Series D			Series E			Series F		
	Z_G	Δbp (°C)		Z_G	Δbp (°C)		Z_G	Δbp (°C)	
		obsd	calcd		obsd	calcd		obsd	calcd
5	5	9.5	28.4						
6	9	19.0	20.3						
7	14	19.2	20.7	16	12.3	13.7			
8	23	18.9	18.7	25	13.7	14.7			
9	37	18.1	17.9	41	13.8	13.2	39	15.6	15.5
10	60	17.2	16.9	66	12.9	12.8	64	16.6	14.1
11	97	16.3	16.1	107	13.9	12.1	103	17.9	13.7
12	157	15.5	15.4	173	13.3	11.6	167	17.3	13.0

a) See the footnote of Table 2.

In some series of compounds the values for the lowest members deviate appreciably as is reasonably expected and may be omitted from the consideration. We get several empirical rules on the boiling points of chain paraffins. The topological index is shown to be in parallel with the boiling point change through Eq. (5).

Rule 1) Of all the isomeric paraffins the normal compound has the highest boiling point.

Rule 2) A monomethyl substitution lowers the boiling point by about 7 ± 1°C. (See Series A, B, and C in Table 2).

Rule 3) A geminal-dimethyl substitution lowers the boiling point by about 2 ± 1°C more than the double of a monomethyl substitution. (Compare pairs of Series A and D, B and E, and C and F in Tables 2 and 3).

Rule 4) The magnitude of the boiling point lowering by a monomethyl or geminal-dimethyl substitution alternates as the site of the substitution runs from the terminal towards insides. (See Series A, B,···F).

No exception has long been observed for Rule 1). It is proved in Ref. 1 as Theorem 4 that the topological index of the normal compound is the largest of all the isomeric structures.

Rule 4) deserves to be noted. As evident from Table 2, 2-methyl and 4-methyl substitutions lower the boiling point by about the same amount, which is larger than the contribution by a 3-methyl substitution. This is also the case for geminal-dimethyl substitutions. In both cases the boiling point lowering by further inner substitutions converges rapidly to a limit. This behavior reminds one of the zig-zag change of melting points of chain compounds with the increase of the chain length. That the topological index has just the same property can be shown as follows.

Let the topological index of a normal paraffin with N carbon atoms (n-N-ane) be $Z_{\bar{N}}$. For a 2-methyl substituted isomer (2-Me-(N-1)-ane) the topological index Z_{2-Me} is expressed as

$$Z_{2-Me} = Z_{\overline{N-1}} + Z_{\overline{N-3}}$$

by using the composition principle. (Eq. (15) of Ref. 1) For larger N's the value $Z_{\bar{N}}$ increases asymptotically as $\alpha^{N+1}/\sqrt{5}$,[15] with $\alpha=(1+\sqrt{5})/2$. Thus the ratio

TABLE 4. Observed and calculated boiling point lowerings of paraffins by a 2-methyl substitution

N	Series G			Series H			Series J		
	Z_G	$\Delta\Delta bp$[a] (°C)		Z_G	$\Delta\Delta bp$ (°C)		Z_G	$\Delta\Delta bp$ (°C)	
		obsd	calcd		obsd	calcd		obsd	calcd
6	10	2.3[b]	5.2						
7	15	9.6	9.3	17	2.1[b]	5.7	13	−1.7[b]	3.8
8	25	8.5	7.1	26	9.5	8.4	19	7.6	9.1
9	40	8.0	7.3	43	8.2	6.8	32	8.6	6.5
10	65	7.1	6.7	69	7.4	6.8	51	8.0	6.9
11	105	6.2	6.5	112	7.0	6.4	83	7.0	6.3
12	170	6.0	6.2	181	6.0	6.1	134	6.0	6.2
Isomer	C_{N-6}			C_{N-7}			C_{N-7}		
Reference	C_{N-5}			C_{N-6}			C_{N-6}		

a) $\Delta\Delta bp$(obsd) $= bp$(ref.) $- bp$(isomer), $\Delta\Delta bp$(calcd)310 log(Z_{ref}/Z_{isomer})/$\sqrt{N}$.
b) Deviating from the additivity.

15) $Z_N = (\alpha^{N+1} - \beta^{N+1})/\sqrt{5}$, where $\alpha=(1+\sqrt{5})/2$ and $\beta=(1-\sqrt{5})/2$.[1]

TABLE 5.   OBSERVED AND CALCULATED BOILING POINT LOWERINGS OF PARAFFINS BY A 2,2-DIMETHYL SUBSTITUTION

N	Series K			Series L			Series M		
	Z_G	$\Delta\Delta bp$[a] (°C)		Z_G	$\Delta\Delta bp$ (°C)		Z_G	$\Delta\Delta bp$ (°C)	
		obsd	calcd		obsd	calcd		obsd	calcd
7	13	9.2[b]	16.6						
8	19	18.4	20.1	31	9.0[b]	16.3	17	0.3[b]	14.4
9	32	19.2	17.3	50	17.7	18.7	24	10.4[b]	19.4
10	51	18.1	17.0	81	17.0	16.5	41	19.4	16.2
11	83	16.2	16.0	131	16.0	16.1	65	17.0	16.3
12	134	15.0	15.4	212	15.0	15.3	106	16.0	15.3
Isomer	$-\!\!\overset{\vert}{\underset{\vert}{C}}_{N-7}\!\!-$			$-\!\!\overset{\vert}{\underset{\vert}{C}}_{N-8}\!\!-$			$-\!\!\overset{\vert}{\underset{\vert}{C}}_{N-8}\!\!-$		
Reference	$-\!\!\overset{\vert}{\underset{\vert}{C}}_{N-5}\!\!-$			$--\overset{\vert}{\underset{\vert}{C}}_{N-6}\!\!-$			$--\overset{\vert}{\underset{\vert}{C}}_{N-6}\!\!-$		

a) $\Delta\Delta bp(\text{obsd})=bp(\text{ref.})-bp(\text{isomer})$, $\Delta\Delta bp(\text{calcd})=310 \log(Z_{\text{ref}}/Z_{\text{isomer}})/\sqrt{N}$.
b) Deviating from the additivity.

TABLE 6.   OBSERVED AND CALCULATED BOILING POINT LOWERINGS OF DECANE ISOMERS BY MONOMETHYL SUBSTITUTIONS[a]

Reference	2-Methyl	3-Methyl	4-Methyl
	7.1 (6.7)	6.3 (4.0)	8.4 (5.1)
	7.1 (6.7)	6.6 (4.1)	8.5 (4.7)
	7.4 (6.8)	7.0 (3.9)	8.4 (5.6)
	8.0 (6.9)	6.1 (3.7)	8.6 (6.1)
	8.4 (6.2)	5.5 (4.8)	−0.7 (2.7)

a) Numerals in parentheses are calculated from Eq. (7).

$Z_{\bar{N}}/Z_{2-\text{Me}}$ converges to a limit $(5+3\sqrt{5})/10=1.171$ with increasing N's. Similarly we get

$$Z_{\bar{N}}/Z_{3-\text{Me}} \to 1.099, \quad Z_{\bar{N}}/Z_{4-\text{Me}} \to 1.125,$$
$$Z_{\bar{N}}/Z_{5-\text{Me}} \to 1.115 \text{ and finally}$$
$$\lim_{m\to\infty} (Z_{\bar{N}}/Z_{m-\text{Me}}) \to \sqrt{5}/2 = 1.118.$$

In order to check the additivity of the lowering of the boiling point by branching, the lowering of the boiling point, $\Delta\Delta bp$, of disubstituted paraffins with respect to a reference mono-substituted compound was studied. Some of the results are shown in Tables 4—6.

Let us consider the octane isomers as an example. The boiling point of 2,5-dimethylhexane is lower than that of 2-methylheptane by 8.5°C (Series G in Table 4), which is very close to the value 8.1°C (Series A) of the lowering of the latter with respect to n-octane. These values are estimated from the topological index through Eq. (5) or (7) to be 7.6 and 7.1°C, respectively. Both for the observed and calculated values, good agreement is observed between Δbp's of Series A and $\Delta\Delta bp$'s of Series G. The $\Delta\Delta bp$ values for Series H and J represent other examples of the boiling point lowering by 2-methyl substitution. Rule 2) seems to be obeyed for Series G, H, and J. However, the boiling point lowerings of 2,3-dimethylated butane, pentane, and hexane are as small as about 2°C with

respect to 2-methylpentane, 3-methylhexane, and 4-methylheptane (not shown), respectively. Sterically hindered substitution seems to raise the boiling point appreciably.

Series K, L, and M in Table 5 give the boiling point lowering by *geminal*-dimethyl substitutions. In Table 6 observed and calculated boiling point lowerings (Δbp and $\Delta\Delta bp$) of 2-, 3-, and 4-methyl subsitutions for dodecane isomers are demonstrated. Thus we get

Rule 5) If two substituents are well separated from each other, the lowering of the boiling point is additive.

Rule 6) Too much crowded substitution does not lower the boiling point effectively.

If one admits the relation (5), all these empirical rules except for Rule 6) can be predicted. Qualitatively the same conclusions can be obtained from the simpler relation (4). It has been known that the boiling point is well correlated with the absolute entropy of a molecule in gaseous state and we have found that the absolute entropy of saturated hydrocarbons are linearly dependent on $\log Z_G$ fairly well.[14] Thus it can be said that the topological index is a good index for the topological properties of molecules and is useful for rough estimation of some thermodynamic quantities. By the term "topological properties" we mean such quantities that may be related with the entropy or the number of the degree of freedom for

TABLE 7.   ISOMERS OF THE SMALLEST TOPOLOGICAL INDEX AND THOSE WITH THE LOWEST BOILING POINTS

N	Smallest Z	Lowest bp	
		1	2
5			
6			
7			
8			
9			
10			
11			
12			

internal rotations of a molecule.

Steric effect seems to be one of the most important factors that could improve the empirical relations (4) and (5). This point has already been discussed by Platt[9] that the polarity number or the number of "steric pairs" p[16] proposed by Wiener[10] is the best parameter for evaluating this effect. Thus the isomer with the lowest boiling point is not necessarily the one with the smallest topological index. This is seen in Table 7.

Cyclic Paraffins

Figure 5 for the plot of all the possible isomers of monocyclic C_6H_{12} hydrocarbons is instructive to realize the effect of branching on the boiling point of cyclic compounds. Plots of other series, though not complete, show similar trend and we get

Rule 7) Among all the isomers of monocyclic saturated hydrocarbons (C_NH_{2N}) the isomer with no branch (cyclo-N-ane) has the highest boiling point.

Rule 8) For polycyclic saturated hydrocarbons isomers without branches have generally higher boiling points than those with branches.

Rule 9) For cyclic compounds with the same ring skeleton, the longer the longest branch the higher the boiling point.

Rule 10) For cyclic compounds with the same ring skeleton, the more the quarternary carbon atoms, the lower the boiling point.

Rule 7) is analogous to Rule 1), that is, the normal paraffin has the highest boiling point among the isomers of chain saturated hydrocarbons. The remaining Rules 8)—10) are consistent with the general aspects of the topological index.[3] As an application of these Rules let us consider some interesting topics.

We can predict that among the possible twenty bornane isomers, i.e., trimethylbicyclo[2.2.1]heptanes,

2,3,7-trimethyl derivative III and 1,3,3-trimethyl derivative V, respectively, give the highest (ca. 170°C) and lowest (ca. 150°C) boiling points, while bornane, 2,7,7-trimethyl isomer IV boils at 160°C.

III   IV   V
Z=116   Z=102   Z=88
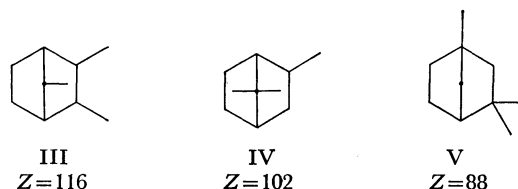
It is also predicted that among the possible isomers of $C_{10}H_{16}$ cyclenes, the isomers VI and VII respectively give the highest (ca. 160°C) and lowest (ca. 145°C) boiling points (See Fig. 7).

VI   VII
Z=138   Z=106
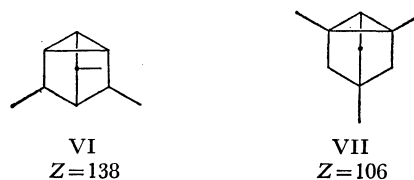
Adamantane is known to be volatile but to melt at as high as 270°C. The topological index is calculated as 163 and the boiling point is estimated as below as 165°C from the interpolation of the plots of tricyclic compounds (Fig. 7). A paradoxical result is also obtained for twistane with Z=177. So we must say that for highly fused ring compounds the topological index alone cannot account for the boiling point.

Appendix

Comparison of Several Empirical Relations of the Boiling Points of Normal Paraffins.   Empirical formulae of the boiling points of the lower members of normal paraffins have been proposed by many authors. Typical of them are as follows:

TABLE 8.   COMPARISON OF THE EMPIRICAL FORMULAE FOR THE BOILING POINT OF NORMAL PARAFFINS[a]

N	Exp. bp (°K)	Error=calcd−obsd (°K)					
		(8)	(9)	(10)	(11)	(12)	(13)
1	111.7	17.9	15.3	−12.2	7.5	7.1	65.2
2	184.5	0.2	−0.7	−6.8	−2.4	−3.0	0.4
3	231.1	0.5	0.3	−0.4	0.3	−0.2	−5.5
4	272.7	−0.1	−0.2	0.7	0.3	0.0	1.1
5	309.2	−0.1	−0.1	0.8	0.2	0.1	−0.1
6	341.9	−0.1	0.0	0.6	−0.1	0.2	0.4
7	371.6	−0.1	0.1	0.3	−0.4	0.1	−0.3
8	398.8	0.0	0.1	0.0	−0.6	0.1	−0.2
9	424.0	−0.1	0.0	−0.3	−0.9	−0.1	−0.3
10	447.3	−0.1	−0.2	−0.4	−1.0	−0.1	0.0
20	617.0	0.9	−4.8	−0.9	2.0	0.1	16.8
40	798.2	13.5	−18.3	−30.2	20.3	−0.2	93.4
80	951.2	68.4	−26.9	−167.7	75.9	−0.2	300.7
100	988.2	100.3	−25.1	−237.2	104.3	−0.3	408.2

a) The number in parentheses indicates the equation number in text.

$$bp = 745.42 \log (N+4.4) - 416.31 \qquad (8)^{17)}$$

$$bp = 1209.59 - 1162.9/(1+0.074189N^{0.85}) \qquad (9)^{18)}$$

$$bp = \{(21720N-11820)/(1+0.000283N^2)\}^{1/2} \qquad (10)^{19)}$$

$$bp = 127.55N^{2/3}/(1+0.07033N^{2/3}) \qquad (11)^{20)}$$

$$\log (1078-bp) = 3.0319 - 0.04999N^{2/3} \qquad (12)^{21)}$$

16) The number p is defined as the number of pairs of carbon atoms which are separated by three carbon-carbon bonds.

17) G. Egloff, J. Sherman, and R. B. Dull, *J. Phys. Chem.*, **44**, 730 (1940).

18) J. R. Platt, *J. Chem. Phys.*, **15**, 419 (1947).

19) Y. Varshni, *J. Ind. Chem. Soc.*, **28**, 535 (1951).

20) K. Nakanishi, M. Kurata, and M. Tamura, *J. Chem. Eng. Data*, **5**, 210 (1960).

21) A. Kreglewski and B. J. Zwolinski, *J. Phys. Chem.*, **65**, 1050 (1961).

Boiling points are in °K and N is the number of carbon atoms. Expressions with many parameters or of complicated forms are not chosen here.[12,13] Now let us add our Eq. (5).

$$bp = 650.3 \log Z_N/\sqrt{N} + 46.55 \qquad (13)$$

By using the asymptotical form of Z_N we get

$$bp = 135.90\sqrt{N} + 46.55 - 91.37/\sqrt{N}. \qquad (14)$$

for larger N.

Although the forms of these formulae are quite different from each other they give fairly good values for paraffins with N from 2 to 10 as shown in Table 8. Since all these relations were obtained so as to fit the lower members of the series most of them including our relations (13) and (14) are in poor agreement with experiments for higher members of the series up to $N=100$. However, the relation (12) gives surprisingly good results.