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Topological Index and Thermodynamic Properties. III.[†] Classification of Various Topological Aspects of Properties of Acyclic Saturated Hydrocarbons

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To elucidate the physical meaning of the structure-activity relationship of alkanes, correlation coefficients between 24 thermodynamic properties of hexane, heptane, octane, and nonane isomers and four different topological indices were calculated. These properties were classified into five different types depending on the signs and magnitudes of their correlation coefficients with the two indices, Z and p_3. It is interpreted that Z and p_3, respectively, represent the dynamical and static features of the topological properties of molecules. The merit of correlation pattern recognition is demonstrated.

There have been proposed a number of empirical formulas relating various properties of chemical substances with their structural parameters, such as the topological index.[1—18] Although the term topological index was proposed first by one of the present authors for the Z-index defined below,[7,19] recently it is used as a common name given to a group of indices for characterizing certain aspects of the topological skeleton of a molecule obtained according to the specified algorithm.[8,10,20—24] Given a good structure-activity relationship for a certain property or a set of properties, two different directions are open for further studies, namely, predictable (or practical) and interpretable (or conceptual) ones.[13] A majority of QSAR (quantitative structure-activity relationship) studies aim the former goal by using as many parameters as possible for attaining accurate predictions.[1,8,9] On the other hand, toward the latter goal, continuing attempts have been undertaken to unveil the physical or microscopic meaning of various magic parameters, the topological indices.[4,7] Thermodynamic properties of saturated hydrocarbons seem to be the best probe for this study, since their isomeric differences seem to be governed mainly by the topological structure of the carbon atom skeleton, and a number of experimental data of good quality are available.[25]

The present authors have shown that the boiling point and entropy of saturated hydrocarbons are correlated fairly well with the Z index and many empirical rules on these properties can be derived by assuming linear relationships between Z and these properties.[7,14—16]

The pioneering works by Wiener[2] and Platt[3] established that almost all the thermodynamic properties can be correlated well with the combination of two different topological indices, *e.g.*, Wiener's path number w and polarity number p or p_3. Randić and Wilkins[13,17] chose another set of parameters, p_2 and p_3, for graph-theoretical ordering of the hydrocarbon isomers to analyze the molecular property correlation, where p_2 is the number of paths of length two, or the so-called Gordon-Scantlebury index, N_2.[18] It is interesting to note that similar two-parameter dependency of thermodynamic properties is observed in a systematic factor analysis by Cramer[12] for a larger group of substances of considerable diversity from helium to anthracene and from alkanes to amides. He claims that his two parameters B and C respectively represent molecular cohesiveness and molecular bulkiness.

What is then the best set of two parameters representing the different topological aspects of branching and cyclization? They should also be as orthogonal as possible to each other, and their physical meaning should be clear or at least interpretable. For this purpose those simple, say, interger topological indices, Z, w, p_2, and p_3, which have been introduced above are desirable. In this paper we have studied the correlation between the twenty four thermodynamic properties of saturated hydrocarbons and the individual and various combinations of these topological indices. The properties studied were found to be well classified into several types depending on the mixing-phase of the correlation coefficients with respect to the two parameters, Z and p_3. Attempts to get the physical interpretation of the two-parameter dependency of these properties are being under way.

I. Topological Indices

Definitions. The carbon atom skeleton of a (saturated) hydrocarbon molecule can be expressed as a non-directed graph G composed of lines (C–C bonds) and N points (C atoms), whose adjacency relation is to be expressed by an $N \times N$ adjacency matrix $\boldsymbol{A}$ with elements $a_{ij}=1$ and 0, respectively, for the bonding and non-bonding ij pairs of points. The distance matrix $\boldsymbol{D}$ is defined as the $N \times N$ matrix with elements d_{ij} as the number of shortest path from point i to j. The half sum of the off-diagonal matrix elements of $\boldsymbol{D}$ is defined as w.[2,7] One half of the number of $d_{ij}=2$ elements in $\boldsymbol{D}$ is defined as p_2 or N_2 (Gordon-Scantlebury index),[18] while that of $d_{ij}=3$ as p_3 or p.[2] The non-adjacent number $p(\mathrm{G},k)$ for G is defined as the number of ways for choosing k disjoint lines from G.[7] The total number of $p(\mathrm{G},k)$ is defined as Z_G (topological index or Z-index).[7] As shown in Fig. 1 we can

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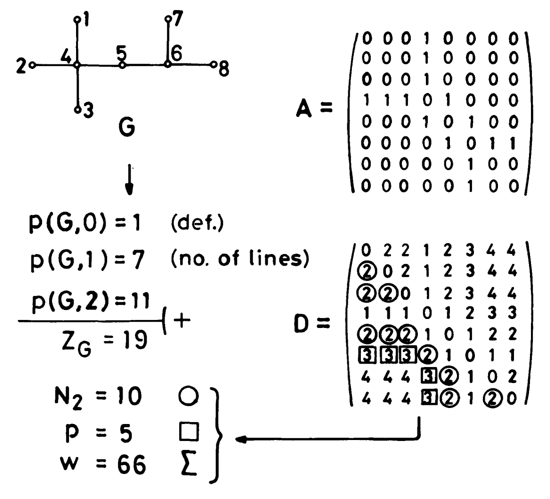

Fig. 1 Enumeration of various topological indices for 2,2,4-trimethylpentane. G: graph, A: adjacency matrix, and D: distance matrix.

TABLE 1. VARIOUS TOPOLOGICAL INDICES OF HEXANE, HEPTANE, AND OCTANE ISOMERS

No.[a]	Name[b]	Z[c]	w	p_3	p_2
6-1	6	13	35	3	4
2	3m-5	12	31	4	5
3	2m-5	11	32	3	5
4	23m-4	10	29	4	6
5	22m-4	9	28	3	7
7-1	7	21	56	4	5
2	3e-5	20	48	6	6
3	3m-6	19	50	5	6
4	2m-6	18	52	4	6
5	23m-5	17	46	6	7
6	33m-5	16	44	6	8
7	24m-5	15	48	4	7
8	22m-5	14	46	4	8
9	223m-4	13	42	6	9
8-1	8	34	84	5	6
2	3e-6	32	72	7	7
3	3m-7	31	76	6	7
4	4m-7	30	75	6	7
5	2m-7	29	79	5	7
6	34m-6	29	68	8	8
7	3m3e-5	28	64	9	9
8	2m3e-5	28	67	8	8
9	23m-6	27	70	7	8
10	24m-6	26	71	6	8
11	33m-6	25	67	7	9
12	25m-6	25	74	5	8
13	234m-5	24	65	8	9
14	22m-6	23	71	5	9
15	233m-5	23	62	9	10
16	223m-5	22	63	8	10
17	224m-5	19	66	5	10
18	2233m-4	17	58	9	12

a) These numbers are used in Figs. 3—8. b) Platt's nomenclature.[3] c) The definitions of these indices are given in the text.

easily enumerate these topological indices with 2,2,4-trimethylpentane as an example. In Table 1 are tabulated the Z, w, p_2, and p_3 values for all the haxane, heptane, and octane isomers.[26,27]

Correlation among Z, w, p_2, and p_3. In Table 2 the correlation coefficients among the four different topological indices for eighteen octane isomers are given. It is evident that p_3 is the least correlated with other three indices. Among them w has rather large $|\rho|$ value of 0.79 with p_3. They are far from being orthogonal to each other. The index p_2 also has relatively large $|\rho|$ values both with Z and w, and is not a good candidate for an element of an orthogonal pair of indices.

TABLE 2. CORRELATION COEFFICIENTS AMONG THE VARIOUS TOPOLOGICAL INDICES FOR THE EIGHTEEN OCTANE ISOMERS

	Z	w	p_3	p_2
Z	1			
w	0.761	1		
p_3	−0.257	−0.787	1	
p_2	−0.936	−0.903	0.543	1

On the other hand, the pair of Z and p_3 is found to be the most orthogonal to each other, whereas the $|\rho|$ value for the pair of Z and p_2 is the largest, though negative. As shown in Table 3 correlations among these indices were also calculated for other isomer sets with N=6, 7, and 9, and also for their cumulative sets (given in parentheses). Correlation patterns are found to be all the same for each isomer set.

Some of the above correlation patterns can be explained by the graph-theoretical properties of these indices. By definition w includes both p_2 and p_3 as its components. As seen in Table 2 the $|\rho|$ values among these three parameters are very large and thus one cannot choose any two of them as a good orthogonal pair of indices, although Randić and Wilkins classified the thermodynamic and some other physical properties according to their correlation patterns with respect to p_2 and p_3.[13] The value of p_2 increases by 1 and 2, respectively, for each tertiary and quarternary branching, just in the opposite direction for the case of the components of Z. Namely, p(G,2), an element of Z, decreases by 1 and 3, respectively, for each tertiary and quarternary branching.[7] On the other hand, the values of Z and p_3 forming a good orthogonal pair are derived from different countings, *i.e.*, Z from disjoint line selection and p_3 from distant point-pair selection.

It is to be noted that even for the orthogonal pair of Z and p_3, their correlation coefficients get dramatically large if more than two isomer sets with different carbon numbers are combined as shown in the parentheses in Table 3. Also for the pair of Z and w the correlation coefficient gets as large as 0.94 even in the cumulative set up to octanes. One can expect ρ=1 for the correlation between many different molecular quantities such as heat of formation and just the number of carbon atoms if an infinitely large number of hydrocarbons are taken! It is not necessarily true for the structure-activity correlation study that the larger the better.

Then in the following discussion we will mainly be

TABLE 3. CORRELATION COEFFICIENTS AMONG THE VARIOUS TOPOLOGICAL INDICES FOR HEXANE TO NONANE ISOMERS

No. of Carbon	No. of Isomer	$Z—p_3$	$w—p_3$	$Z—w$	$p_3—p_2$
6	5	0.000	−0.333	0.924	0.080
7	9	−0.091	−0.648	0.796	0.394
	(14)[a]	(0.507)	(0.457)	(0.923)	(0.566)
8	18	−0.257	−0.787	0.761	0.543
	(32)	(0.543)	(0.512)	(0.940)	(0.727)
9	35	−0.142	−0.782	0.665	0.461
	(67)	(0.587)	(0.511)	(0.938)	(0.739)

a) The numbers in parentheses are obtained for the set of hydrocarbons cumulated from the hexane isomers.

TABLE 4. CORRELATION COEFFICIENTS BETWEEN THERMODYNAMIC PROPERTIES AND THE TOPOLOGICAL INDEX AND POLARITY NUMBER

Type number	Property	ρ (Z)			$\rho(p_3)$			$\bar{\rho}$ (Z)	$\bar{\rho}(p_3)$
		N[a]=6	7	8	6	7	8		
A1	Heat of vaporization	0.983	0.985	0.955	0.015	−0.147	−0.262	0.97	−0.19
A2	Entropy	0.961	0.919	0.930	−0.132	−0.233	−0.485	0.93	−0.36
A3,5	Heat of formation[b,c]	0.979	0.981	0.896	0.078	−0.079	0.059	0.93	0.02
A4	Boiling point	0.977	0.966	0.888	0.082	0.038	0.088	0.92	0.07
A′6	Entropy of vaporization	0.979	0.931	0.836	−0.077	−0.385	−0.595	0.88	−0.46
A′7	Entropy of fusion[d]	0.943	0.911	0.764	−0.538	−0.356	−0.600	0.83	−0.52
A′8	Cryoscopic constant[d]	0.830	0.826	0.726	−0.549	−0.283	−0.589	0.77	−0.50
A′9	Heat of fusion[d]	0.974	0.937	0.672	−0.496	−0.393	−0.508	0.79	−0.47
B1	Density of liquid	0.590	0.306	0.104	0.798	0.914	0.974	0.23	0.93
B2	Critical pressure	−0.383	−0.284	−0.465	0.871	0.970	0.966	−0.40	0.95
B3	Refractive index	0.696	0.375	0.133	0.705	0.877	0.963	0.28	0.90
B4	Pressure coefficient of vaporization	0.803	0.335	0.026	0.493	0.766	0.864	0.23	0.78
C1,4	Molal refraction[e]	−0.119	−0.124	−0.037	−0.982	−0.975	−0.990	−0.07	−0.98
C2	Molal volume	−0.592	−0.308	−0.112	−0.793	−0.912	−0.973	−0.24	−0.93
C3	Refractivity intercept	0.802	0.317	0.151	−0.519	−0.930	−0.933	0.29	−0.87
W1	Specific dispersion	−0.773	−0.552	−0.387	−0.614	−0.723	−0.864	−0.49	−0.79
W2	Critical temperature	0.919	0.712	0.322	0.332	0.558	0.764	0.52	0.64
W3	Critical volume	0.915	0.434	0.293	−0.290	−0.682	−0.725	0.42	−0.65
W4	Critical density	−0.905	−0.432	−0.292	0.312	0.677	0.716	−0.42	0.65
X1	Melting point[d]	0.131	−0.295	−0.402	−0.226	0.290	0.333	−0.30	0.24
X2	Critical pV/RT	−0.516	−0.325	−0.597	0.493	0.151	0.321	−0.51	0.30
X3	Free energy of formation	0.922	0.686	−0.075	0.295	0.143	0.826	0.28	0.56

a) Number of carbon atoms. b) Only this property is correlated with −Z. c) A5 is heat of combustion, which has the same correlation coefficients as heat of formation. d) Data are not available for several isomers. e) C4 is specific refraction, which has the same correlation coefficients as molal refraction.

concerned with the correlation between the thermodynamic properties of isomeric hydrocarbons and the two topological indices Z and p ($=p_3$).

II. Structure-Activity Correlation

Thermodynamic Properties. From the American Petroleum Institute (API) Research Project 44[25] twenty four thermodynamic properties were chosen for five hexane, nine heptane, and eighteen octane isomers as listed in Table 4. For some of the selected cases the values of thirty five nonane isomers were also analyzed. The type symbol, such as A or B, is tentatively assigned to each property according to the discussion in the later part of this paper.[28] The correlation coefficients between these quantities and Z and p_3 were calculated as shown in Table 4. For some of the properties the data of a few isomers are missing, but no serious problem arose in comparing and discussing all the correlation coefficients given in Table 4 without further statistical correction.

Classification of Thermodynamic Properties. By looking at the patterns of the numbers in each row of Table 4, one may notice that they can roughly be grouped into four. Namely, the nine type A properties have large (0.7—1.0) positive $\rho(Z)$. However, as for $\rho(p_3)$ some of them have an appreciably large value as large as −0.6 and are assigned as type A′, while the rest of them have very small $|\rho(p_3)|$ values. Type B properties have large (0.8—1.0) positive $\rho(p_3)$ values, while type C large (−0.9—−1.0) negative $\rho(p_3)$'s. The $\rho(Z)$ values of both type B and C properties are very small. For other properties in Table 4 , both the $\rho(Z)$ and $\rho(p_3)$ values are medium to small. However, if one looks at these figures more carefully, they may be grouped into two. To make these groupings more clear the ρ values of N=6, 7, and 8 isomers for each property were tentatively averaged with weights of 1, 2, and 4, respectively, to give $\bar{\rho}(Z)$ and $\bar{\rho}(p_3)$ in Table 4. Then

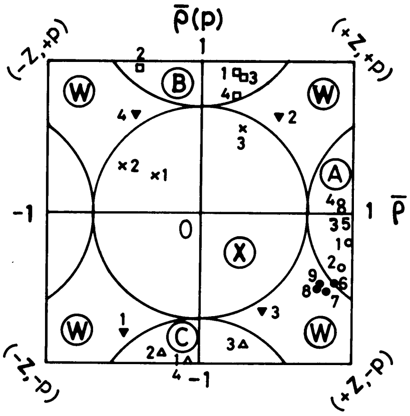

Fig. 2. Plot of $(\bar{\rho}(Z),\bar{\rho}(p_3))$ for the various thermodynamic properties averaged over hexane, heptane, and octane isomers.
○: type A, ●: type A′, □: type B, △: type C, ▼: type W, ×: type X.
The numbers near the points refer to the property numbers given in Table 4, where the $\bar{\rho}(Z)$ and $\bar{\rho}(p_3)$ values are also given.

it was found that for the entries other than types A, B, and C the correlation coefficients of $|\bar{\rho}(Z)|$ and $|\bar{\rho}(p_3)|$ are smaller than 0.5 and 0.8, respectively. Again they are divided into types W and X depending that the $|\rho(p_3)|$ value is larger or smaller than 0.6. Both the $|\rho(Z)|$ and $\rho(p_3)$ values for type X properties are smaller than 0.6.

Next the $\bar{\rho}(Z)$ and $\bar{\rho}(p_3)$ values for the twenty four properties were plotted in the rectangular coordinate plane as in Fig. 2. A pair of $(\bar{\rho}(Z), \bar{\rho}(p_3))$ is then found to be a good index for characterizing the nature of the topological factors on which the specified property depends. Namely, all the five entries of type A (boiling point, entropy, and heats of vaporization, formation, and combustion) fall into the far right arc in Fig. 2, whereas the four entries of type B (density of liquid, critical pressure, refractive index, and pressure coefficient of vaporization) and three of type C (molal refraction, specific refraction, molal volume, and refractivity intercept), are, respectively, encircled in the top and bottom arcs. Notice that by this plot all the four entries of type A′ (cryoscopic constant, heat of fusion, entropies of vaporization and fusion) get close to each other and are clearly distinct from W3 (critical volume). This supports our tentative grouping of the thermodynamic properties. Although the distance between the four A′ entries and A2 (entropy) is rather small, the latter discussion will differentiate them. It is interesting to note that all the four entries of type W (specific dispersion, critical temperature, critical volume, and cirtical density) find their respective places at the four corners showing all the possible different combinations of the modes of $\bar{\rho}(Z)$ and $\bar{\rho}(p_3)$ but are clearly distinct from the three properties of type X (melting point, critical pV/RT, and free energy of formation). It is interesting to note that these four entries are distinctively classified by Randić and Wilkins by the different combinations of the signs of the correlation with p_2 and p_3.[13] Their argument is based on the relative trends of the correlation patterns, while our criterion is based on the quantitative features of the correlation.[29]

Thus we can affirmatively classify the thermodynamic properties of alkanes into the following groups and select their typical entries as follows:

Type A: Heat of vaporization:
large $\rho(Z)$ and small $|\rho(p_3)|$
Type B: Density of liquid:
large $\rho(p_3)$ and small $|\rho(Z)|$
Type C: Molal refraction:
large $-\rho(p_3)$ and small $|\rho(Z)|$
Type W: Specific dispersion:
medium $|\rho(Z)|$ and $|\rho(p_3)|$
Type X: Melting point:
small $|\rho(Z)|$ and $|\rho(p_3)|$

However, there still remains a question if the pair of Z and p_3 parameters are the best combination for this sort of classification. To check this point the correlation coefficients of the above-mentioned five typical properties for the other parameters, w and p_2, were calculated and compared with the results for Z and p_3 in Table 5, where the $|\rho|$ values larger than 0.9 is printed in bold face. From this Table it is difficult to select such a useful pair of indices other than the pair of Z and p_3 that is capable of characterizing each type of properties. No $|\rho|$ value except for that of p_2 for Type A exceeds 0.9 suggesting inappropriateness of parameter p_2 for this purpose.

This conclusion is different from the criterion taken by Randić and Wilkins, who claim the effectiveness of the classification of the physical properties by the combination of p_2 and p_3.[30]

In Table 5 are also given important data for the $\rho(Z)$ and $\rho(p_3)$ values of thirty five nonane isomers, whose features on the ρ values are essentially the same, revealing that our tentative classification would be valid for relatively large saturated hydrocarbons.

Pattern Recognition of Correlation. Having established the classification of the thermodynamic properties into five types, let us see the similarity of the correlation pattern among each type. Figures 3 and 4 give the plots of four of type A properties (A1—A4) of the heptane and octane isomers against Z. The isomers are arranged in the increasing order of Z. The Wiener's path number w is also plotted against Z. While for heptane isomers correlation is fairly good, it gets worse for octane giving zigzag patterns.

It is worthy of notice that the zigzag patterns in the left half region of octanes of boiling point (bp) and heat of formation ($-\Delta H_f$) in Fig. 4 have an opposite trend to w but coincide with the corresponding patterns of type B plots in Fig. 6, where all the four curves of B1—B4 amazingly run in parallel with p_3 (See

Table 5. Correlation coefficients of the five typical thermodynamic properties for four different topological indices

Type	Typical property	Parameter	Number of C atoms			Parameter	C atoms	
			7$^{a)}$	8$^{b)}$	9$^{c)}$		7$^{a)}$	8$^{b)}$
A	Heat of vaporization	Z	**0.985**$^{d)}$	**0.955**	**0.938**	w	0.872	0.787
		p_3	−0.147	−0.262	0.007	p_2	**−0.928**	**−0.911**
B	Density of liquid	Z	0.306	0.104	−0.104	w	−0.296	−0.597
		p_3	**0.914**	**0.974**	**0.980**	p_2	0.019	0.264
C	Molal refraction	Z	−0.124	−0.037	0.069	w	0.479	0.669
		p_3	**−0.975**	**−0.990**	**−0.982**	p_2	−0.194	−0.325
W	Specific dispersion	Z	−0.552	−0.387	−0.329	w	0.030	0.349
		p_3	−0.723	−0.864	−0.870	p_2	0.305	0.006
		$-Z-5p_3$	**0.936**	**0.981**	**0.963**			
X	Melting point	Z	−0.295	−0.402	0.120	w	−0.246	−0.322
		p_3	0.290	0.333	0.255	p_2	0.347	0.498
		$-Z+2p_3$	0.387	0.454	0.021			

a) Data taken from nine heptane isomers but seven for melting point. b) Data taken from eighteen octane isomers but fourteen for melting point. c) Data taken from thirty five nonane isomers but nineteen for melting point. d) Those figures whose absolute magnitudes exceed 0.9 are underlined.

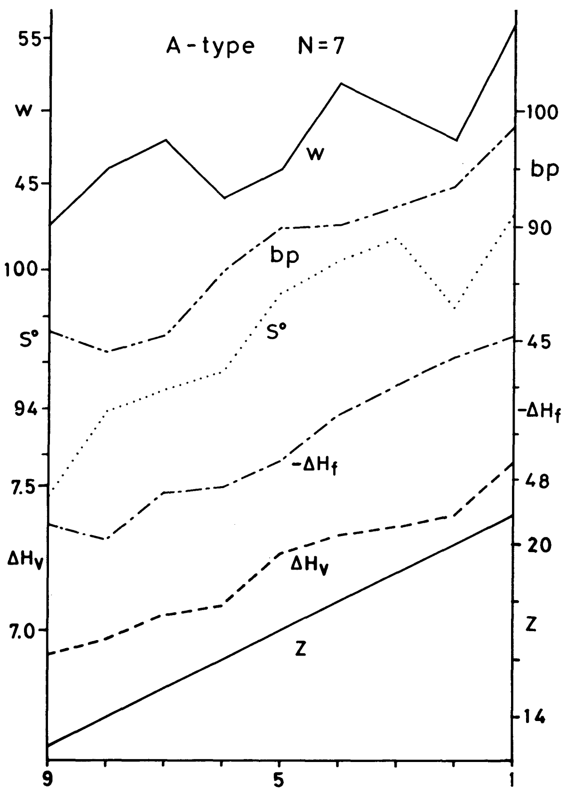

Fig. 3. Thermodynamic properties of heptanes. Type A. The numbers in the abscissa refer to the isomer numbers given in Table 1. The properties and their units are: A1, heat of vaporization (ΔH_v) in kcal · mol^{-1}; A2, entropy ($S°$) in cal · deg^{-1} mol^{-1}; A3, heat of formation ($-\Delta H_f$) in kcal · mol^{-1}; A4, boiling point (bp) in °C. (1 cal$_{th}$=4.184 J)

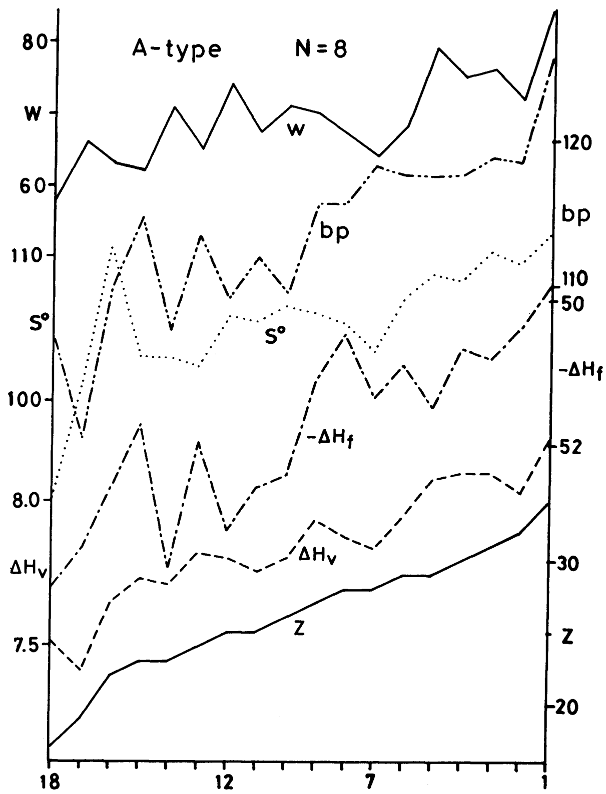

Fig. 4. Thermodynamic properties of octanes. Type A. See the footnotes of Fig. 3.

also Fig. 5 for type B properties of heptanes). Quite similarly type C properties show a good correlation with $1/p$ as demonstrated for C1—C3 in Figs. 7 and 8.

As have been shown in the above discussion the merits of drawing the correlation patterns like Figs. 3—8 lie not only in making certain of the classification of the structure-activity relationship but also in digging out the second variable hidden under the main correlation pattern. Further, if a good set of complementary indices like Z and p_3 are available, another correlation plot as Fig. 2 is found to be powerful for the analysis of structure-activity relationship.

Two-parameter Correlation. As has been inferred above, the p_3 character seems to be mixed in the correlation pattern of the boiling point against Z for octane isomers in Fig. 4. Then correlation coefficients were calculated between the A4 values of octane isomers and various in-phase linear combinations of Z and p_3. The optimum value was obtained to be $\rho(Z+p_3)=0.947$, which is to be compared with $\rho(Z)=0.888$ in Table 4.

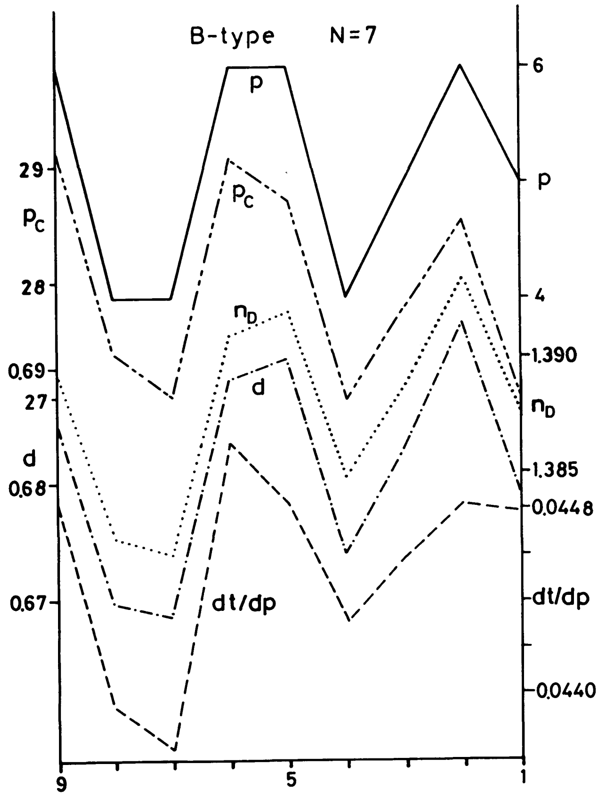

Fig. 5. Thermodynamic properties of heptanes. Type B. The numbers in the abscissa refer to the isomer numbers given in Table 1. The properties and their units are: B1, density of liquid (d^{25}) in g·ml^{-1}; B2, critical pressure (p_c) in atm.; B3, refractivity index (n_D); B4, pressure coefficient of vaporization (dt/dp) in °C·mmHg^{-1}. (1 mmHg = 133.322 Pa)

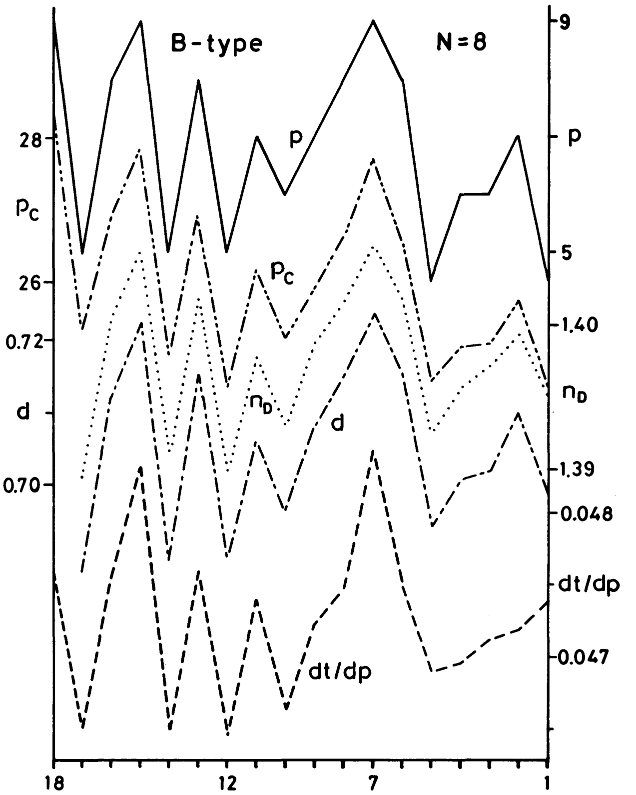

Fig. 6. Thermodynamic properties of octanes. Type B. See the footnotes of Fig. 5.

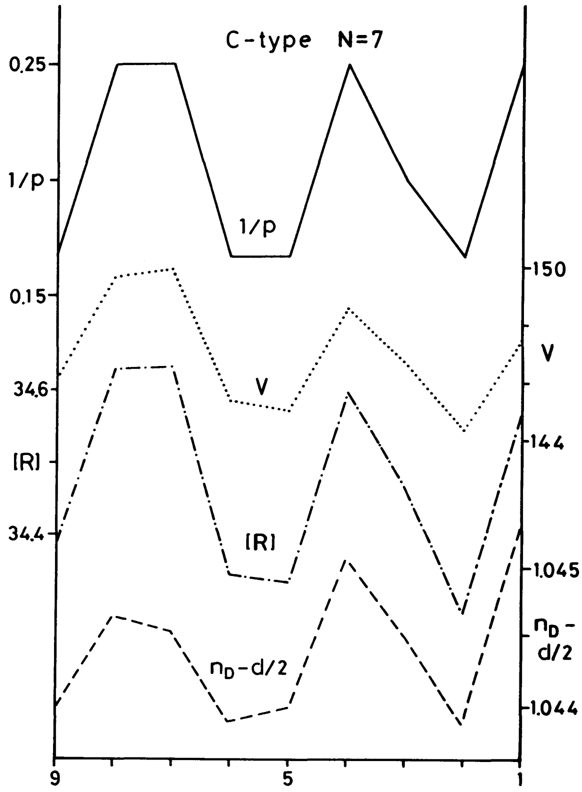

Fig. 7. Thermodynamic properties of heptanes. Type C. The numbers in the abscissa refer to the isomer numbers given in Table 1. The properties and their units are: C1, Molal refraction ([R]) in ml·mol^{-1}; C2, Molal volume (V) in ml·mol^{-1}; C3, Refractivity intercept ($n_D-d/2$).

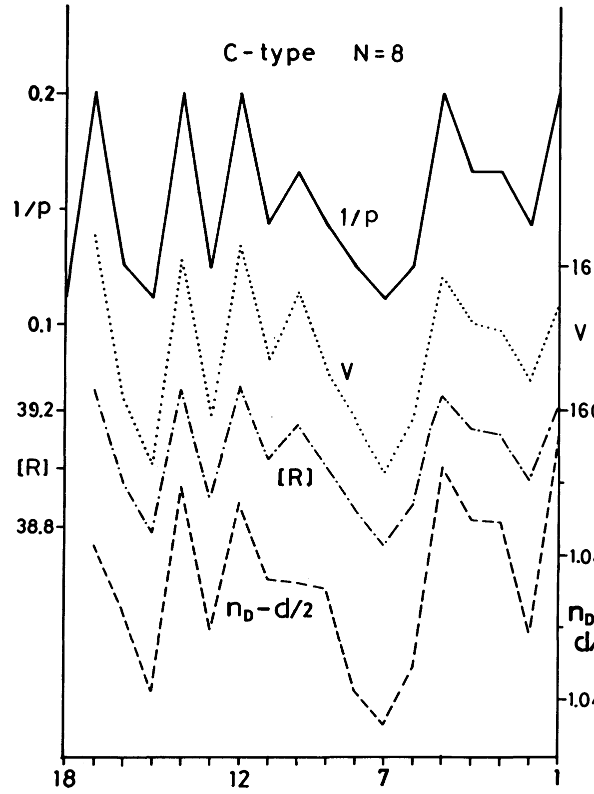

Fig. 8. Thermodynamic properties of octanes. Type C. See the footnotes of Fig. 7.

TABLE 6. EFFECT OF MIXING OF PARAMETERS Z AND p_3 ON THE CORRELATION COEFFICIENTS FOR SEVERAL THERMODYNAMIC PROPERTIES OF OCTANE ISOMERS

Property[a)]	$\rho\ (Z)$[b)]	$\rho\ (p_3)$[b)]	$(\rho^2(Z)+\rho^2(p_3))^{1/2}$	Best ρ Value	Best ρ Combination
A1	+	−	0.990	0.990	Z
A2	+	−	1.049	0.963	$Z-p_3$
A3,5	+	+	0.898	0.981	$Z+5p_3$
A4	+	+	0.892	0.947	$Z+p_3$
A′6	+	−	1.026	0.922	$Z-2p_3$
A′7	+	−	0.971	0.846	$Z-2p_3$
A′8	+	−	0.935	0.813	$Z-2p_3$
A′9	+	−	0.842	0.735	$Z-2p_3$
W1	−	−	0.947	0.981	$-Z-5p_3$
W2	+	+	0.829	0.938	$Z+5p_3$
W3	+	−	0.782	0.732	$Z-12p_3$
W4	−	+	0.773	0.724	$-Z+12p_3$
X1	−	+	0.522	0.454	$-Z+2p_3$
X2	−	+	0.678	0.622	$-Z+p_3$
X3	−	+	0.829	0.826	p_3

a) See Table 4. b) Numerical values are given in Table 4.

Similar calculations were performed for the properties of types A′, W, and X of octane isomers by varying the relative values of a and b for $\rho(aZ+bp_3)$. The results are given in Table 6, where the values of $|\rho|=(\rho^2(Z)+\rho^2(p_3))^{1/2}$ are also given. This quantity was found to be a good indicator for estimating the magnitude of the optimum value to be obtained with a mixing parameter $aZ+bp_3$. The value of $|\rho|$ itself does not have a definite meaning and thus sometimes may exceed unity. However, within each series of properties of types A, A′, W, and X, good parallelism is observed between $|\rho|$ and the optimum $\rho(aZ+bp_3)$ value.

The fact that the four properties of type A′ have the same optimum combination of Z and p_3 as $Z-2p_3$ corresponds to the clustering of the points for these properties in the $\rho(Z)-\rho(p_3)$ plot of Fig. 2.[31)]

Note also that the signs of a and b giving the optimum value are correctly predicted by the corresponding signs of $\rho(Z)$ and $\rho(p_3)$. This is dramatically shown in the four properties of type W. All these entries are found in the four different quadrants in the $\rho(Z)-\rho(p_3)$ plot of Fig. 2. The above discussions support our tentative assignment of type W and A′ properties. Among the four entries in type W, two of them (W1 and W2) achieved fair improvement in the ρ values, while the rest of them (W3 and W4) got only a little improvement. The optimum ρ values for the latter, however, are still larger than those for X1 and X2. If one looks at the data of octane isomers in Table 6, only X3 may be regrouped into type W having fairly large optimum ρ value. However, as evident in Table 4, for property X3, as well as X1, the fluctuation of the $\rho(Z)$ and $\rho(p_3)$ values is very large compared to other properties even to type W properties.

In this study only the optimum ρ value was sought for the mixing parameters of $aZ+bp_3$. Although there is a possibility to get a better result with $aZ+b/p_3$ or other combination of Z and p_3, the analysis has clarified the essential features of the two-parameter topological properties of saturated hydrocarbons.

Interpretation of Topological Factors. Then what do the two-parameter features in the structure-activity relationship mean? Among the four entries in type B properties, density of liquid d (B1) and refractive index n_D (B3) of alkanes are doubtlessly determined by the bulkiness of molecules. The fact that molal refraction $[R]$ (C1) and molal volume V (C2) of type C have large negative correlation with p_3 can also be explained by the bulkiness of molecules, since they are reciprocally related to density, respectively, as $[R]=M(n_D^2-1)/(n_D^2+2)d$ and $V=M/d$, where M is the molar mass. Since the specific refraction is expressed as $(n_D^2-1)/(n_D^2+2)d$, it should have quite the same correlation coefficients as molal refraction, and we did not include its values in Table 4. Refractive intercept $n_D-d/2$ (C3) belongs to type C but its physical meaning is left unclear.

Critical pressure (B2) is expressed as $p_c=a/27b^2$, where a and b are the constants in the van der Waals equation of state.[32)] The parameters a and b are interpreted respectively to reflect intermolecular interaction and molecular size. If we assume that a is almost constant among the isomeric hydrocarbons, the critical pressure is inversely proportional to the square of b, or molecular size. Then the higher the density, the smaller the b value, leading to a parallelism between d and p_3. Similarly critical volume V_c (W3) and critical temperature T_c (W2) are related to a and b as $V_c=3b$ and $T_c=8a/27Rb$, leading to negative and positive correlation with p_3, respectively. Of course, critical density d_c (W4) is inversely proportional to V_c. Although T_c, V_c, and d_c belong to type W, the results of Table 6 show that all of them get larger ρ value if small amount of out-of-phase Z character is introduced into $\rho(aZ+bp_3)$. Thus no matter what mechanism is responsible for the good correlation between the path number p_3 and these p-related properties, the parameter p_3 surely can take account of the topological bulkiness factor. One may well call p_3 as the static topological parameter, while the Z index as the dynamical topological parameter. The reason for the latter naming will be explained as follows.

We have shown in the previous paper[15] that the entropy $S°$ (A2) of alkanes is well correlated with the Z index except for sterically crowded and highly symmetrical molecules. The main factor in the parallelism between Z and $S°$ is due to the fact that the branching of alkanes decreases the Z value and also the freedom of rotation which eventually lowers $S°$.[33–35] Further, through the following relation

$$S° = \int_0^T C_p/T' \, dT'$$

and the Trouton's law, *i. e.*, bp (A4) is proportional to ΔH_v (A1), three of type A properties except heat of formation (A3) can be related to each other. All these properties are determined by the dynamical balance between the vigorous motion of molecules and intermolecular force. This picture is a little different from what the term cohesiveness means. Moreover, as the term molecular cohesiveness proposed by Cramer[12,17] seems to involve molecular packing and bulkiness to some extent, we prefer to say that the Z index takes account of the dynamical topological factor such as the rotational motion of molecules, and we may call Z as the dynamical topological parameter.

Deviation of the boiling point data from the Z-correlation as shown in Fig. 4 can be explained by the onset of stacking or bulkiness effect in the highly branched alkanes. A systematic study has not been done for viscosity, since a good set of data was not available. However, a preliminary study reveals that viscosity surely belongs to type W.

Now it is established that most of the thermodynamic properties, except type X properties as melting point (X1), are linear functions of two orthogonal topological parameters, namely, dynamical Z relating to the rotational degree of freedom and static p_3 governing the bulkiness of molecules. It is then deduced that the form of the linear function of a given property of hydrocarbons reflects how the two topological factors are competing in the molecular level. More detailed study, such as physical modelling and molecular dynamics type simulation calculation, can be proceeded further along the topological understanding obtained in this paper.

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29) They actually did not obtain the correlation coefficients but observed the relative tendency of the physical properties against the increase of the parameters concerned.

30) According to Randić and Wilkins our W4 and B2 belong to the same (+,+) group. Their similar character can be shown as the proximity of their points in Fig. 2. This is also the case with the (+,−) group of W1 and C2, and (−,+) group of W2 and A5. This fact suggests the different criteria of the classification of the properties taken by us and by Randić and Wilkins.

31) Actually in Fig. 2, the plot is made for the $\bar{\rho}$ averaged over N=6—8, but as seen in Table 4, the corresponding signs of ρ values within types A′ and W are all the same for different N.

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