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Topological Index and Thermodynamic Properties. IV.[3] Size Dependency of the Structure-Activity Correlation of Alkanes

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Correlation coefficients between twelve thermodynamic properties (ΔS, ΔH_f, ΔG_f, bp, d, n_D, R_m, V_m, p_c, T_c, V_c, d_c) of 624 isomers of nonane through dodecane and five different topological indices (Z, p_3, w, p_2, A_3) were calculated, where the new index A_3 is proposed to be defined as the half sum of the off-diagonal elements of the cube of the adjacency matrix A. These properties can be classified into several types, according to the behavior of the two correlation coefficients, $\rho(Z)$ and $\rho(p_3)$, against the change of the size of molecules. ΔS and bp depend largely on Z, while d and n_D on p_3, irrespective of the size change of molecules. On the other hand, ΔH_f of smaller alkanes is largely dependent on Z, but for larger alkanes it turns out to be a p_3-dependent property. Various interesting behaviors of the structure-activity relationships including the "pentane effect" were observed and discussed.

There are two different standpoints in the study of structure-activity correlation for molecular properties, namely, application-oriented and theory-oriented, or in other words, practical and conceptual standpoints.[1,2] Choosing the latter road we showed, in paper III of this series,[3] that thermodynamic properties of the lower members ($N<9$) of alkanes can roughly be classified into a few types depending on their relative magnitudes of the correlation coefficients for the two different topological indices, Z and p_3. The former index Z[4] proposed by one of the present authors well reflect the dynamical topological features, such as rotational degree of freedom, while the latter index p_3,[5] Wiener's polarity number, represents the static topological factors governing the bulkiness of molecules. Boiling point and entropy are the typical quantities which depend largely on Z,[3,6] and density of liquid, refractive index, and some other properties form another type of thermodynamic properties whose topological characteristics are represented well by p_3.

However, it was observed in III that for several properties the correlation pattern fluctuates with the size of molecules. Do not these types of correlation of thermodynamic properties change all the way toward larger molecules? No systematic study for analyzing the size dependency of the structure-activity correlation patterns for alkanes has been reported. Further, correlations among the various topological indices for larger molecules have not yet been systematically analyzed. The purpose of the present paper is to study not only the behaviors of the thermodynamic properties of larger alkanes but also the size dependencies of these correlations and of the various topological indices of the corresponding graphs. The obtained results will be helpful both for further theoretical elucidation and quantitative prediction of the thermodynamic properties of molecular aggregates.

I. Definitions of Various Topological Indices

In this paper, only the topological indices of integer values will be considered. The Z index has been defined by one of the present authors.[4] Wiener's path number, (w), polarity number, (p_3),[5] and Gordon and Scantlebury's p_2[7] have been frequently introduced.[8-10] Besides them some new indices are introduced in this study. The quantity A_3 is the half sum of the cube of matrix A of a graph G. Namely,

$$A_3 = \sum_{i<j} (A^3)_{ij}.$$

The idea of Wiener's polarity number, p_3, can be extended to the definition of p_n as half the number of n in the off-diagonal elements of the distance matrix D of G.[11] However according to our experience, none of p_4, p_5, and p_6 was shown to be more effective than the above topological indices for analyzing the structure-activity relationship for alkanes. Thus in this paper, we will mainly deal with the five integral topological indices, Z, w, p_3, p_2, and A_3.

II. Thermodynamic Properties of Alkanes

In paper III of this series twenty-four different thermodynamic properties of lower members ($N<9$) of alkanes were classified into five types, A, B, C, W, and X, according to the relative magnitudes of the correlation coefficients for Z and p_3 parameters.[3] Namely, Type A properties, such as boiling point, are largely dependent on Z, whereas Type B (density of liquid etc.) and C (molar refraction etc.) properties have large positive and negative correlation with p_3, respectively. The correlation coefficients of Type W properties (critical temperature etc.) for both Z and p_3 are medium in value, and Type X properties such as melting point have really no correlation with either Z or p_3.

In this paper correlation coefficients of entropy (ΔS), heat of formation (ΔH_f), boiling point (bp),

liquid-state density (d), refractive index (n_D), molar refraction (R_m), molar volume (V_m), and free energy of formation (ΔG_f) with the above five indices for nonanes (35 isomers), decanes (75), undecanes (159), and dodecanes (355) were calculated. For critical pressure (p_c), critical temperature (T_c), critical volume (V_c), and critical density (d_c), analysis is not complete, because those data were available only up to decanes even in the up-dated version of the API Report.[12]

The data of the physical properties of isomers through nonane are almost all measured ones. For decane, the data of 42 isomers are the average of the independently calculated values obtained by Zwolinski,[13] Greenshields,[14] and Taylor, Pignocco, and Rossini.[15] By their methods, the calculated values of isomers are fairly in concordant with the measured ones, so that we think those calculated values are reliable. However, almost all the data of undecane and dodecane are calculated ones. Although we are doubtful about the reliability of those data, in order to analyze systematically, the correlation coefficients of twelve physical properties of the isomers of undecane and dodecane with the five indices are also calculated.

III. Liquid-State Density, Refractive Index and Related Properties

Correlation coefficients between each of the four properties (d, n_d, V_m, R_m) and various topological indices (Z, w, p_3, p_2, A_3) for the isomers of nonane, decane, undecane, and dodecane are given in Table 1.

Figure 1 shows the size dependency of the ρ values of d, n_D, V_m, and R_m. Although the majority of the data of undecane and dodecane are those calculated with a large set of structural parameters, the points of undecanes and dodecanes in Fig. 1 smoothly lie on the curves extended from the experimental ones for hexane through nonane. Thus we can conclude that there might be no large difference between the estimated and real values.

For these properties, correlation with Z and p_2 is too poor as compared with the case of smaller ($N<9$) alkanes. Actually liquid-state density and refractive

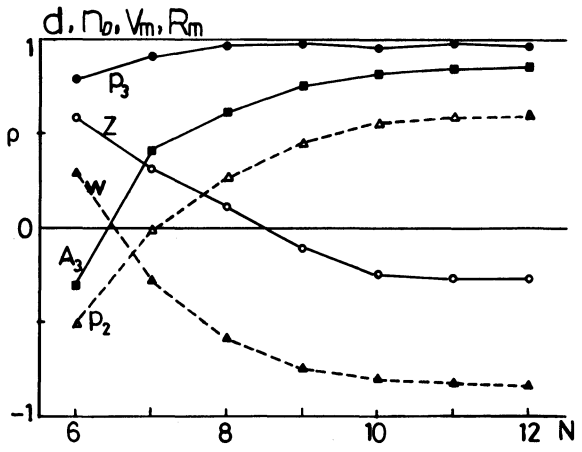

Fig. 1. The size dependency of the ρ values of d against the five topological indices for alkanes. The results for n_D, V_m, and R_m are identical to d.

Table 1. Correlation Coefficients between the Various Topological Indices and Several Thermodynamic Properties Depending Largely on p_3

Topological index	Property	C_9	C_{10}	C_{11}	C_{12}
p_3	d	0.980	0.963	0.978	0.980
	n_D	0.967	0.942	0.949	0.990
	V_m	−0.979	−0.963	−0.979	−0.981
	R_m	−0.986	−0.925	−0.967	−0.980
A_3	d	0.759	0.818	0.844	0.855
	n_D	0.734	0.813	0.837	0.873
	V_m	−0.754	−0.814	−0.842	−0.855
	R_m	−0.721	−0.731	−0.786	−0.828
w	d	−0.742	−0.802	−0.827	−0.834
	n_D	−0.733	−0.779	−0.809	−0.843
	V_m	0.741	0.804	0.831	0.840
	R_m	0.743	0.773	0.802	0.842
p_2	d	0.442	0.554	0.585	0.597
	n_D	0.451	0.563	0.590	0.618
	V_m	−0.436	−0.548	−0.581	−0.596
	R_m	−0.398	−0.455	−0.513	−0.552
Z	d	−0.104	−0.241	−0.263	−0.266
	n_D	−0.113	−0.255	−0.272	−0.269
	V_m	0.097	0.235	0.258	0.266
	R_m	0.069	0.165	0.209	0.236

d: liquid-state density (g ml^{-1}, 25 °C), n_D: refractive index (25 °C), V_m: molar volume (ml mol^{-1}, 25 °C), R_m: molar refraction (25 °C).

index were assigned to belong to B-type, while molar volume and molar refraction to C-type. All these properties have been known to be governed by the static topological features such as bulkiness of molecules.[3] Generally the absolute magnitudes of the $\rho(p_3)$ values for these properties increase quite similarly with the number of carbon atoms. It is surprizing to see that the absolute magnitudes of the linear correlation coefficients between p_3 and the four properties, d, n_D, V_m, and R_m, are all higher than 0.98 for the 355 isomers of dodecane. As seen in Fig. 1 for the size dependency of the $\rho(p_3)$ value for d, the Z index gradually loses its correlation with these Type properties with the increase of the molecular size. On the other hand, the ρ values for w and A_3 dramatically increase with the size of molecules but with opposite signs. The A_3 index was found to show remarkably good correlation with these properties when linearly combined with Z as aA_3+bZ, the ratio of b/a decreasing with the size of molecules. The results are listed in Table 2. It is interesting to see Fig. 2, where two randomly scattered correlation patterns of Z-p_3 and A_3-p_3 are seen to be merged into a fairly good linear plot when they are linearly combined with an appropriate ratio. If one carefully compares the $\rho(p_3)$ and the optimum $\rho(aA_3+bZ)$ values in Tables 1 and 2, no dramatic but fair improvement can be seen. So at this stage no merit is obtained by introducing the A_3 parameter for the QSAR analysis. However, as will be shown later the role of A_3 is highlighted for the correlation of A Type properties such as boiling point.

Table 2. Optimum Combinations of A_3 and Z Indices for Correlating the Four Topological Indices (A_3, w, p_2, Z)

Isomer	Property	Combination	ρ
C_9	d	A_3+0.39Z	*0.984*
	n_D	A_3+0.38Z	0.944
	V_m	A_3+0.38Z	*−0.983*
	R_m	A_3+0.38Z	−0.963
C_{10}	d	A_3+0.23Z	0.961
	n_D	A_3+0.22Z	*0.945*
	V_m	A_3+0.22Z	−0.958
	R_m	A_3+0.25Z	−0.897
C_{11}	d	A_3+0.15Z	*0.981*
	n_D	A_3+0.15Z	*0.964*
	V_m	A_3+0.15Z	*−0.981*
	R_m	A_3+0.16Z	−0.940
C_{12}	d	A_3+0.1Z	*0.983*
	n_D	A_3+0.1Z	*0.996*
	V_m	A_3+0.1Z	*−0.984*
	R_m	A_3+0.1Z	−0.967

The value in italic exceeds the corresponding correlation coefficients of p_3 parameter.

Now, let us take a closer look at the correlation between p_3 parameter and these four properties of B and C types. If we plot the values of d, n_D, V_m, and R_m of each group of isomers against p_3, most points are found to lie closely around a straight line, but a few points deviate from it, as exemplified in Figs. 3(a—d) for undecane isomers. For molar refraction the deviation is not obvious but can be detected from the correlation coefficients. The deviating points (the minority group) are represented with diamond marks.

Table 3. The Structures of Alkane Isomers (N=9—12) Deviating from the V_m-p_3 Plots. The Asterisks for Undecane and Dodecane Indicate that Except for Normal Alkanes the Data are Estimated Values

C_9	C_{10}	C_{11}*	C_{12}*
++	++-	++--	++-- +++
	+++	+++-	+++- +++-
	-++-	++--	++-- -++-
	+++	+++	++-- +++-
	-+-	+++	-++- ++
	++-	++-	++-- -++-
		-++	+++- ++
			+++ +++
			++- ++
			-++-

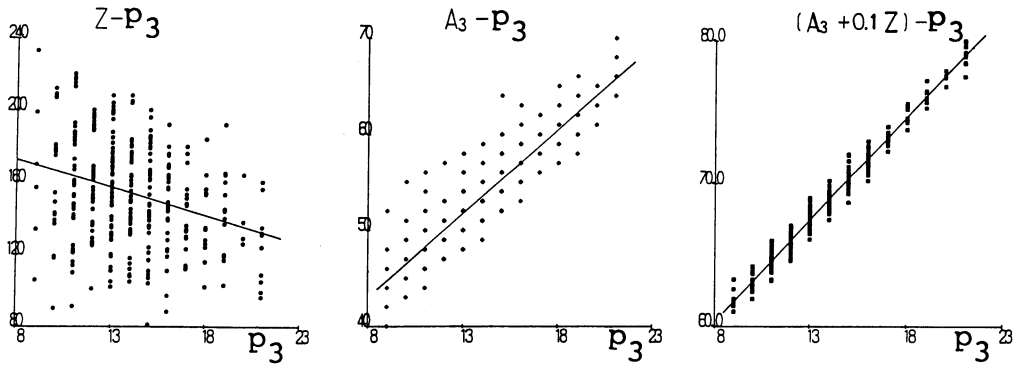

Fig. 2. The plots of Z—p_3, A_3—p_3, and (aA_3+bZ)—p_3, for dodecane isomers.

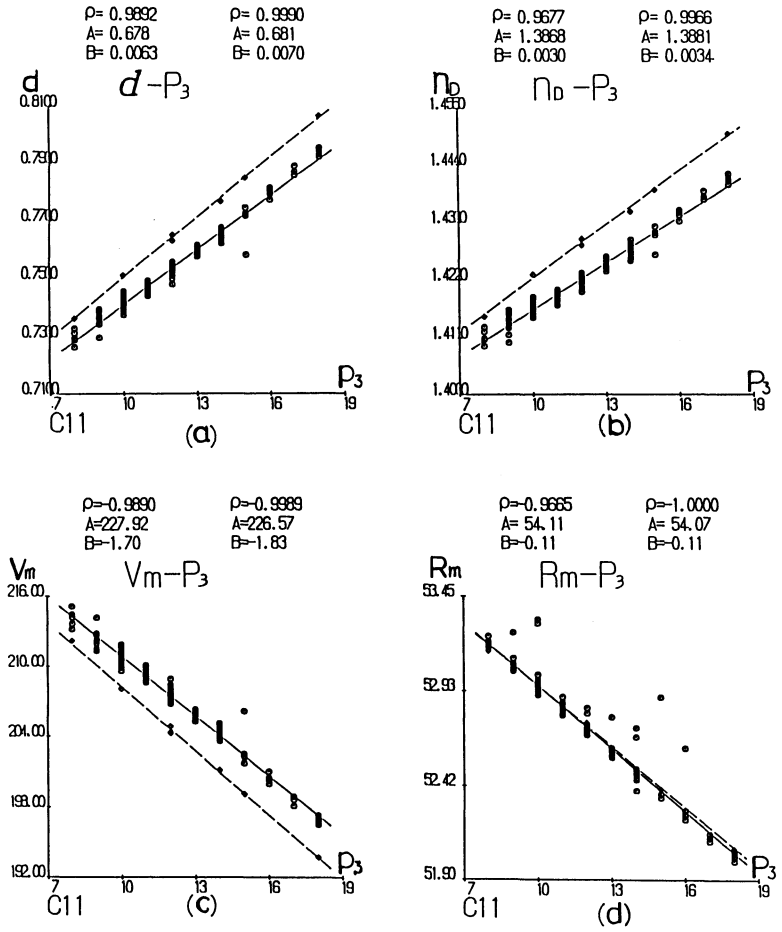

Fig. 3. The plots of d–p_3, n_D–p_3, V_m–p_3, and R_m–p_3 for undecane isomers. The ρ value and the coefficients A and B for $A+Bp_3$ corresponding to the majority and minority groups of undecane are, respectively, given in the top-left and right of each figrue.

The numerical results obtained from separate fittings are also given in the figures. For dodecane isomers quite a similar feature was found. We find that for these properties, except for R_m, all the deviating points correspond to a special group of compounds, whose structures are listed in Table 3.

It is remarkable that all the compounds but normal paraffins in Table 3 contain the common skeleton as ++. Further, among all the 624 alkanes studied, no compound other than those listed in Table 3 contains this skeleton. So we can safely assert that the ++ skeleton in alkanes works to decrease V_m, and increase d and n_D.†

IV. Pentane Effect

In general interactions between nonbonded pairs of alkane molecules in the liquid state are complicated enough to evade rigorous theoretical treatment. To simplify the question, we may consider only the dominant interactions. In calculating the conformational density of states of normal hydrocarbons, Terlin et al.,[16] proposed the so called "pentane effect". Namely, when four consecutive C–C bonds take the gauche–gauche conformation as those in cyclohexane, severe steric hindrance arises between the two methylene groups separated by four C–C bonds.

The measured volume of liquid compounds is interpreted to be composed of two factors. One is the volume which is really occupied by the component atoms, while the other is the spatial cavities, surrounded by either intra- or intermolecular group of atoms. The more efficient the molecules occupy the space, the smaller the cavities become. The skeleton of ++ is considered to decrease the V_m through the following two ways. First, a molecule with ++ skeleton generally tends to take a spherical shape compared to other isomers and is expected to expose

† In Table 3 those undecane and dodecane molecules are marked with asterisks whose thermodynamic properties are estimated. Even by omitting these data the present conclusion will not be changed.

lesser molecular surface than other molecules leading to smaller V_m value. Secondly, this is the most important, large steric hindrance within a molecule with a ++ skeleton causes the effective volume of the molecule to reduce considerably. As early as 1951, Platt[11] pointed out that steric hindrance reduces the effective volume of a molecule. Since under strong steric hindrance atoms are forced to get close to each other, the distance within nonbonding pair of atoms gets smaller than the van der Waals radii. Namely the so-called interpenetration occurs and the effective volume of a molecule is reduced.

Now, we can say without question that although the topological index p_3 is suitable for describing the "bulk" properties, such as liquid-state density molecular volume, and refractive index, etc., it fails in reflecting the effect of the ++ skeleton, or steric hindrance within a molecule.

The fact that normal paraffins belong to the minority group can be explained by the strong intermolecular interaction. Detailed discussion will be give in Section V.

We have attempted to get a single linear correlation for all the isomers. By assigning p_3+2 to the isomers with the ++ skeleton instead of p_3, all the isomers were found to lie on a straight line. The regression equations and correlation coefficients for d are obtained as follows:

For dodecane: $d = 0.68252 + 0.00600p_3'$
$\rho = 0.991$ (355 points)

For undecane: $d = 0.67790 + 0.00630p_3'$
$\rho = 0.990$ (159 points)

For decane : $d = 0.67754 + 0.00608p_3'$
$\rho = 0.973$ (75 points)

where

$$p_3' = \begin{cases} p_3+3 & \text{isomer which has ++ skeleton} \\ p_3 & \text{other} \end{cases}$$

All the correlations are of high quality including n_D and V_m, so that the p_3' index has a predictable power for these properties.

V. Entropy, Boiling Point, and Related Properties

The correlation coefficients between the topological indices and entropy (ΔS), boiling point (bp), heat of formation (ΔH_f), and free energy of formation (ΔG_f) of larger alkanes (N=9—12) are tabulated in Table 4. The size dependencies of these correlations are shown in Fig. 4(a—d).

For ΔS the $|\rho|$ values for Z, w, p_2, and A_3 do not change appreciably from hexanes to dodecanes. The discontinuous change at nonanes can be attributed to 3-methyl-4-ethylhexane, whose point deviates from the majority of their isomers. Although this molecule has no high symmetry, its entropy is extremely small compared with other isomers. So we deem that this data is erroneous. The recalculated ρ values by omitting this point are found to lie on more smoothed curves as marked with an asterisk in Fig. 4(a). Although the ρ value for p_3 gradually increases from hexane (0.1) to dodecane (0.7), one can safely conclude that entropy is governed by the dynamic feature of molecular topology and belongs essentially to A type.

For lower members of alkanes the correlation

Table 4. Correlation Coefficients between the Various Topological Indices and Several Thermodynamic Properties Depending Largely on Z

Topological index	Property	C_9	C_{10}	C_{11}	C_{12}
	bp	0.749	0.542	0.483	0.413
Z	ΔS	0.448	0.789	0.825	0.827
	ΔH_f	0.299	0.019	−0.111	−0.172
	ΔG_f	−0.373	−0.387	−0.425	−0.416
	bp	0.280	0.071	0.060	0.030
w	ΔS	0.674	0.841	0.807	0.778
	ΔH_f	−0.262	−0.503	−0.652	−0.695
	ΔG_f	−0.789	−0.775	−0.808	−0.794
	bp	−0.521	−0.292	−0.208	−0.136
p_2	ΔS	−0.610	−0.894	−0.937	−0.924
	ΔH_f	−0.463	0.212	0.350	0.419
	ΔG_f	0.632	0.603	0.645	0.642
	bp	−0.202	−0.007	0.063	0.137
A_3	ΔS	−0.665	−0.885	−0.914	−0.910
	ΔH_f	−0.088	0.483	0.602	0.657
	ΔG_f	0.801	0.786	0.817	0.814
	bp	0.355	0.407	0.400	0.408
p_3	ΔS	−0.518	−0.636	−0.664	−0.692
	ΔH_f	0.575	0.712	0.784	0.804
	ΔG_f	0.779	0.818	0.843	0.845

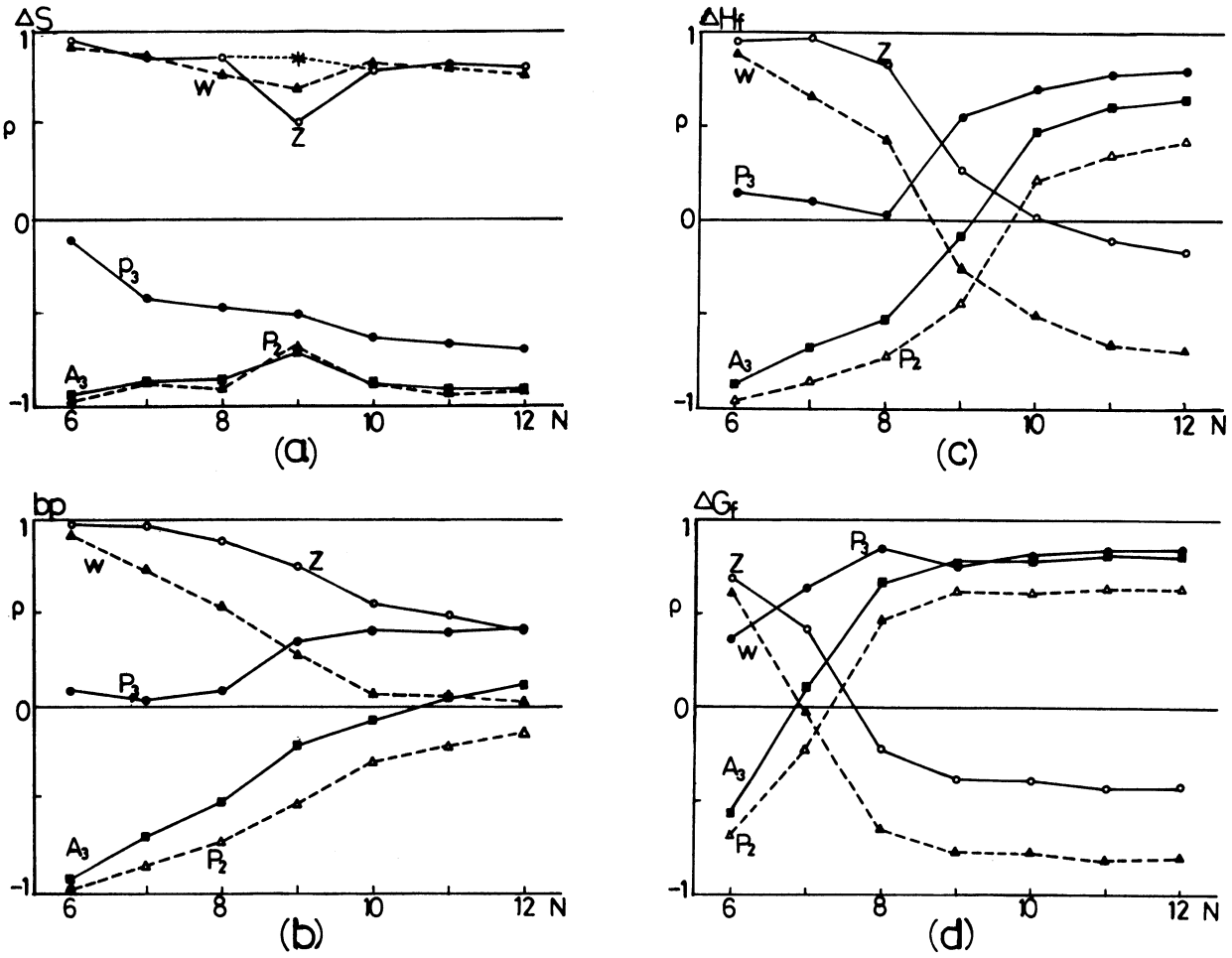

Fig. 4. The size dependency of the ρ values of ΔS, bp, ΔH_f, and ΔG_f against the five topological indices for alkanes. The asterisk for the Z curve in Fig. 4a was calculated by omitting one deviating point. The results for other topological indices are not shown.

pattern of boiling point, one of the typical A type properties, is very similar to that of entropy. However, as the size of molecules gets larger, the $|\rho|$ values of w and A_3 sharply drop down to zero while those of Z and p_2 slowly decrease. On the contrary $\rho(p_3)$ gradually increases but does not reach as high as 0.5. Thus boiling point of alkanes at least up to decane may well be classified into A-type. Although for dodecane isomers Z index still shows the largest $|\rho|$ value among all the indices studied, boiling point turns to belong to W-type, with medium $\rho(Z)$ and $\rho(p_3)$ values. It is to be noted that fairly large ρ value (>0.7) can be obtained by combining the Z and A_3 parameters as aA_3+bZ. (See Table 5 and Fig. 5). The ratio of b/a decreases with the size of molecules, whereas the $|\rho(A_3)|$ value decreases sharply down to zero.

Figure 5 shows that the deviant points correspond to the isomers with short branches. This is also the case with other properties, such as ΔS, ΔH_f, and ΔG_f. We have not found any appropriate topological index

Table 5. Optimum Combinations of A_3 and Z Indices for Boiling Point and Entropy, and Optimum Combination of p_3, p_4, p_5 for Heat and Free Energy of Formation

Isomer	Property	Combination	ρ
C_9	bp	$0.9A_3+Z$	0.886
	ΔS	$A_3+0.05Z$	−0.667
	ΔH_f	p_3+p_4	0.683
	ΔG_f	p_3-7p_5	0.958
C_{10}	bp	$1.8A_3+Z$	0.788
	ΔS	$A_3-0.20Z$	−0.912
	ΔH_f	$p_3-2.5p_5$	0.796
	ΔG_f	$p_3+0.7p_4$	0.763
C_{11}	bp	$2.7A_3+Z$	0.765
	ΔS	$A_3-0.15Z$	−0.945
	ΔH_f	$p_3+1.1p_4$	0.879
	ΔG_f	$p_3-1.2p_5$	0.915
C_{12}	dp	$4.2A_3+Z$	0.718
	ΔS	$A_3-0.10Z$	−0.942
	ΔH_f	$p_3+1.2p_4$	0.895
	ΔG_f	p_3+p_4	0.898

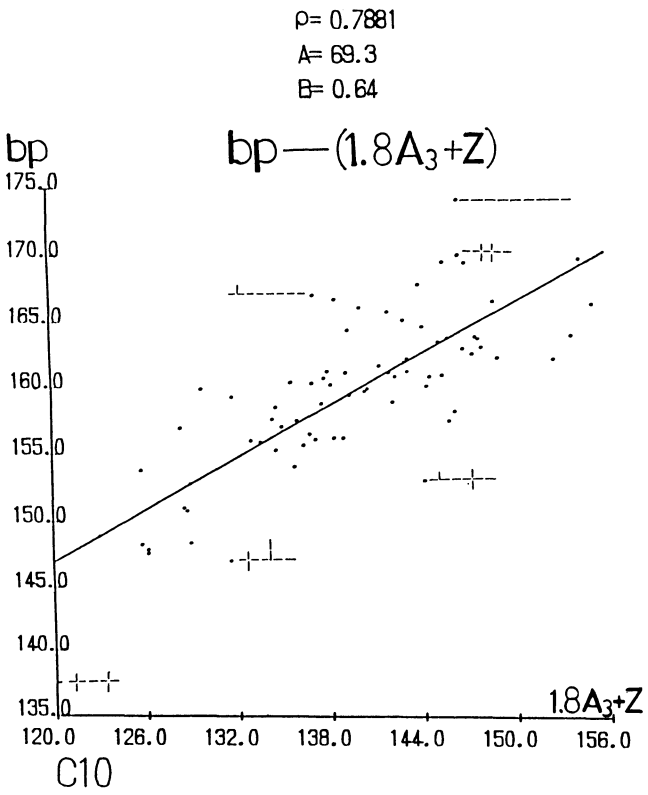

Fig. 5. The plots of bp-(aA_3+bZ) for decane isomers.

to discriminate those short-branched isomers from others. If we can find such a topological index that can effectively characterize those kinds of molecules, all these problem will be solved.

Heat of formation, ΔH_f, for lower members of alkanes also belongs to A-type. The ρ values for the five parameters exhibit "cross-over" patterns as shown in Fig. 4(c). Namely ΔH_f changes its character into B-type above decane.

Free energy of formation, ΔG_f, of W-type, also shows a similar crossover pattern. (See Fig. 4(d)). However, the "transition point" to B-type for ΔG_f is lower than that of ΔH_f but is higher than that of the majority of B-Type properties shown in Fig. 1.

VI. Properties at the Critical Point

The correlation coefficients among the various topological indices for the four properties at the critical point, T_c, p_c, V_c and d_c, of nonane and decane isomers are presented in Table 6. However, data are not available for the higher members of alkanes.

In Fig. 6(a—d) are shown the size dependency of the ρ values of p_c, d_c, V_c, and T_c. Obviously w is the best for the description of d_c, V_c, whereas p_3 is the best for d_c and T_c. However, if they are to be classified, p_c belongs to B-type for all N and the remaining three properties change from W-type to B-type at around heptane and octane.

From the van der Waals equation of state, we get the

Table 6. Correlation Coefficients between the Various Topological Indices and Critical Constants

Topological index	Property	C_9	C_{10}
p_3	d_c	0.921	0.927
	V_c	−0.910	−0.922
	p_c	0.947	0.963
	T_c	0.850	0.848
A_3	d_c	0.871	0.859
	V_c	−0.870	−0.835
	p_c	0.912	0.904
	T_c	0.499	0.630
w	d_c	−0.931	−0.945
	V_c	0.938	0.933
	p_c	−0.881	−0.877
	T_c	−0.415	−0.551
p_2	d_c	0.639	0.641
	V_c	−0.647	−0.608
	p_c	0.680	0.684
	T_c	0.155	0.551
Z	d_c	−0.356	−0.374
	V_c	0.376	0.347
	p_c	−0.376	−0.393
	T_c	0.189	0.165

relations, $p_c=a/(27b^2)$, $T_c=8a/(27Rb)$, $V_c=3b$, giving $a=9RT_cV_c/8$ and $b=V_c/3$. The parameters a and b can be interpreted respectively to reflect the intermolecular interaction and molecular volume.[3] The values of a can be calculated from the data of T_c and V_c, as shown in Table 7 for nonane isomers. From this table, one may notice that those compact molecules with large steric hindrance, such as 2244m-4, 22m3e-4 23m3e-4, 24m3e-4, and 33e-4 (m and e, respectively stand for methyl and ethyl) have rather smaller value of a. Same thing also happens in decane isomers.

The more compact the molecule is, the weaker the molecules interact with each other in the liquid state. Further, it is noticed that the normal paraffin has the largest a value among all the isomers. As has been discussed in Section IV, we can further say that, the intermolecular interaction of molecules with high steric hindrance is weaker than for other molecules. The reason why the volume of those compounds decreases is not because they interact with each other strongly, but just as we discussed in Section IV.

Since "critical state" is a kind of state in which liquid phase and gaseous phase not only coexist, but also have the same density without any phase boundary between them, molecules in this state do not approach each other as in the liquid state. This means that the intermolecular interaction is not so strong that the volume of the bulk is determined mainly by the molecular size, as implied in the relation, $V_c=3b$. As shown in Table 7, each normal paraffin has actually the largest size (or V_c value) of all the isomers.

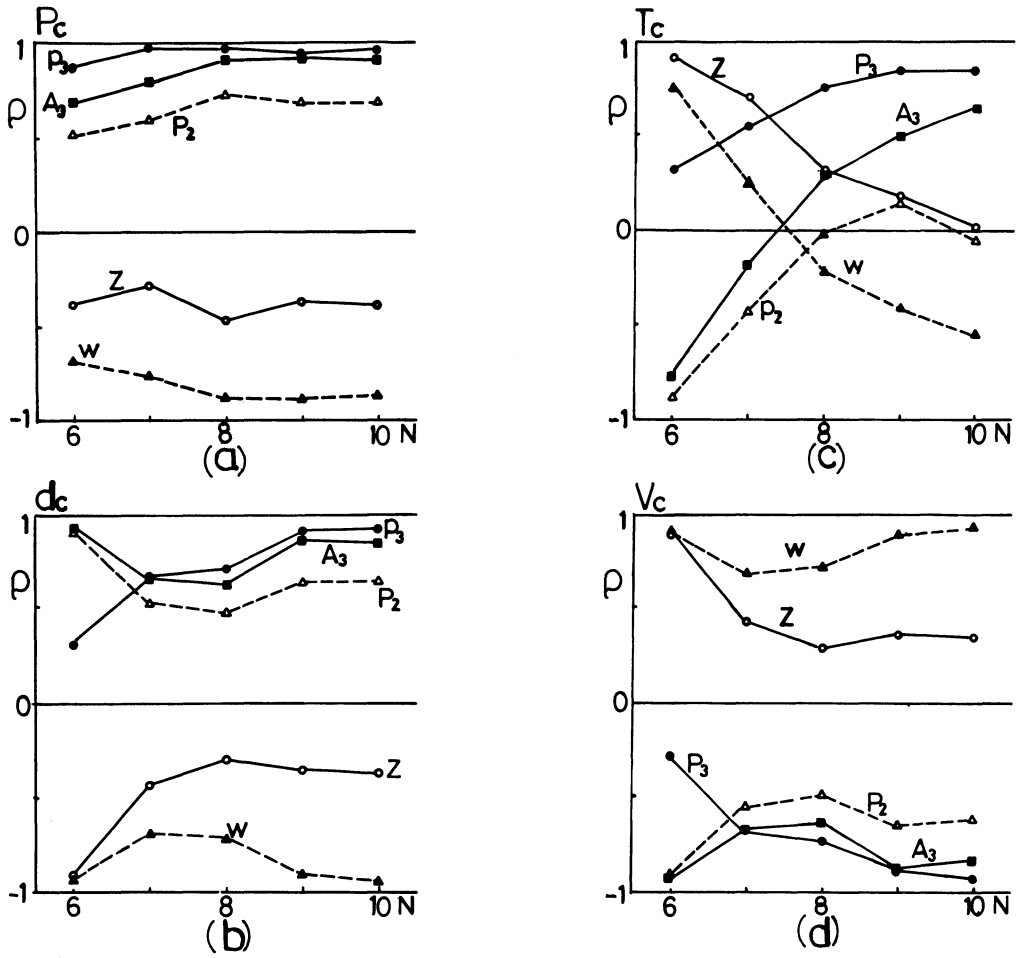

Fig. 6. The size dependency of the ρ values of p_c, d_c, T_c, and V_c against the five topological indices for alkanes.

But, liquid normal paraffin has the smallest volume among all the isomers having the same p_3 value. So it is clear that the decrease in volume of normal paraffins is due to the strong intermolecular interaction as to decrease the holes among molecules.

In liquid state, for alkanes, the most important intermolecular attraction is the London dispersion force, and its energy is proportional to the square of the polarizability and to inverse sixth power of the separation; i.e., $U_{\text{London}} \propto \alpha^2/\gamma^6$. Because of its loose structure, normal paraffin may have the largest polarizability and therefore it has the largest London dispersion force. We suppose this is the reason why the normal paraffins have the strongest intermolecular attraction.

VII. Concluding Remark

The size dependency of the correlations of twelve physical properties and topological types are summarized in Fig. 7. Since type C properties have large negative correlation with p_3, they can essentially be classified into type B. In Fig. 7, slant zebra indicates A-type, whose properties are largely dependent on Z index; stars indicate B-type, whose properties have large positive or negative correlations with p_3 index; checker and dots indicate W-type and X-type, respectively.

As seen from Fig. 7, the fact that entropy belongs essentially to A-type does not change even with the increase of molecular size. Boiling point can be classified into A-type up to decane, but it turns to belong to W-type above undecane. For heat of formation, as the number of cabon atoms in a molecule increases from six to twelve, its character changes from A-type to W-type for octane, and into B-type beyond decane. Liquid-state density, molar volume, refractive index, molar refraction and critical pressure are classified into B-type up to dodecane. Critical temperature, critical volume, and critical density turn to belong to B-type as the molecular size increases. Free energy of formation has almost no linear correlation both with Z and p_3 for lower members of alkanes, but it can be classified into B-type beyond undecane.

In paper III of this series, it has been pointed out that p_3 may be regarded as a kind of topological

Table 7. Critical Volume, Temperature and van der Waals' Constant a of Nonane Isomers

p_3	Compound	V_c	T_c	$8a/(9R)=T_cV_c$
	n-9	0.548	594.6	325.84
	2m-8	0.541	586.6	317.35
6	26m-7	0.535	577.9	309.18
	22m-7	0.526	577.6	303.82
	225m-6	0.519	567.9	294.74
	2244m-5	0.504	574.6	289.60
	3m-8	0.529	590.0	312.11
	4m-8	0.523	587.6	307.31
7	25m-7	0.522	581.1	303.33
	24m-7	0.517	576.8	298.21
	224m-6	0.507	573.5	290.76
	3e-7	0.511	590.4	301.69
	4e-7	0.505	587.9	296.89
	35m-7	0.510	583.2	297.43
	23m-7	0.515	589.6	303.64
8	2m4e-6	0.504	580.0	292.32
	33m-7	0.506	588.4	297.73
	44m-7	0.501	585.4	293.29
	235m-6	0.509	579.2	294.81
	244m-6	0.500	581.5	290.75
	34m-7	0.503	591.9	297.73
9	2m3e-6	0.497	588.1	292.29
	223m-6	0.498	588.0	292.82
	3m4e-6	0.490	593.7	290.91
	3m3e-6	0.487	597.5	290.98
	234m-6	0.494	594.5	293.68
10	24m3e-5	0.489	591.2	289.10
	233m-6	0.491	596.0	292.64
	22m3e-5	0.486	590.4	286.93
	2234m-5	0.490	592.6	290.37
11	334m-6	0.484	602.3	291.51
	33e-5	0.473	610.0	288.53
12	23m3e-5	0.477	606.8	289.44
	2334m-5	0.481	607.5	292.21
	2233m-5	0.478	607.5	292.39

bulkiness factor, or a static topological parameter, and Z may be regarded as a dynamical topological parameter. The present work confirms those inferences about Z and p_3 from the results of larger molecules.

We think p_3 is not a good parameter in reflecting the steric hindrance and complex interactions, and this conclusion is contrary to the results by some other authors.[11,17]

Boiling point, which is determined by the dynamical balance between the motion and interaction of molecules, has the best correlation with Z. This conclusion agrees with paper III. But for larger molecules, the correlation of Z with bp is not as good as that for smaller molecules. From Section V, it is revealed that the optimum linear combination among topological indices for bp is aA_3+bZ, and we have envisaged in Section III that aA_3+bZ has a certain

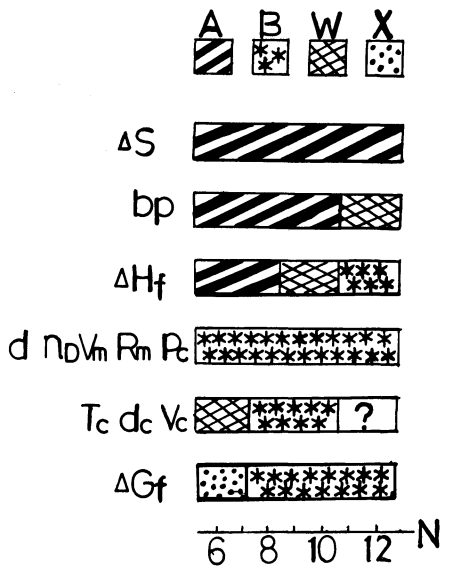

Fig. 7. Diagram showing the size dependency of the correlation types of physical properties and molecular topology for alkanes.

property close to p_3. Thus we may consider bp is also affected by bulkiness properties, and as the number of carbon atoms increases, the bulkiness properties become dominant. This is also the case with ΔH_f and ΔG_f.

The property of the parameter, A_3 is interesting, because when it is properly combined with Z, it will reflect various physical properties, whereas it has almost no correlation with any property by itself. It awaits further analysis.

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