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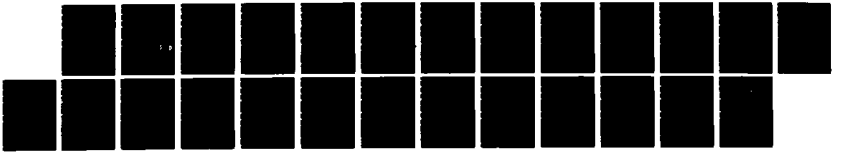

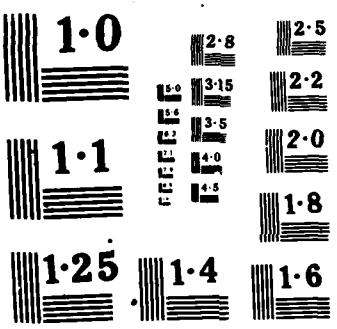

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1. REPORT NUMBER: Technical Report No. 22	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle): THE FRACTAL NATURE, GRAPH INVARIANTS, AND PHYSICOCHEMICAL PROPERTIES OF NORMAL ALKANES	5. TYPE OF REPORT & PERIOD COVERED: Technical Report
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): D.H. Rouvray and R.B. Pandey	8. CONTRACT OR GRANT NUMBER(s): N00014-85-K-0365
9. PERFORMING ORGANIZATION NAME AND ADDRESS: University of Georgia, Department of Chemistry, Athens, GA 30602	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR051-861
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, Department of the Navy, Arlington, VA 22217	12. REPORT DATE: 6/6/86 13. NUMBER OF PAGES: 22
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report) 15a. DECLASSIFICATION/ DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

DTIC ELECTE JUN 13 1986 S D

18. SUPPLEMENTARY NOTES

To be published in Journal of Chemical Physics

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Graph theory
Graph invariants
fractals
alkanes
physicochemical properties

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The variation in the physicochemical properties of linear normal alkane molecules with the graph invariants carbon number and the Wiener index is investigated. It is demonstrated that the variation can be interpreted in terms of the fractal dimension of these species. A general formula expressing the precise nature of the relationship has been derived.

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The Fractal Nature, Graph Invariants, and Physicochemical Properties of Normal Alkanes

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Abstract

The variation in the physicochemical properties of linear normal alkane molecules with the graph invariants carbon number and the Wiener index is investigated. It is demonstrated that the variation can be interpreted in terms of the fractal dimension of these species. A general formula expressing the precise nature of the relationship has been derived.

Introduction

As the most extensively studied of all the homologous series, the alkanes may now be said to be generally well understood. Extensive compilations of data on their physicochemical properties have been amassed[1] and numerous structure-property correlations have been performed using a wide variety of different graph invariants.[2] Such correlations tend to have only a limited range of applicability, however, and attempts to extend the range usually lead to excessively complicated expressions.[3] One important reason for the difficulties encountered in modelling the alkanes in this way is that, for any given

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TECHNICAL REPORT NO. 22

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Prepared for publication in

Journal of Chemical Physics

University of Georgia
Department of Chemistry
Athens, Georgia 30602

June 6, 1986

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physicochemical property, the increments to that property from each subsequent addition of a methylene (CH_2) unit along the series are not constant. The contributions from the methylene components become progressively smaller as the carbon number, n, increases.[4] This type of behavior is evident from Figure 1, which shows the plot of boiling point against n for normal alkanes up to the C_{40} member.

In recent years many different graph invariants have been proposed for the characterization of chemical species. These are usually referred to in the chemical literature as topological indices.[5,6] Such indices reflect in different ways the size and shape of the molecules they characterize and also provide some measure of the degree of branching present.[7] The relationship between such indices and the physicochemical properties of the alkanes is clearly not a linear one (note the pronounced curvature in Fig. 1). Even if the plots are made on logarithmic scales, some of the curvature remains, as will be apparent from Figure 2, which shows the variation of ln n with ln (boiling point) for normal alkanes. To explain this curvature we shall make use of fractal geometry and demonstrate that this curvature arises from the fractal nature of the alkanes themselves.

The concept of the random fractal has been used to characterize any object whose form is extremely irregular, ramified and/or fragmented at length scales on which a self-similarity exists.[8] Widespread use of the concept has been made in both chemistry and physics.[9-12] Although the full description of a fractal involves several different universal scaling functions and exponents, such as the fractal dimensionality, the topological dimensionality, the order of ramification, the connectivity, and lacunarity[13], we shall focus here only on the fractal dimensionality. The fractal dimensionality is one of the most important scaling exponents and quantifies the manner in which the mass of an object increases with its size.[14] If m is the mass of the object and r its radius of gyration,

we may write:

$$\underline{m} \propto \underline{r}^{\underline{d_f}}, \tag{1}$$

where $\underline{d_f}$ is the fractal dimensionality of the object.

The Use of Graph Invariants

The carbon number, $\underline{n}$, in an alkane molecule was first employed over 100 years ago as a means of characterizing these molecules.[15] It represents the simplest possible graph invariant, for it may be defined as the number of vertices in the hydrogen-suppressed graphs of alkane species.[2] As such, the carbon number may be deemed to be a topological index, though it is one which has very low discriminating power. All isomers corresponding to a given value of $\underline{n}$ will have the same index. Such an index is thus completely unsuitable for the characterization of branched species. Since this index came into vogue, many other topological indices have been developed with the specific aim of characterizing the branching in molecular species.[2] We now describe one such index which we shall use in our investigation of the behavior of linear alkanes.

The topological index we employ was introduced by Wiener[16] and is nowadays commonly referred to as the Wiener index. Although the index was first put forward in 1947, its manifold applications in chemistry, physics, and several other sciences have only recently come to the fore. Details of the index and its applications are to be found in a review by one the present authors.[17] The Wiener index may be defined as one half the sum of the entries in the distance matrix, D(G), of the graph G of the molecule under consideration. Normally G is taken as the hydrogen-suppressed graph of the species. Thus, as will be

apparent from Figure 3, the Wiener index, W(G), for the molecule of normal butane is 10. For normal, i.e. unbranched, alkanes, Wiener proved[16] the following general, closed formula for W(G):

$$W(G) = \frac{1}{6}(\underline{n}^3 - \underline{n}). \qquad (2)$$

We shall concern ourselves here only with normal alkane species. In Figures 4 and 5 plots of W(G) versus the boiling points of normal alkanes up to C_{40} member are presented using respectively ordinary and logarithmic scales.

Modelling the Curvature

The pronounced curvature evident in Figures 1 and 4 is typical of plots of most physicochemical parameters against some appropriate graph invariant used to characterize the structure of species. An attempt to model relationships of this general type, led Walker[18] to postulate a biparametric equation of the following form:

$$P = \underline{a}\,[W(G)]^{\underline{b}} \qquad (3)$$

where P is some physicochemical property, and $\underline{a}$ and $\underline{b}$ are constants to be determined for the range of values of the property P under consideration. For limited ranges, estimates of $\underline{a}$ and $\underline{b}$ are commonly obtained from logarithmic plots such as that shown in Figure 5. For more extended ranges, however, it is clear that this method is not applicable, for the plots are then far from being straight lines.

Since the first few points of the plot in Figure 5 (corresponding roughly to

$1 < \underline{n} < 10$) may be fitted reasonably well on one straight line, and the last few points (corresponding to $30 < \underline{n} < 40$) may be fitted on another straight line, it is of interest to inquire if the two extreme slopes have physical significance. Let the slope of the first few points be $\underline{b}_1$ and that of the second few points be $\underline{b}_2$. Clearly we have $\underline{b}_1 > \underline{b}_2$, and the range of $\underline{b}$ values lying between $\underline{b}_1$ and $\underline{b}_2$ will correspond to a crossover region characterized by a transition from one power law behavior (having exponent $\underline{b}_1$) to another power law behavior (having exponent $\underline{b}_2$). The Walker-type relationship in equation (3) should thus more correctly be written as several different relationships. For the extreme cases referred to above, the two relationships may be written in the form:

$$P = \underline{a}_1 [W(G)]^{\underline{b}_1} \quad (\underline{n} \text{ small}) \tag{4a}$$

$$P = \underline{a}_2 [W(G)]^{\underline{b}_2} \quad (\underline{n} \text{ large}) \tag{4b}$$

where $\underline{a}_1$ and $\underline{a}_2$ are appropriate constants.

The type of behavior described by equations (4a-4b) has previously been observed and commented upon by several authors.[19-21] The exponents $\underline{b}_1$ and $\underline{b}_2$, which we shall focus on exclusively hereafter, can be interpreted in terms of the fractal nature of normal alkane species. Detailed studies of the alkanes near to their boiling point have led to the conclusion that the molecules behave more or less as rigid rods when they are short[22] and as random chains when they are very long.[23] For our purposes it is thus reasonable to assume, as a good first approximation, that short normal alkane molecules ($1 < \underline{n} < 10$) are completely stiff, whereas long normal alkane molecules ($\underline{n} > 35$) are completely flexible. It is, of course, well-known[24] that $\underline{n} = 35$ will not be long enough to yield a completely flexible chain; this figure was selected somewhat arbitrarily because

of the paucity of boiling point data[1] on species having $\underline{n} > 40$. In fact, $\underline{n} \approx 30$ lies in the crossover region between rigid rod and flexible chain type behavior.[24] Strictly speaking, therefore, precise behavior of one type or the other cannot be ascribed to alkanes in this region.

Alkane Fractal Dimensionalities

In our model we thus imagine short alkane molecules to exist in the form of stiff rods, as illustrated in Figure 6. The end-to-end length, $\underline{r_n}$, of such a chain has been shown[25] to be proportional to $\underline{n}$:

$$\underline{r_n} \propto \underline{n} . \tag{5}$$

On the other hand, the flexible chain characteristic of long alkanes, which we illustrate in Figure 7, is known[24] to have an end-to-end length, $\underline{r_n}$, that assumes the following proportionality:

$$\underline{r_n} \propto \underline{n}^{\frac{1}{2}} . \tag{6}$$

There is thus a clearcut change in the power law which obtains in going from a stiff, rodlike short alkane chain to a flexible, gaussian, random-walk-like long alkane chain.

From equation (1), we may therefore conclude that for small values of $\underline{n}$, $\underline{d_f} = 1$, whereas for large values of $\underline{n}$, $\underline{d_f} = 2$. The difference in these fractal dimensionalities reveals that we are dealing with two self-similar configurations of the alkanes based on two different topological length scales. These are (i) a rodlike configuration for small $\underline{n}$ which persists to some upper cutoff value

$\underline{n}_c$; and (ii) a flexible chainlike configuration for large $\underline{n}$ where $\underline{n} > \underline{n}_c$. It is these two different fractal dimensionalities which we use to explain the curvature observed in the plots of physicochemical properties of the alkanes versus the carbon number, $\underline{n}$, or indices, such as the Wiener index, which correlate closely[26] with $\underline{n}$. As is evident from equation (2), the Wiener index for large $\underline{n}$ may be expressed to a good approximation as follows:

$$W(G) \alpha (\underline{n}^3 - \underline{n}) = \underline{n}^3 (1 - \underline{n}^{-2}) \sim \underline{n}^3 . \quad (7)$$

Rearrangement of the two expressions given in equations (4a-4b) to model the variation of the physicochemical property, P, with the Wiener index, yields the new equations:

$$W(G) \alpha P^{\frac{1}{\underline{b}_1}} \quad (\underline{n} \text{ small}) \quad (8a)$$

and

$$W(G) \alpha P^{\frac{1}{\underline{b}_2}} \quad (\underline{n} \text{ large}) . \quad (8b)$$

Because the physicochemical properties of the alkanes will depend in general upon the configuration of the molecules and the configuration adopted will in turn depend upon $\underline{n}$, P can be expressed in terms of the following relationship:

$$P \alpha \underline{n}^{\underline{k}} , \quad (9)$$

where $\underline{k}$ is an exponent which we suppose assumes the values $\underline{k}_1$ and $\underline{k}_2$ thus:

$$W(G) \alpha \underline{n}^{\underline{k}_1/\underline{b}_1} \qquad (\underline{n} \text{ small}) \tag{10a}$$

$$W(G) \alpha \underline{n}^{\underline{k}_2/\underline{b}_2} \qquad (\underline{n} \text{ large}) . \tag{10b}$$

If no cognizance is taken of the actual configurations adopted by the alkane species, i.e. if no account is taken of the differing self-similarities and their fractal dimensionalities, it is possible to derive two further relationships. Using the value of W(G) given in equation (7), and comparing it with the exponents in equations (10a-10b), we obtain the relationships:

$$\underline{k}_1/\underline{b}_1 = 3 \qquad (\underline{n} \text{ small}) \tag{11a}$$

$$\underline{k}_2/\underline{b}_2 = 3 \qquad (\underline{n} \text{ large}) . \tag{11b}$$

To relate the results in equations (11a-11b) to the fractal dimensionality, $\underline{d}_f$, of $\underline{r}_n$, we make use at this point of an appropriately modified form of the expression in equation (1):

$$\underline{r}_n^{\underline{d}_f} \alpha \begin{cases} W(G)^{\underline{b}_1/\underline{k}_1} & (\underline{n} \text{ small}) \qquad (12a) \\ W(G)^{\underline{b}_2/\underline{k}_2} & (\underline{n} \text{ large}) . \qquad (12b) \end{cases}$$

Scaling Theory Applied to the Alkanes

To interrelate the two sets of exponents $\{\underline{b}_1, \underline{k}_1\}$ and $\{\underline{b}_2, \underline{k}_2\}$, which we have defined as being valid in the two limiting cases (i) $\underline{n} < \underline{n}_c$ and (ii) $\underline{n} > \underline{n}_c$, use is now made of scaling arguments similar to those presented by de Gennes.[27]

The size of the molecules, characterized by $\underline{r}_{\underline{n}}$, will clearly be different for the two cases. Only at the point where $\underline{n} = \underline{n}_c$ will the two cases by precisely equal, namely when

$$\underline{r}_{\underline{n}} (\underline{n} < \underline{n}_c) = \underline{r}_{\underline{n}} (\underline{n} > \underline{n}_c) \quad \underline{n} \rightarrow \underline{n}_c . \tag{13}$$

At this point, it then follows from equations (12a-12b) that:

$$W(G)^{\underline{b}_1/\underline{k}_1\underline{d}_{f1}} = W(G)^{\underline{b}_2/\underline{k}_2\underline{d}_{f2}} \tag{14}$$

and therefore that:

$$\frac{\underline{b}_1}{\underline{k}_1 \ \underline{d}_{f1}} = \frac{\underline{b}_2}{\underline{k}_2 \ \underline{d}_{f2}} . \tag{15}$$

Since from our earlier discussion we already know that $\underline{d}_{f1} = 1$ and $\underline{d}_{f2} = 2$, we are now in a position to state our final new result as:

$$\frac{\underline{b}_1}{\underline{b}_2} = \frac{\underline{k}_1}{2\underline{k}_2} . \tag{16}$$

Experimental Test for the Derived Relationship

To test whether the new relationship derived above in equation (16) is a valid one, determinations were made of the various slopes exhibited in the plot shown in Figure 5. Using a least squares regression analysis, we computed the slope of the first nine points in the Figure (corresponding to C_2 through C_{10} alkanes), the slope of the last nine points (corresponding to alkanes C_{32} through C_{40}), as well as the slopes of several other sets of nine points chosen from the Figure.

The slope for the first set of nine points was found to be 0.1133°K, and that for the last set equalled 0.1753°K. If each of the slopes obtained is divided by the slope for the first set of points (0.1133°K), the ratios should converge to the value 0.5 as n increases. A plot of these ratios against the average value of n represented by each set of nine points chosen is presented in Figure 8.

Unfortunately, reliable boiling point data for the alkanes are not available beyond the C_{40} member, and so this perforce represents an abrupt cutoff point for our plot in Figure 8. From this plot, however, it may be seen that whereas the ratio b_1/b_2 starts out from the precise value of unity, by the time the last set of nine points is reached (corresponding to an average C_{36}) the ratio has fallen to the value 0.646. It seems highly likely that this fall toward the theoretical limit of 0.5 would continue if sufficient boiling point data were available to extend our plot beyond this artificially imposed limit.

Conclusion

A formula has been derived showing how the fractal dimensionalities, d_f, for r_n characterizing normal alkane species are related to the exponents b_1 and b_2 in Walker-type plots of ln P versus ln W(G) for n small and n large. The entirely reasonable assumption has been made that the two extreme d_f values are one for short-chain normal alkanes and two for long-chain normal alkanes. We have demonstrated that the ratios of the slopes obtained from plots in ln P versus ln W(G) should asymptotically approach the theoretical limit value of 0.5 as n becomes very large. Analysis of these plots for normal alkanes up to and including the C_{40} member reveal that the ratio falls in value from unity for the C_2-C_{10} sets of points to 0.646 for the C_{32}-C_{40} set of points. It appears very likely that the observed fall in value of the ratio would continue if data were available for

chains containing more than forty carbon atoms, so that the theoretical value of 0.5 would be more closely approached. From our results we may therefore conclude that the Wiener topological index is able to provide valuable information on the state of randomness of normal alkane chains at the boiling point. The general approach we have outlined here could clearly be extended to the study of a variety of other systems and many different physicochemical parameters.

Acknowledgments

One of us (D.H.R.) thanks the U.S. Office of Naval Research for partial support of this work. Both authors would like to express their gratitude to Ms. C. Pirie for calculating the various slopes of the plot in Figure 8.

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Captions to Figures

Figure 1. Plot of boiling point temperature against carbon number for normal alkanes from the C_1 to the C_{40} member.

Figure 2. Plot of natural logarithm of boiling point temperature against natural logarithm of the carbon number for normal alkanes from the C_1 to the C_{40} member.

Figure 3. Schematic derivation of the Wiener index for the molecule of normal butane.

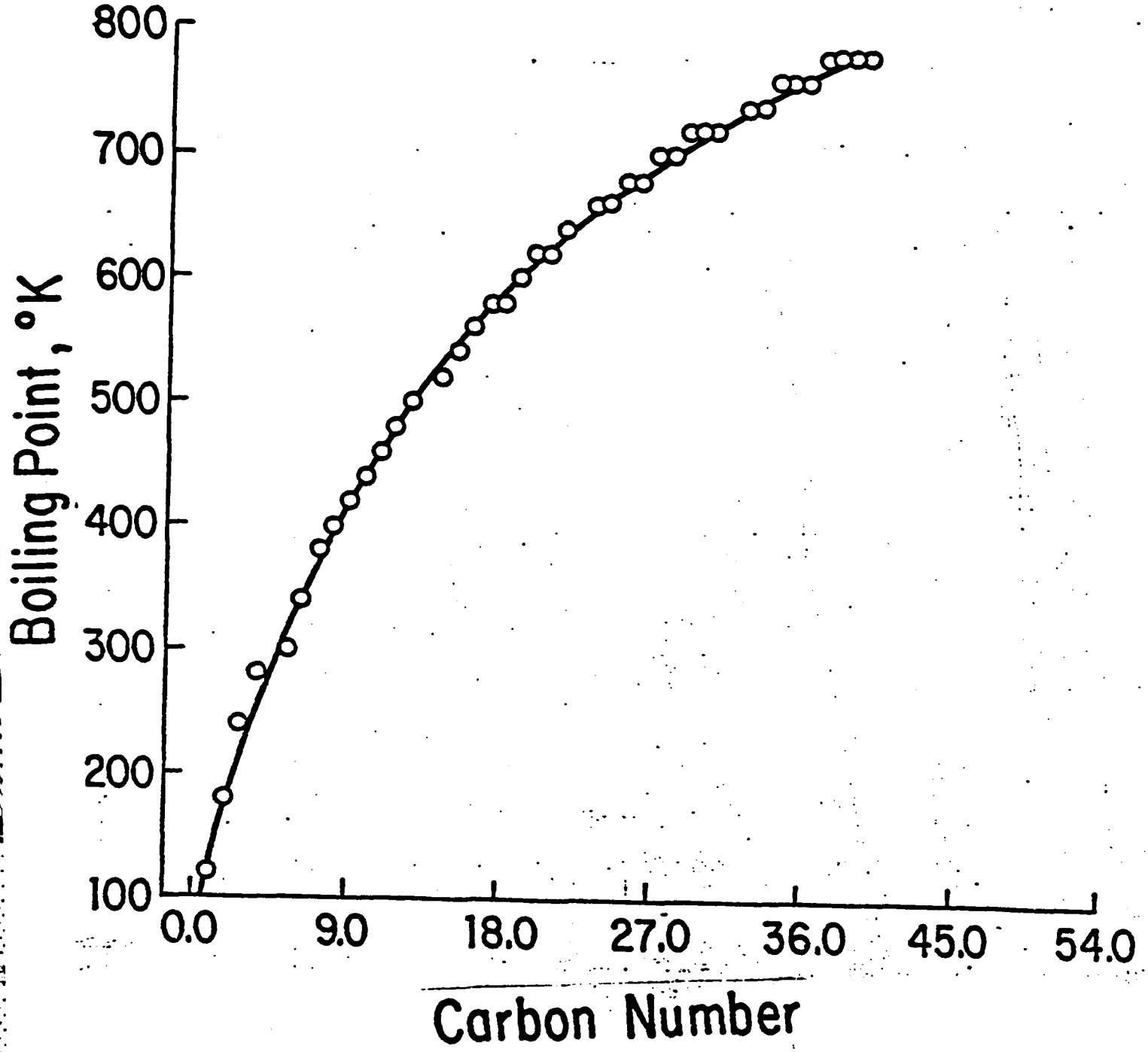
Figure 4. Plot of the boiling point temperature against Wiener index for normal alkanes from the C_2 to the C_{40} member.

Figure 5. Plot of the natural logarithm of boiling point temperature against natural logarithm of the Wiener index for normal alkane species from the C_2 to the C_{40} member.

Figure 6. An illustration of the end-to-end length, $\underline{r_n}$, for short, stiff, normal alkane species ($1 < \underline{n} < 10$).

Figure 7. An illustration of the end-to-end length, $\underline{r_n}$, for long, flexible, normal alkane species ($\underline{n} > 35$).

Figure 8. Plot of the slopes for different sets of nine points (taken from Figure 5) against the average value of $\underline{n}$ represented by each set of points.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700
600
500
400
300
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27.0
36.0
45.0
54.0
Carbon Number

Figure 1

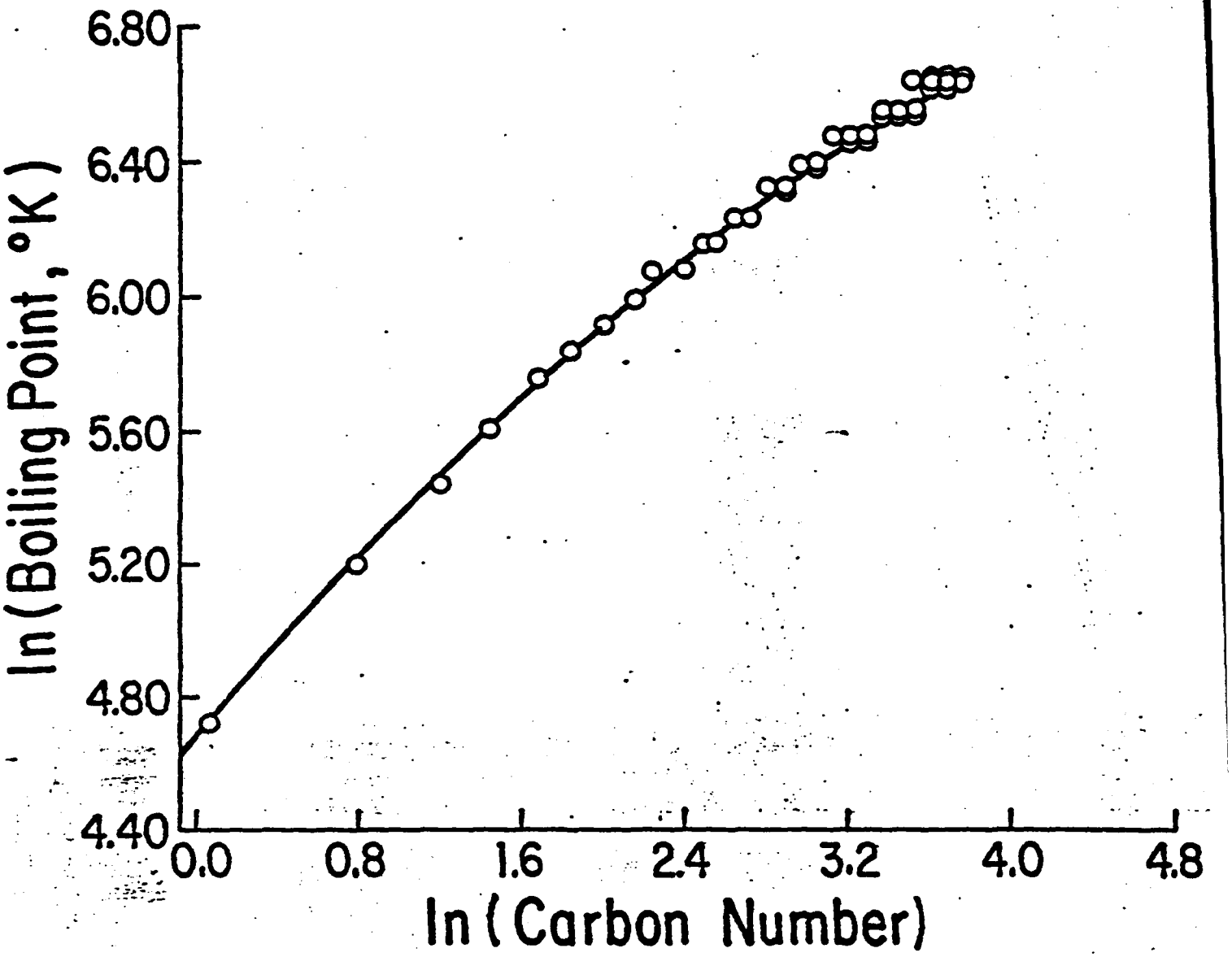

6.80
6.40
6.00
5.60
5.20
4.80
4.40
ln (Boiling Point, °K)
0.0
0.8
1.6
2.4
3.2
4.0
4.8
ln (Carbon Number)

Figure 2

Chemical Graph

$$\begin{array}{c} \\ 1 \\ 2 \\ 3 \\ 4 \end{array} \begin{array}{c} \begin{array}{cccc} 1 & 2 & 3 & 4 \end{array} \\ \begin{pmatrix} 0 & 1 & 2 & 3 \\ 1 & 0 & 1 & 2 \\ 2 & 1 & 0 & 1 \\ 3 & 2 & 1 & 0 \end{pmatrix} \end{array}$$

Distance Matrix

$$\frac{1}{2}\sum_i\sum_j d_{ij}$$

Index Definition

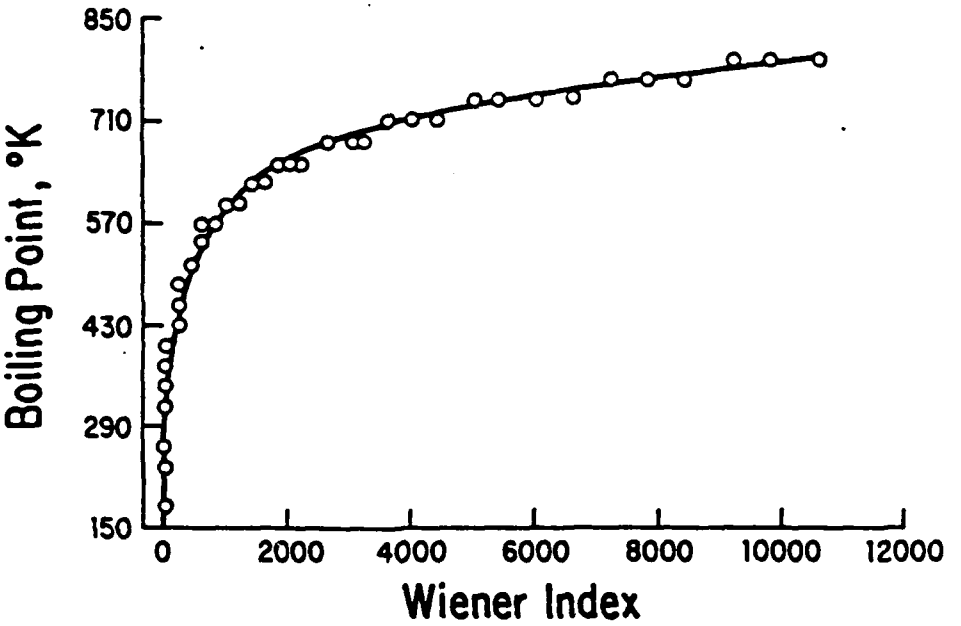
$$(1 \times 3) + (2 \times 2) + (3 \times 1)$$

Summation

$$W(G) = 10$$

Wiener Index

Figure 3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430
290
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Boiling Point, °K
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2000
4000
6000
8000
10000
12000
Wiener Index

Figure 4

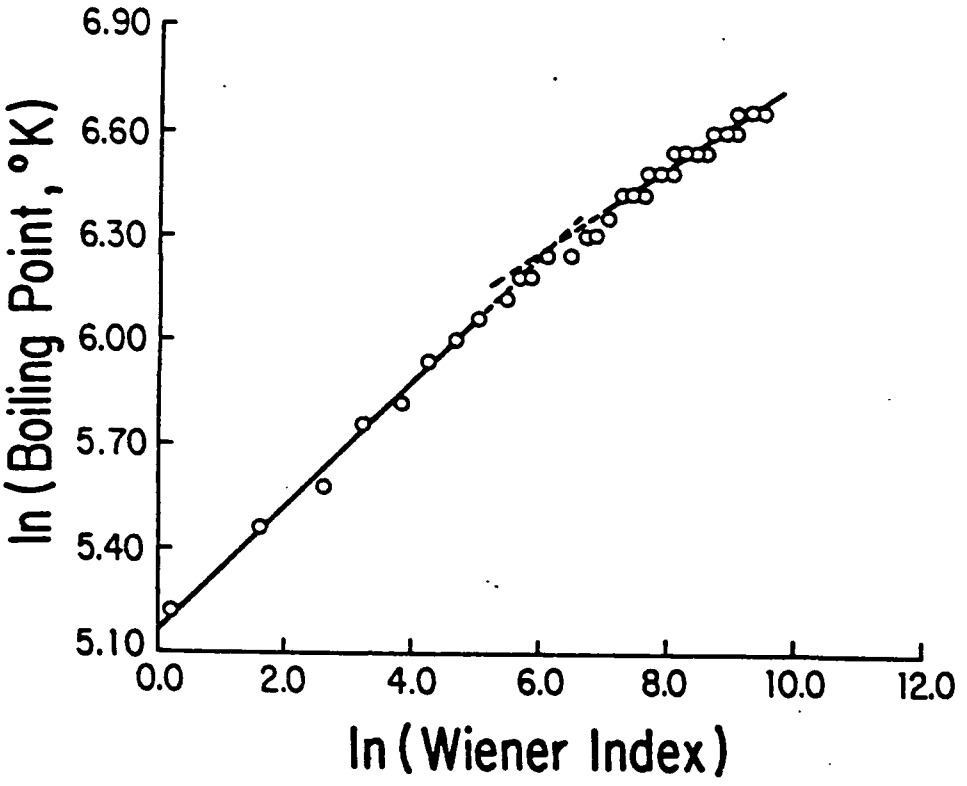
6.90
6.60
6.30
6.00
5.70
5.40
5.10
ln (Boiling Point, °K)
0.0
2.0
4.0
6.0
8.0
10.0
12.0
ln (Wiener Index)

Figure 5

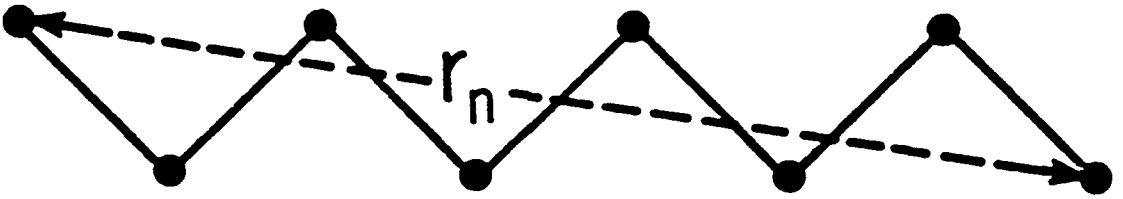

Figure 6

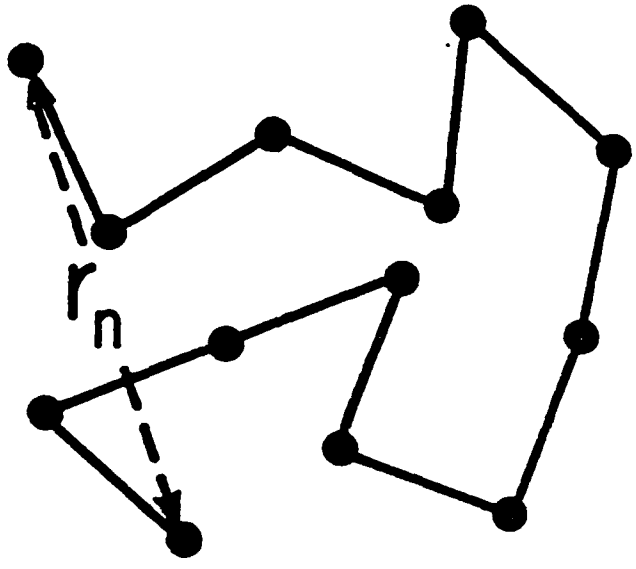

Figure 7

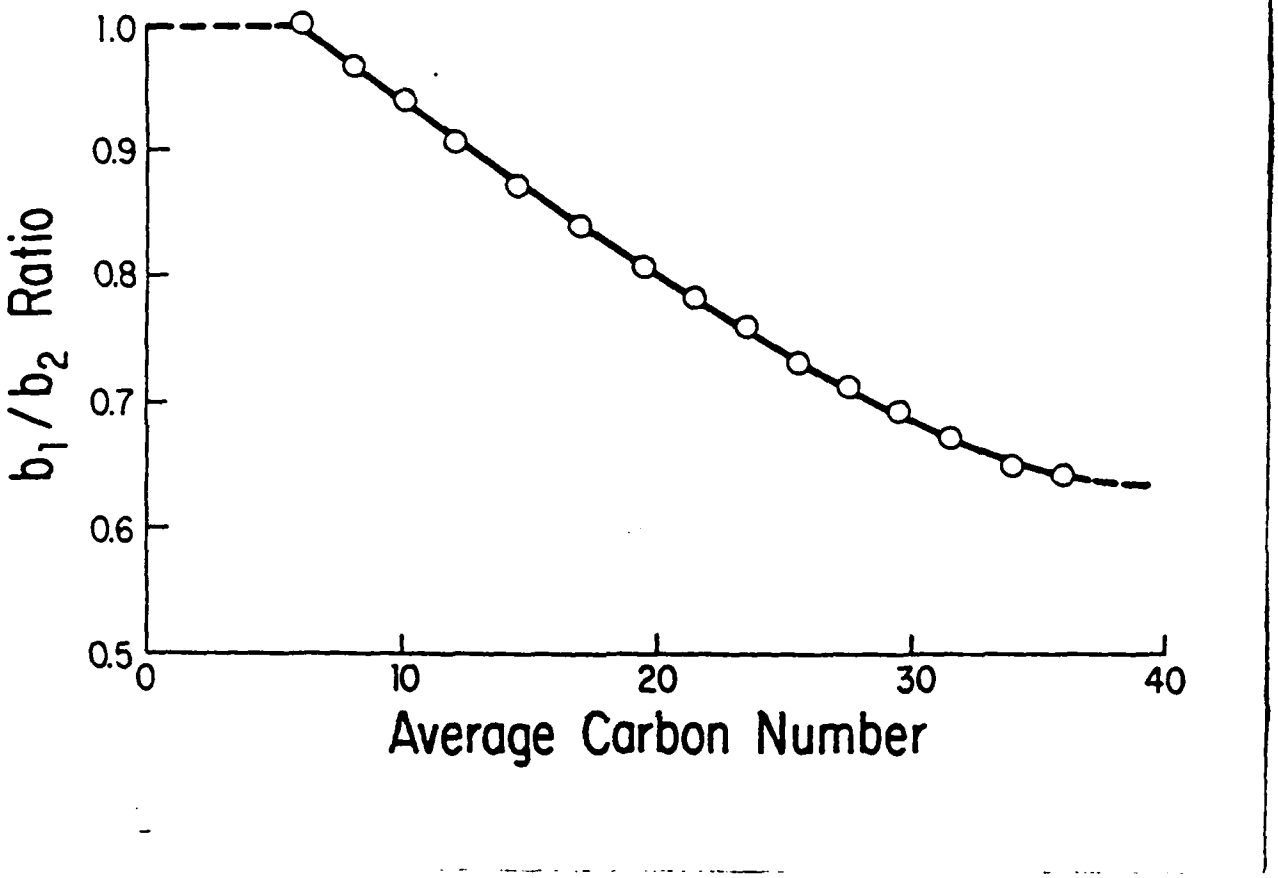

Figure 8

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