

PREDICTION OF MOLECULAR FLEXIBILITY IN HALOGENATED ALKANES VIA FRACTAL DIMENSIONALITY

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Abstract

The topological connectedness and experimentally determined boiling point for each of a series of halogenated normal alkane molecules were used to derive fractal dimensionalities of these molecules by a simplified version of the method of Rouvray and Pandey. The results, which relate to the time-averaged molecular conformations of the species in the bulk liquid phase, were then used to obtain estimates of the flexibility of the molecules in question. The effects of the halogen atoms are pronounced and reveal a number of interesting trends. Such analysis is of particular value in the medical context, since perfluorinated alkanes and other perfluorinated species are now being employed widely in medical operations as substitutes for body fluids.

1. Introduction

Halogenated alkane species have been the subject of much critical comment in the news media in recent years because of their toxicity and role in the destruction of the stratospheric ozone layer [1,2]. What is less widely known, however, is that many such species are so chemically unreactive that they are scarcely harmful at all. In fact, they appear to be environmentally benign. Examples of those that have proven to be beneficial to humankind include (i) short-chain perfluorinated species used in substitute body fluids such as artificial blood [3] and as replacement for the vitreous humor in the eye after retinal surgery [4], (ii) polymeric species such as polytetrafluoroethylene (Teflon), noted for their great thermal stability and resistance to oxidation, which have found application in making buildings weather resistant [5] and in the production of waterproof clothing, automatic bread bakers, and nonstick frying pans [5], (iii) copolymerized species such as Hostaflon or Tefzal made from ethylene and tetrafluoroethylene and used as plastic sheeting on construction sites and on greenhouses because of their outstanding strength and durability [5], and (iv) random copolymers, such as Vitron or Fluorel (made from vinylidene fluoride and perfluoropropylene) which form elastomers that are being used for seals, gaskets and hoses in the automobile and aerospace industries [6].

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The great utility and wide range of applicability of perfluorinated and partially fluorinated alkane species is a direct outcome of the unique combination of physical and chemical properties possessed by these species. Among some of the more remarkable properties, mention should be made of their legendary chemical inertness. They are not attacked by acids, bases, oxidants, reductants or heat below 700 °C [7]; even under the most extreme conditions, they are able to resist oxidation, reduction or degradation. They are also known to repel powerfully the close approach of a wide variety of chemical species including water and oil molecules [5]. However, they do dissolve a number of gases including oxygen, nitrogen and carbon dioxide. It is this characteristic that renders liquid perfluorinated alkanes suitable as substitute blood products; it also makes possible the survival of experimental animals and fish when totally immersed in oxygenated emulsions of perfluorinated systems [8]. A further advantage, especially for the latter type of application, is that perfluorinated species are of very low toxicity to members of the animal kingdom and human beings [7].

The properties of fluorinated alkane species clearly differ profoundly from those of their nonfluorinated counterparts. The principal reason for the difference is the carbon–fluorine bond. Carbon–fluorine bonds are exceptionally strong, the average recommended values for the C–F and C–H bonds being, respectively, 109.50 and 98.25 kcal [9]. The great stability of the species formed when alkanes are fluorinated is reflected in the data assembled in table 1. This table shows that there

Table 1
Listing of certain parameters for progressively fluorinated methane molecules

Molecule	Heat of formation (in kcal/mol at 298 K; ref. [11])	Heat of atomization (in kcal/mol; ref. [12])	C–F bond length (in Å; ref. [13])	Boiling point (in K at 760 mm; ref. [14])
CH ₄	– 17.88	397.19	(1.087)	111.51
CH ₃ F	– 55.90	402.86	1.383	194.62
CH ₂ F ₂	– 108.22	420.95	1.351	221.52
CHF ₃	– 166.60	445.88	1.328	188.72
CF ₄	– 223.02	469.64	1.319	145.12

is a dramatic increase in the heat of formation liberated as the methane molecule is progressively fluorinated. In support of this trend, it is seen that the heat of atomization increases and the C–F bond length decreases with increasing fluorination. The substitution of a fluorine atom for a hydrogen in an alkane is unlikely to introduce any significant strain into the system. Fluorine atoms are intermediate in size between carbon and hydrogen atoms, the precise radii being in the ratio H:F:C :: 1.08 : 1.30 : 1.53 [10]. Since the fluorine atoms are located on the periphery of the molecule, they are able to function as a shield that is protective of the

underlying carbon framework when present in sufficient number. This observation explains not only the high resistance to chemical attack of these species, but also their relatively low level of attractive intermolecular interaction.

Consideration of the physicochemical properties of halogenated alkane species reveals a number of irregularities that appear to shatter any illusion that the behavior of such species is governed by simple trends. Although the boiling points listed in table 1 correlate roughly with the molecular dipole moments, the correlation is not a linear one, an observation that seems to apply to several of the other physicochemical properties too [14]. While the reasons for this kind of nonlinearity may be speculated upon, there can be little doubt that a substantial part is due to the nature of the interactions occurring between the molecules. Such reasoning suggests that a closer look at the size and conformation of the interacting molecules may provide some useful insights. We propose to do this here for series of halogenated alkane molecules by making use of a simplified version of a technique put forward by Rouvray and Pandey [15, 16]. This technique yields information on the time-averaged conformation of molecular species in the liquid state by viewing them as fractal objects. After a determination of the fractal dimensionalities has been made, it is comparatively simple to obtain estimates of the relative size and structural flexibility of the species under study.

2. The mathematical formalism

To set the scene for the technique employed here, we first describe the relevant theoretical landscape. As indicated above, the mathematical formalism we use derives from a somewhat simplified version of that published in the original papers of Rouvray and Pandey [15, 16]. The technique in its current state of development applies only to unbranched chain molecules that are members of some well-defined series such as a homologous series. The individual molecules in the series are represented by means of chemical graphs whose vertices and edges are normally weighted when heteroatoms are present in the structure. From the graphs, scalar numerical invariants (topological indices) are derived and these are then used to characterize the molecules [17]. The two topological indices that have been used to date for this purpose are the well-known carbon number index [17] and the Wiener index [18]. In this work, we shall adopt the latter index, with due allowances being made for the fluorine atoms in the structures we investigate.

Let us start by focusing our interest on some physicochemical property P exhibited by a bulk liquid phase comprised of identical molecules M . We assume that the molecule M can be characterized by some appropriate topological index T . Following a now standard procedure [17], we may write for the M a Walker-type relationship [19] of the form:

$$P = a \times (T)^b, \quad (1)$$

where a and b are undetermined constants. The latter can be estimated by obtaining the slope and intercept of a plot of $\ln P$ against $\ln T$ for a set of related systems (each based on a molecule closely related to M such as the members of a homologous series). It is known [15], however, that the parameters a and b change in value slightly as one progresses through the successive members of a given series. The true situation is therefore more accurately reflected by a set of k relationships written for a series containing k different molecules as follows:

$$P_i = a_i \times (T_i)^{b_i} \quad (1 \leq i \leq k). \quad (2)$$

In our subsequent analysis, we shall concentrate on only two molecules in the above series: a short molecule which will be associated with the value $i = 1$ and a long molecule associated with the value $i = 2$. For two such molecules, it is evident [15] that we shall always have $b_1 > b_2$ if we use either the carbon number or the Wiener index and consider boiling points.

The physicochemical properties of the bulk phase are known to be strongly dependent on the time-averaged size of the molecules that constitute it [15]. A convenient measure of molecular size for our purposes is provided by (i) the mean square radius of gyration, or (ii) the mean square end-to-end length of the molecule. For chain molecules, these two quantities are in fact interrelated and differ only by a constant of proportionality [20]. We take the measure in (ii) as being more directly amenable for our analysis. The end-to-end length r of a flexible molecular chain M satisfies [21] a proportionality relationship of the general type:

$$r \propto n^q, \quad (3)$$

where n is the number of atoms in the chain and q is typically a fractional number. This relationship can also be expressed in an equivalent formulation by making use of the fractal dimensionality [15,22] of the molecule M thus:

$$r \propto m^{1/d_f}, \quad (4)$$

where m is the mass of M and d_f its fractal dimensionality. Because of the dependence of physicochemical properties on the time-averaged conformation of molecules in the bulk phase, we may write for the property P_i of the molecule i the following relationships:

$$P_i \propto r_i \propto m_i^{1/d_{fi}}. \quad (5)$$

Moreover, from the set of relationships in (2), it is seen that the proportionality:

$$m_i^{1/d_{fi}} \propto T_i^{b_i} \quad (6)$$

will also be implied for the molecule i .

At this point, scaling arguments similar to those employed by de Gennes [23] are introduced. For the two molecules designated by the subscripts 1 and 2 in the set of k molecules referred to earlier, the inequalities (i) $m_1 < m_c$ and (ii) $m_2 > m_c$ will apply, where m_c represents some critical molecular mass. If now m_1 and m_2 are imagined to approach ever closer to the critical mass m_c , we can write in the limit:

$$T_1^{b_1 d_{f_1}} = T_2^{b_2 d_{f_2}} \quad (m \rightarrow m_c). \quad (7)$$

Clearly, at this limit the two topological indices and the two exponents will become identical. We may therefore equate the exponents to obtain our final relationship:

$$\frac{b_1}{b_2} = \frac{d_{f_2}}{d_{f_1}}. \quad (8)$$

It is this relationship that we shall now exploit in our study of the physicochemical properties of various halogenated normal alkane molecules.

3. The systems studied

All of the systems investigated in our study were halogenated, normal, i.e. straight-chain, alkane molecules containing only one type of halogen in the molecule. Two principal criteria were adopted in selecting the systems, namely (i) their inherent interest as representatives of the scientifically and commercially important class of halogenated alkanes, and (ii) the availability of reasonably reliable experimental data for the systems. Following on from our earlier work [15,16], we made use of the boiling point measured at 760 mm Hg for the species we considered. Criterion (ii) proved to be a fairly severe constraint on the systems that could be studied, for, although boiling points are generally more widely available than any other experimentally determined property, there is a great paucity in the data for partially halogenated alkane species containing more than one halogen atom. In some instances, plots that we made were perforce terminated at some arbitrary cut-off point owing to a lack of appropriate data points.

For our study, we elected to investigate four different halogenated alkane systems, viz. (i) monofluorinated alkanes, (ii) monochlorinated alkanes, (iii) monobrominated alkanes, and (iv) perfluorinated alkanes. In the case of the first three systems, the substituent halogen atom was always located on the terminal methyl group of the parent alkane molecule, and boiling point data were available for the entire range $1 \leq n \leq 40$ [24]. In the case of the perfluorinated alkanes $C_n F_{2n+2}$, boiling point data spanned only the range $1 \leq n \leq 16$ with four missing points [14]. Because of the generally low thermodynamic stability of other perhalogenated alkane systems, data points were available for only the first few members of each series. It was thus not feasible for us to investigate these systems here, although an analysis and a discussion of the stability of such systems will be presented elsewhere [25].

For the normal alkanes themselves, boiling point data exist for the entire range $1 \leq n \leq 40$ [26]. These were utilized in our previous studies [15,16] and are referred to here only when comparisons need to be drawn with our earlier results.

For the mathematical characterization of the various systems we investigated, use was made of two different molecular descriptors, both of which reflect the size of the molecule. The first of these descriptors, the molecular volume, affords a direct measure of molecular size and may be calculated by summing additively all the relevant atomic or atomic group contributions to the volume. Since there are several different schemes available for such calculations, we decided to adopt that due to Bondi [26]. This enabled us to derive the following sets of equations for calculation of molecular volumes in cm^3/mol .

$$\text{C}_n\text{F}_{2n+2} : v_1 = 12.00 + 16.86n, \quad (9)$$

$$\text{C}_n\text{H}_{2n+1}\text{F} : v_2 = 9.16 + 10.23n, \quad (10)$$

$$\text{C}_n\text{H}_{2n+1}\text{Cl} : v_3 = 15.06 + 10.23n, \quad (11)$$

$$\text{C}_n\text{H}_{2n+1}\text{Br} : v_4 = 17.84 + 10.23n. \quad (12)$$

The second of the descriptors, the Wiener topological index [17,18,27], can be calculated by taking one half the sum of the entries in the distance matrix [18] of the relevant molecular graph. These indices were derived after making allowances for the heteroatoms according to the recommendation of Barysz et al. [28]. The values used as distance matrix entries for the heteroatoms are listed in table 2. It

Table 2

Listing of the values used for heteroatom distance matrix entries for calculation of the Wiener index [28]

Atom	Diagonal entry (d_{ii})	Bond	Nondiagonal entry (d_{ij})
F	0.333	C-F	0.667
Cl	0.647	C-Cl	0.353
Br	0.829	C-Br	0.171

has been argued [29] that around 90% of the value of the Wiener index reflects molecular size, while the remaining 10% reflects the shape. Since all of the molecules we studied were of the same shape – all are in the form of unbranched chains – the index functions here as another measure of size.

4. Presentation of results

The curves obtained for the plots of boiling points versus molecular volume and Wiener index for the monofluoroalkanes and the perfluoroalkanes are reproduced in figs. 1–4. As might be expected for systems that display more or less additive behavior, the curves are similar in form to those of normal alkane molecules [16]. There are, however, some important differences too. Figure 1(a), showing the plot of boiling point versus molecular volume for monofluoroalkanes, has a curvature that is convex with respect to the molecular volume axis as expected. Yet the same plot on logarithmic scales in fig. 1(b) reveals an unexpected elongated S-shaped curve, which we believe has not been reported previously. A similar situation obtains in the case of the plots of boiling point versus the Wiener index for the monofluoroalkanes reproduced in fig. 2. When the perfluoroalkanes are considered, no S-shaped curves are observed either for the molecular volume plots in fig. 3 or for the Wiener index plots in fig. 4. We speculate on the reasons for these differences in our discussion.

To derive fractal dimensionalities for the species under consideration, the plots presented in figs. 5–7 were constructed. From our eqs. (2) and (8), it is evident that the fractal dimensionalities can be obtained from boiling point curves plotted on logarithmic scales. The slopes b_i were determined for sets of eight successive data points by regression analysis; experience showed that any number less than eight would not yield smooth plots. For convenience, the initial slope b_1 is always taken as the denominator in the ratios of slopes. This means that the ratios are always less than unity and, from eq. (8), that the relevant fractal dimensionalities are equal to the reciprocals of these ratios. Such curves were obtained for both the average molecular volume and the average Wiener index. In fig. 5, results are presented for the monohalogenated alkanes, and fig. 6 reproduces the plot for the perfluoroalkanes. These curves reveal very clearly the effects of halogenation, with the perfluoroalkanes having the highest (apart from the unsubstituted alkanes) and the monobromoalkanes the lowest fractal dimensionalities.

Table 3

Listing of the mass-scaling exponents (fractal dimensionalities) obtained for halogenated alkane species from molecular volume plots

Average carbon number	Monofluoro-alkanes	Monochloro-alkanes	Monobromo-alkanes	Perfluoro-alkanes	Unsubstituted alkanes
1	1.00	1.00	1.00	1.00	1.00
9.5	1.09	1.06	1.05	1.18	1.18
19.5	1.29	1.23	1.20	1.32	1.43
29.5	1.53	1.40	1.35	–	1.69
36.5	1.55	1.47	1.41	–	1.80

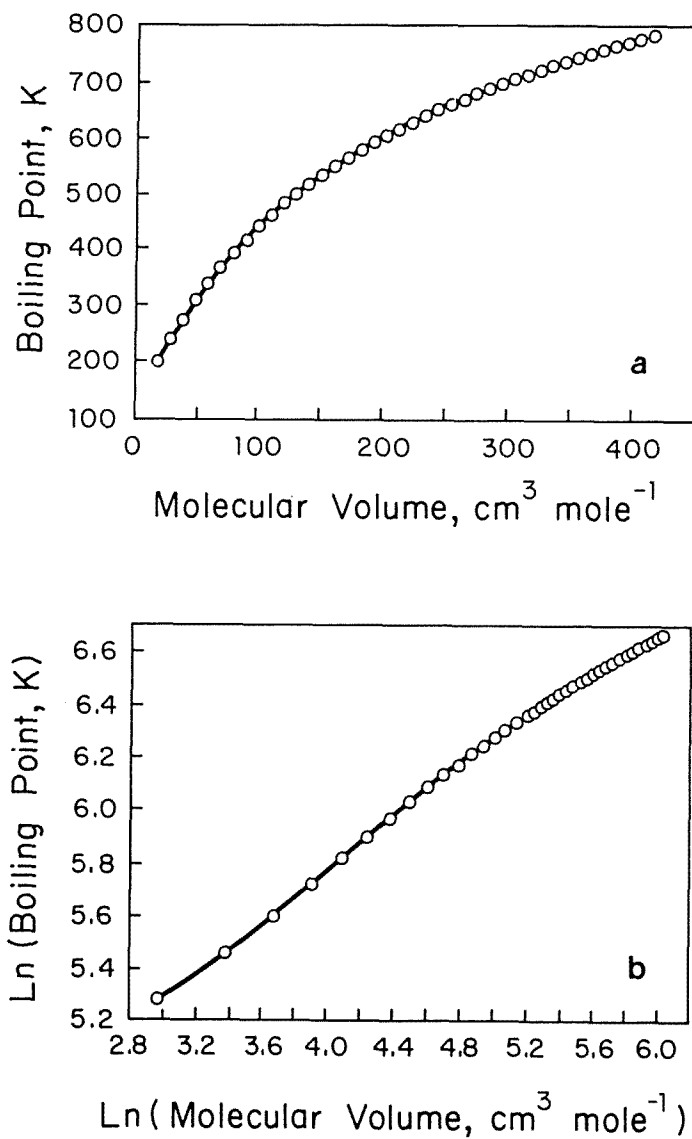


Fig. 1. Plots of boiling point versus molecular volume for mono-fluorinated normal alkanes on (a) linear and (b) logarithmic scales.

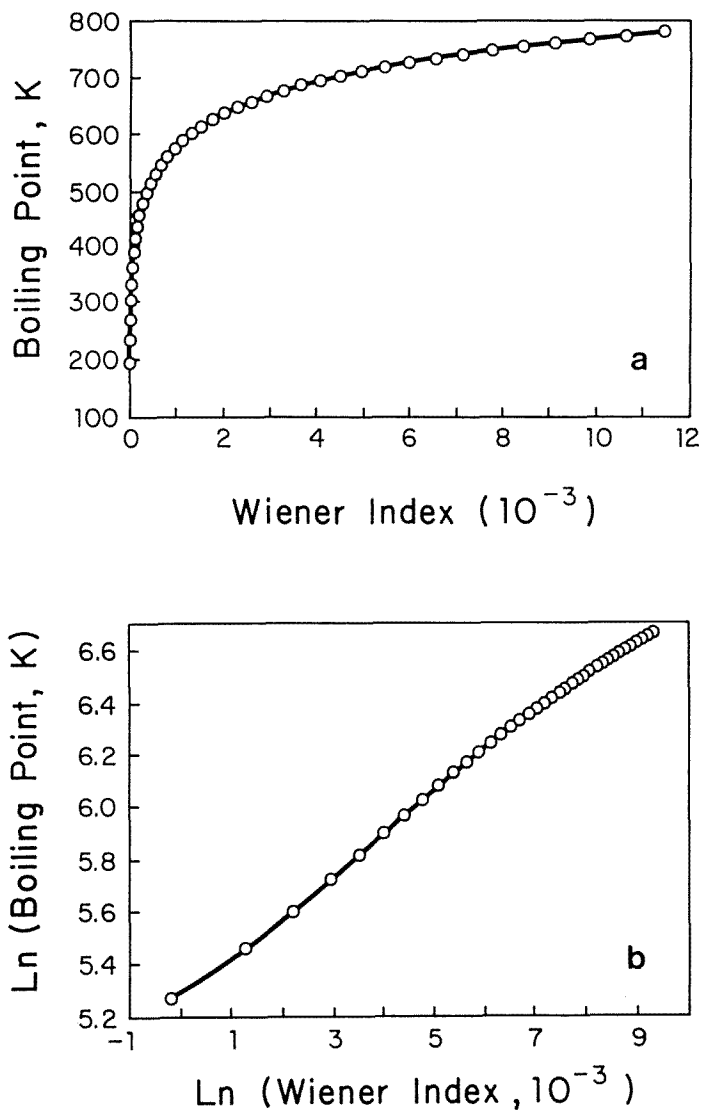


Fig. 2. Plots of boiling point versus the Wiener index for mono-fluorinated normal alkanes on (a) linear and (b) logarithmic scales.

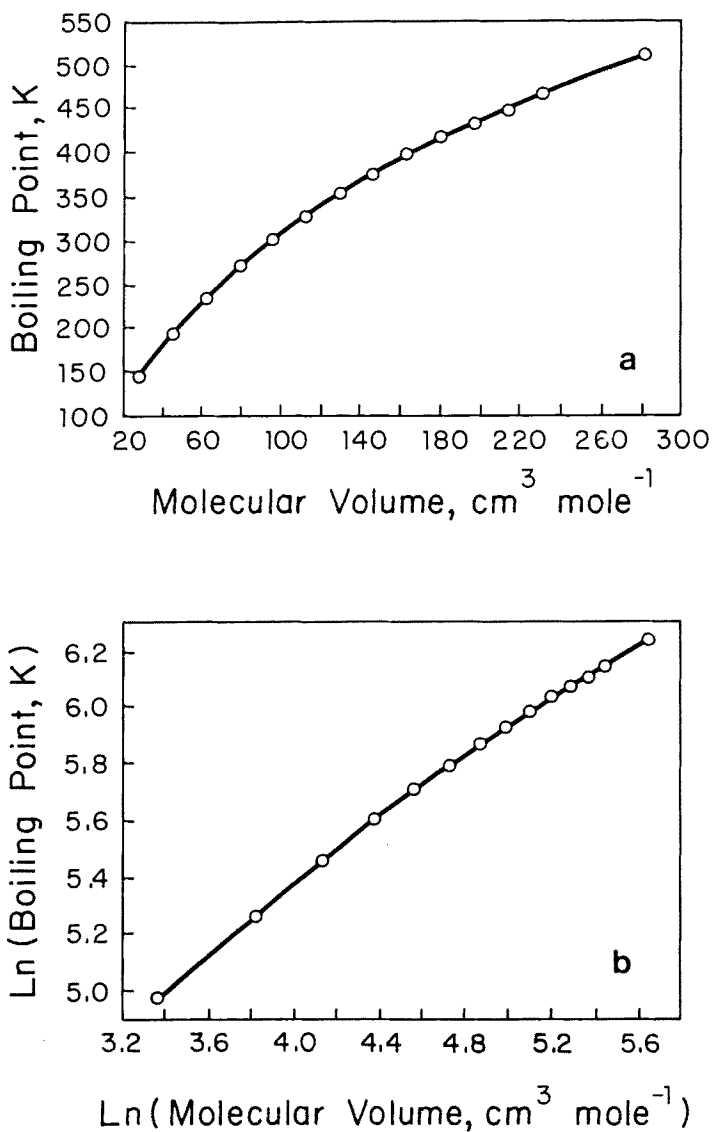


Fig. 3. Plots of boiling point versus molecular volume for perfluorinated normal alkanes on (a) linear and (b) logarithmic scales.

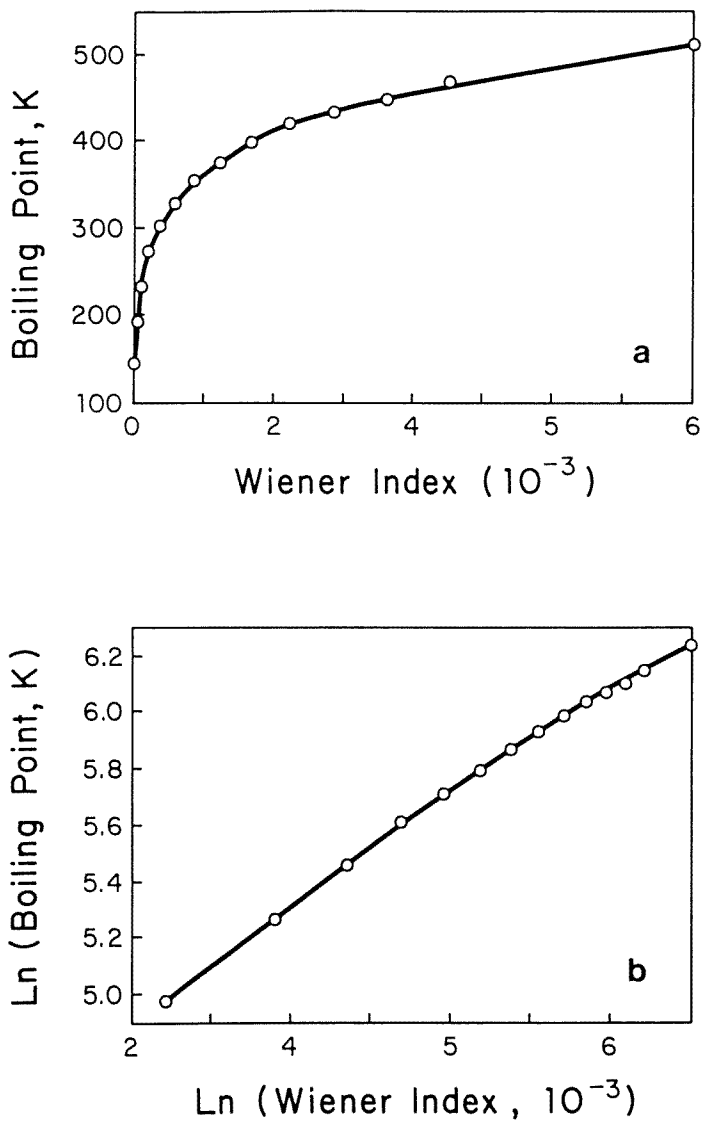


Fig. 4. Plots of boiling point versus the Wiener index for perfluorinated normal alkane species on (a) linear and (b) logarithmic scales.

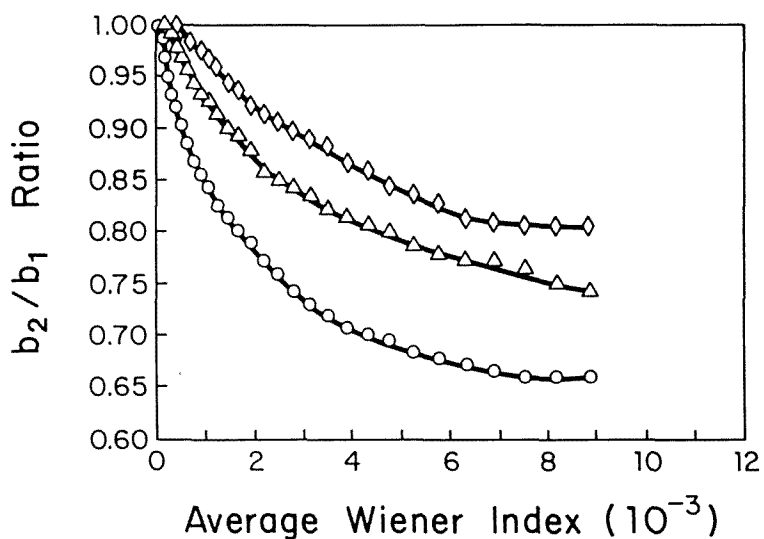


Fig. 5. Plots of the b_2/b_1 ratio versus the average Wiener index for mono-fluorinated (circles), mono-chlorinated (triangles), and mono-brominated (diamonds) normal alkane molecules.

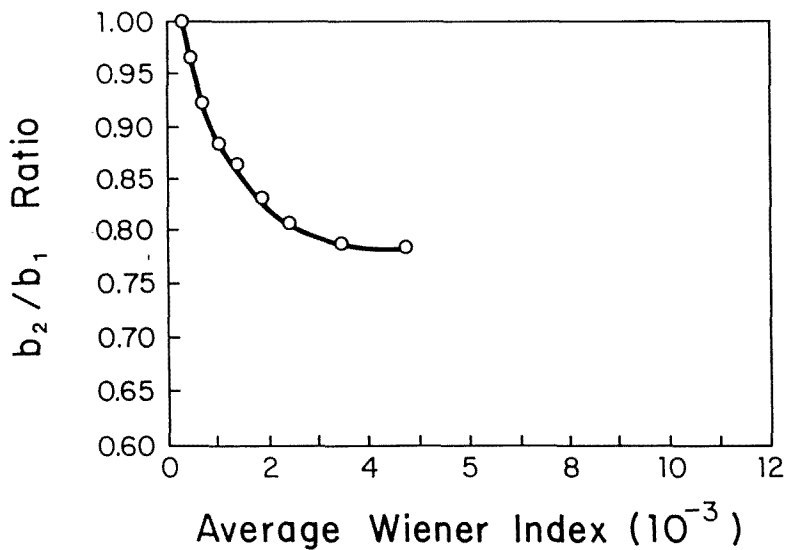


Fig. 6. Plot of the b_2/b_1 ratio versus the average Wiener index for perfluorinated normal alkanes.

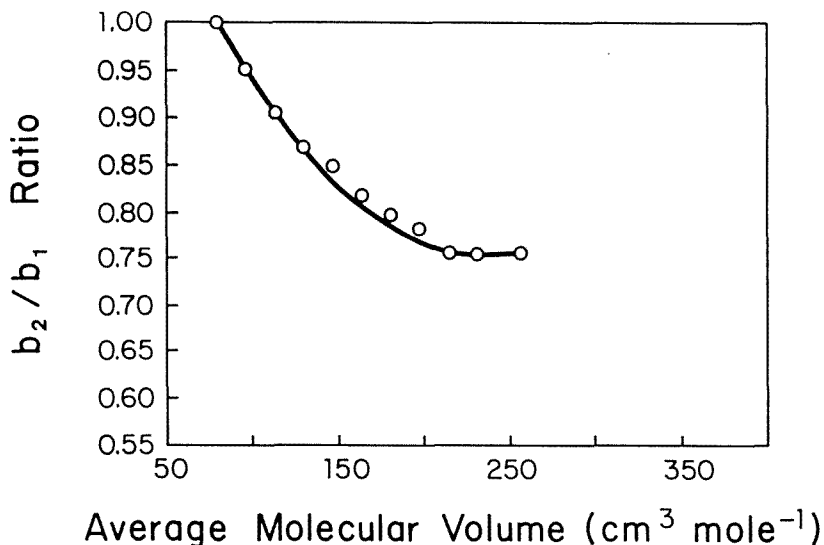


Fig. 7. Plot of the b_2/b_1 ratio versus the average molecular volume for perfluorinated normal alkanes.

In an attempt to have access to more data points for the perfluorinated alkane systems, we decided to extrapolate the boiling point data from $n = 16$ to $n = 20$. Using a regression equation based on the last three experimentally known points ($n = 10, 12$ and 16), we were able to generate the boiling points shown in table 4.

Table 4

Extrapolated values of the boiling point for perfluorinated alkane molecules

Carbon number	Extrapolated boiling point [K]
11	434.81
13	467.95
14	483.50
15	498.43
17	526.75
18	540.13
19	553.10
20	565.72

Since the correlation coefficient for this regression and for regression using all the data points exceeded 0.999 in both cases, the derived values for the boiling points are probably reliable. The plot of the b_2/b_1 ratio against the average molecular volume

for the perfluorinated alkanes including the extrapolated points is reproduced in fig. 7. The curve appears to be leveling off at an apparent asymptotic value of 0.755, which corresponds to the fractal dimensionality of 1.32 given in table 3. Since we did not feel justified in extrapolating beyond the $n = 20$ boiling point, this fractal dimensionality is the best asymptotic value that can be given for the perfluoroalkanes at the present time. It is sufficient, however, to reveal that the perfluorinated alkanes behave similarly to the monofluorinated alkane species, but rather differently from the other monohalogenated species, as shown in our subsequent discussion.

5. Discussion of results

We start by outlining a number of the problems inherent in the approach that we have developed here. One of the most troublesome and, incidentally, one that confronts all workers who employ topological indices for property prediction, concerns the heteroatoms in the structures investigated. The difficulty lies in deciding what weighting factors should be adopted to characterize the heteroatoms. Although several different solutions to this problem have been advocated [30], there is at present no generally agreed or optimal solution. All the proposed solutions suffer from the drawback that the heteroatom weightings are associated with some measure of arbitrariness. This seems to be especially true in the case of fluorine atoms, since widely fluctuating values have been suggested for these at different times in the case of molecular connectivity indices [31, 32]. Although the latter indices were not used here, we feel that the weighting factors employed in our calculation of molecular volumes and Wiener indices should be viewed with a healthy skepticism.

It is our opinion that the unexpected shapes of some of the plots obtained can be traced back ultimately to the problem of the weighting factors used for the halogen atoms in the systems we investigated. It was found that the shapes of the plots on logarithmic scales of boiling point versus both the molecular volume and the Wiener index were in the form of elongated S-curves in the case of monofluoroalkane species. Similar types of plots were obtained in the cases of the monochloro- and monobromoalkanes, with the S-shape becoming more pronounced with increasing size of the halogen substituent. We believe that the true curves are likely to be strictly convex with respect to the descriptor axis and that the shapes we have observed are actually artefacts arising from a somewhat inaccurate weighting procedure adopted for the halogen atoms. At present, it would seem that the weighting methods now in use do not weight halogen atoms in a completely satisfactory manner. This particular problem will probably not be resolved until substantially improved weighting procedures are developed in the future.

Having made this point, however, we incline to the view that overall the results presented here afford an essentially accurate picture of the behavior of halogenated alkane species. In particular, the observed changes produced by the different halogen atoms when substituted into alkane species accord with our intuition

on the behavior of such atoms. Let us consider a number of interesting trends that are revealed. In the case of the monohalogenated alkanes, the terminal halogen atom appears to act as an anchor. The larger the halogen atom, the lower the calculated fractal dimensionality becomes, and hence the more rigid the chain molecule will be. The introduction of a terminal halogen atom into normal alkanes thus reduces their flexibility and the reduction of flexibility becomes greater with increasing size of the halogen atom. In the case of the perfluorinated alkanes, the complete substitution with fluorine atoms results in an increase in molecular rigidity with respect to unsubstituted alkane species. The perfluorinated species, however, still appear to have a fairly high degree of flexibility, which is roughly equivalent to that for the monofluorinated alkane species.

As will be evident from the foregoing, the measure of molecular flexibility that we employ here is related to the fractal dimensionality of the molecular species in question. From eq. (4), we know that both the mean square radius of gyration and the mean square end-to-end length of the species are proportional to their mass raised to a power equal to the reciprocal of their fractal dimensionality. Thus, a fractal dimensionality greater than unity implies the existence of a radius or end-to-end length less than that for a rigid chain containing the same number of links. Because all of the fractal dimensionalities we have determined are greater than unity (apart from those for C_1 species, which are arbitrarily set to unity), it follows that none of the molecules will be in the form of a rigid chain and all will display at least some flexibility. The degree of flexibility is clearly related to the mean square end-to-end length which is proportional to the reciprocal of the logarithm of the fractal dimensionality. If the relationship is assumed to be an inverse one, we may conclude that the molecular flexibility will be proportional to the logarithm of the fractal dimensionality. Thus, if no correction is made for molecular mass, the molecular flexibilities for the C_{20} species will be in the ratios $C_nH_{2n+1}F : C_nH_{2n+1}Cl : C_nH_{2n+1}Br : C_nF_{2n+2} : C_nH_{2n+2} = 1.106 : 0.899 : 0.792 : 1.206 : 1.553$. Correction for molecular mass yields the respective ratios $0.453 : 0.364 : 0.313 : 0.434 : 0.643$, which reveal that the flexibility of C_{20} normal alkanes is over twice that of the corresponding monobrominated species and roughly one and a half times that of the $C_{20}F_{42}$ molecule.

6. Conclusion

We have demonstrated that it is possible to derive valuable information and insights on the behavior of halogenated normal alkane species using only very simple input data. This has been accomplished using the experimentally determined boiling points and the theoretically calculated atomic radii. The topological connectivity of the species investigated also needs to be known. From these comparatively simple starting data, we have obtained results for the fractal dimensionalities and flexibilities of a variety of halogenated normal alkane species in the liquid state.

We have thereby shown that the earlier work of Rouvray and Pandey [15] on the normal alkanes can indeed be extended to other systems as they had predicted. Two major difficulties were encountered in achieving our results, viz. (i) a lack of appropriate data for the boiling points, especially for the perfluoroalkanes, and (ii) the unreliability of the weighting factors adopted for the halogen atoms in deriving our molecular descriptors. The first we attempted to overcome by extrapolating boiling points through to the C₂₀ member of the perfluoroalkane series; we believe that the extrapolated values have a high probability of being accurate. The second problem cannot be effectively solved until better methods of weighting for heteroatoms become available. Even allowing for these problems, however, we incline to the view that the broad picture presented here is valid, namely that the perfluoroalkanes are possessed of a flexibility which is roughly equal to that of the monofluoroalkanes but only two-thirds that of unsubstituted alkanes. This picture appears to accord with known facts concerning the stiffness of the perfluoroalkanes vis-à-vis the alkanes [33–36].

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