

On Isomeric Variations in Decanes

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Abstract

Ordering of structural forms (skeletons of isomers) leads to an array which is shown to provide a natural scheme for discussion of numerous molecular properties and isomeric variations. Regular variations along the rows and columns of the array reveal periodic character of such properties as the heats of formation, the boiling points, the heat capacity, the critical density, etc. The basis for the ordering which displays a regular dependence of numerous properties are graph invariants p_2 and p_3 which represent the count of paths of length two and three, respectively. It appears that the significance of ordering structures has escaped attention of chemists. We argue here in favor of ordering scheme designed for molecules, more specifically the scheme which results in Tables of Isomers. In particular we discuss Decanes and their selected properties and show how well an array of structures based on path enumeration display periodic variations of selected properties in decanes.

Introduction

Properties of alkanes, their variations among isomers, have attracted attention of many chemists over last several decades^{1,2}, and continue to be studied³⁻¹⁴. Availability of sizable sample of data makes it difficult to resist the challenge of a search for a structure-property correlation. There are several conceptually different approaches: (1) empirical bond-additivities; (2) empirical factor analysis; (3) structural (graph theoretical) additivities. Some properties correlate among themselves (e.g. the boiling points and the chromatographic retention times¹⁵), other don't (e.g. enthalpies of formation which one attributes to "surface" property, and indices of refraction, similarly viewed as "volume" property). Much effort in the past has been focused on increased accuracy of alternative additivity schemes, while questions relating to the basis of such schemes and why they work at all have been for the most part avoided. Limitations of quantum mechanics in this area are well known¹⁶ but it appears that the potential of graph theory has not been fully recognized¹⁷. Wiener¹⁸ and Platt¹⁹ were among first to recognize different character of graph theoretical schemes, where the emphasis is on the meaning of the invariants adopted and factors playing the dominant role, rather than on precise fitting of variations by increase in the number of parameters adopted. Thus Wiener was able by use of only two invariants: W the total number of paths in molecular graph and P the number of paths of length three between terminal (methyl) carbons to account for the major part in variation in numerous thermodynamic properties not only of alkanes, but also alcohols, fatty acids and related compounds. Revived interest in chemical graph theory²⁰ brought again to the attention of chemists isomeric variations and the challenge of classification, characterization and ordering of numerous molecular data. Ordering in particular as an operation has been overlooked, yet it offers important insights, even when the initial ordering rules, as in the case of the Mendeleev System of Elements, had to be subsequently revised. We will show that ordering of skeletal forms of isomers also lead to an array which has analogous properties to the Periodic Table of Elements in displaying regular variations among simply independent collection of data.

On ordering

Problem to be faced when ordering structures is twofold: (1) the structures have to be represented by some parameters and (2) an ordering rule has to be proposed. Ordering will depend critically on both these factors and one can envisage many different characterizations as well as many diverse ordering rules. In application to molecules then some characterizations and some rule may point to regularities on the collection of data, other need not, and as such are no longer subject of chemical interest. The most relevant mathematical topic for ordering of structures is comparison of sequences and their subsequent ordering. The field was opened by Muirhead²¹ and has been subsequently expanded²² culminating in Karamata²³ theorem which secures conditions under which ordering of sequences (structures) has for a consequence ordering of properties. As illustrations of various ordering rules consider: Construction of partial sums for sequences and their subsequent comparison; if members of one sequence of partial sums dominate the respective members of the other sequence the corresponding structures can be ordered, the former structure dominates the other. If the relative magnitudes for the partial sums oscillate the structures cannot be compared and ordered. This ordering rule in essence was found of interest in some problems of physics²⁴ and chemistry^{25,26}. In fact they have been, in somewhat modified form rediscovered by Ruch and used in the study of chirality²⁷. Another illustration of ordering concerns MO levels in atoms (and molecules in general). It is well known that group theory can be used to find the pattern of splitting of atomic levels when atom is found in reduced symmetry environment. Group theory, however cannot say anything about the relative magnitudes of the levels, however in some instances additional deductions are possible! This was shown by E. Bright Wilson²⁸ who examined nodal contours of orbitals and using some theorems from calculus ordered numerous orbital energies in several highly symmetrical systems. Noteworthy, details of contours of MO are not essential, the results rests critically on topological characteristics of the nodal properties. Finally, as yet another ordering rule we may mention induced order of structures based on ordering of selected atomic properties. If one decide that whenever selected atomic

properties (such as proton chemical shifts of selected CH groups in benzenoid hydrocarbons)²⁹ overlap one cannot order structures then a collection of atomic properties will determine molecular order (which again will be in general only partial).

The illustrations mentioned hint to possibility of different rules for different needs. In view of diversity of structures (chemical and other) and diversities of properties one can only expect further developments in this area. Here we want in particular to concentrate on an ordering scheme based on enumeration of paths in molecular graph. Preliminary report^{30,31} demonstrated for selected properties of octanes the kind of results we obtain: isomers are arranged in two-dimensional arrays and when the structures are replaced by selected numerical magnitudes trends in the relative values become visible as one moves along the rows and columns of the array. Subsequently the study has been extended³² to dozen and more molecular properties showing that the ordering is general and holds for diverse properties, properties that do not correlate among themselves. It appears that for most thermodynamical properties dependence of the bond contributions is regular and various properties can be classified in various (+,+), (+,-), (-,+), and (-,-) types, where + and - indicate an increase or decrease along the rows and columns. In addition we can have types like (+,0) which signify dependence on only one of the two ordering parameters. Already such simple classification can provide an answer to question which pair of properties can be and which cannot be expected to correlate among themselves. While 18 isomers of octane already provide a sufficiently large pool of data the necessarily qualitative aspect of comparison of relative magnitudes to discern trends allows individual values to oscillate, and even occasionally obscure the trend. There are other contributions which the simple ordering neglects and in some instances they may accumulate reversing the relative magnitudes. The more recent report on nonanes³³, in all 35 isomers, was conducted to reinforce the conviction that indeed ordering of structures reflects some inherent structural feature, which then influence the relative magnitudes for selected properties. It seems difficult to expect that demonstrated ordering of structures is accidental or without some deeper content.

With this paper we want to focus attention of underlying concepts and discuss some minor variations in properties that such ordering produce adding thus to the significance of the ordering and its practical application. It should be mentioned that ordering of structures and properties as an operation is complementary to existing analysis, such as empirical correlations or factor analysis. In particular it provides an independent verification of the data. Significant deviations in the relative magnitudes from those expected on the basis of ordered structures likely points to some errors or alternatively may hint to some neglected structural contribution (not used for the order). The hitherto found regularities on octanes and nonanes justify²⁹⁻³³ (1) extension to other compounds; and (2) justify attaching more significance to minor deviations. Here we will discuss selected properties of decanes, as next higher homologues, and will pay attention to several apparent discrepancies though minor, in order to see whether they also can be attributed to some structural causes.

Enthalpies of formation for decane isomers

We have selected enthalpies of formation of decane isomers as the property to be examined in some details. As a source we have taken calculations of Scott³⁴. Instead of offering an alternative empirical additive scheme we will focus attention to changes in ΔH_f° and will seek any regularity in the relative magnitudes when isomers are arranged in two-dimensional ordering based on enumeration of paths of length two and three. One should observe the different emphasis in our work. While an empirical additive scheme such as one used here due to Scott predicts ΔH_f° within few tenths of kcal mole⁻¹ (the statistical uncertainty is somewhat larger only for most tetra and penta substituted (branched) skeletons) we do not make predictions but consider possible underlying factors which may be responsible for resulting variations. For example in Table 1 we have collected numerous coincidental magnitudes for ΔH_f° (or almost coincidences).

Table 1

Coincidencies in ΔH	
Pairs of isomers	ΔH_f° kcal mole ⁻¹
3,6-dimethyloctane	61.75
5-ethyl-2-methyloctane	61.76
3,4,5-trimethylheptane	60.22
2,3-dimethyl-4-ethylhexane	60.24
2,2-dimethyl-4-ethylhexane	62.54
2,4,4-trimethylheptane	62.54
2,4,5-trimethylheptane	62.25
2,5-dimethyl-3-ethylhexane	62.27
3-methyl-4-ethylheptane	60.05
4-methyl-3-ethylheptane	60.04
2-methyl-3-ethylheptane	60.65
4,5-dimethyloctane	60.62
3,5-dimethyloctane	61.90
2-methyl-4-ethylheptane	61.90

In Table 2 we extended tabulation for other cases of isomers having same count of graph invariants p_2, p_3 .

That some of the coincidencies hapen is not so suprising. For instance 3-methylnonane and 4-methylnonane differ by a shift of the substituted methyl along the chain, and such difference in structure appears to be "observed" only by long range interactions involving several bonds. Hence, similar values

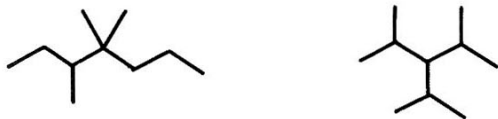
Table 2

Additional similar values in ΔH

Pairs of isomers	ΔH_f°
4-methyl	60.75
5-methyl	60.73
2,3-dimethyl	61.21
3,6-dimethyl	61.75
4,5-dimethyl*	60.62
2-methyl-3-ethyl	60.65
3-methyl-5-ethyl	61.30
3-methyl-2-ethyl	60.05
3-methyl-4-ethyl	60.04
3,3-dimethyl	62.56
2,3,6-trimethyl	62.85
2,4-dimethyl-4-ethyl	61.12
2,2-dimethyl-3-ethyl	60.27
3,4,4-trimethyl	61.27
2,3,4,5-tetramethyl	61.33

* In Ref. 34 this item has been incorrectly shown as 4,4-dimethyl

for molecular properties may be anticipated. But some of the structures in Table 1 and Table 2 are visibly different. For instance 3,4,4-trimethylheptane and 2,4-dimethyl-3-isopropylpentane:



The molecules differ in the length of the main chain, type of carbon atoms (e.g., there is quaternary carbon in the former isomer) and consequently in types of bonds. Why should such apparently different structures nevertheless have similar magnitudes for a number of properties? The answer follows once we recognize p_2 and p_3 , the number of paths of length 2 and length 3 as the principal contributors to molecular additivity²⁹⁻³³.

As already discussed for smaller alkanes the count of p_2 and p_3 , the paths of length two and paths of length three respectively allows associating with each isomer an ordered pair, to be viewed as coordinates. The resulting coordinate grid is shown in Fig. 1 and can alternatively be viewed as Table (Fig. 2). Notice, first that for many sites in the grid (or table) there are more than one isomer assignment. Consequently such isomers are then expected to be very similar in their properties. Hence, the validity of the approach can first be attested by examining all the cases of several isomers belonging to a same site and see if indeed their properties are same (or approximately same). Table 1 and Table 2 is in fact provide in part such a comparison for heats of formation. It seems that the dominant character of the regular variation of the relative magnitudes of heats of formation (enthalpies) is well represented with the respective values of p_2, p_3 . There are variations within such classes, but the major part of the dependence appears to be satisfactorily accounted for. We will later seek for possible cause of the minor variations within each class, the present approach, we can ascertain provides valid basis for classification of isomers. Next, to look for is the regularity in trends along any axis of the grid. Existence of such trends and regular variation would justify using term "periodic" for the table of isomers. In Fig. 3 and Fig. 4 we show variation of heat of formation and variation of entropy for decane isomers ordered according to p_2, p_3 values. The regular variation of the two properties is evident particularly for the cases of larger differences, as is with isomers of the first columns of Table 3. In the case of the entropy in number

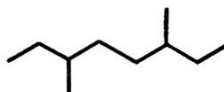
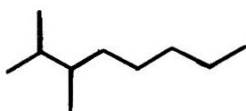
of cases because of small differences the regularities in relative magnitudes are perhaps obscured by possible contributions of other factors. The results in Fig. 3 and Fig. 4 should be combined with the already reported variations in the boiling points of decanes³², and should be all examined together. It appears that there is no doubt that the ordering of isomers along (p_2, p_3) reveals simple "periodicity" although it is also clear that in some instances other factors may be of importance and cause apparent deviations.

Fig. 3

Fig. 4

Possible role of other factors

An obvious next parameter to consider is p_4 , the role of paths of length four, simply just to see what is the effect of truncating the sequence of p_i numbers. However, there are also other factors that we have neglected also, such as the distribution of neighbors (path counts only takes the number of neighbors into consideration). Alternatively, one may be interested in examining bond types, if indeed a property is bond-additive. Still, there are spatial and geometrical factors, such as the number of conformations for an isomer, steric hindrance and so on. We may recollect that Wiener's approach is based on two parameters and that it accounts quite well for the dominant features of structure-property correlations. Hence, one should not liberally increase the number of parameters, until one is forced to do so³⁵. Our attention is focused on isomers of a same class, and we will seek those structural factors in which structures differ. Since in several instances we see isomers that have same p_4 , yet they differ in their property numerically (e.g., 2,3-dimethyloctane and 3,6-dimethyloctane) we conclude that p_4 is not the



principal suspect.

Let's examine more closely bond types involved. We suspect bond types as possible factor, because many thermodynamical properties of alkanes correlate well with the connectivity index, which in fact is based on bond types. In Table 3 we have examined all cases of two and more isomers belonging to a same (p_2, p_3) class. Only in eight cases we find that molecules already classified in a same group differ in bond-type composition. These are classes like (10,9), (11,9), etc. to which more than a single column is assigned in Table 3. If bond type plays significant role we expect that classes with only single bond-type composition should show smaller variations, while other should show that larger variations which are attributed to isomers of different bond-type content. At least this should be in an ideal situation if no other factors cause further visible effects. We can find some support for the contention. In the case of the class (12,9) single value of 64.15 kJ/mole for ΔH_v is by some 1.5 kJ/mole larger than the remaining two values, and it belongs to the isomer with different bond composition. Another illustration is within the class (11,11) which splits into three subgroups and we find that the reported ΔH_v also group into the following: (61.25; 61.38), (60.22), and (59.26; 58.59). In the class (10,10) only single isomer makes a separate subgroup (3E3M) and its ΔH_v is visibly different from the rest of the group which shows much lesser variations: 60.56; 60.62; 60.71; and 60.65.

The above discussion should be taken as indicative, not conclusive. There are too few cases to be compared, and too few properties for which such small differences can be visible. Variations for example in the values of the boiling points are generally much larger, and same again is with the values of entropies.

On deviations from the apparent regularity

In few instances visible deviations in the relative magnitudes from the trends on (p_2, p_3) grid can be observed. For heats of formation such is the case of points (13,9) and (13,10) with the values 63.58 and 64.37, while

the reverse is expected. In case of the boiling points reversal of the relative values is for (13,9) and (14,9) the values being 147.8°C and 153.8°C , while the remaining values (if we ignore the variations within each class which are few degrees in magnitude) show remarkable regularities in variation along (p_2, p_3) grid. In case of calculated entropies the noticeable deviation occurs at (11,8), the value of 119.71 which appear somewhat too small. None of the mentioned examples should be overlooked, but at the present stage of understanding details of molecular additivities it seems that there are two options: (1) increase the number of parameters to bring those "exceptions" back into the line; or (2) keep the number of parameters minimal and tolerate few "exceptions", hoping that further accumulation of data may lead to inclusion of responsible structural factors. We prefer this later option and hope that more close look at the "worst" cases may be instructive. As an illustration of such attitude we may mention the improvement of the correlation of the chromatographic retention volumes with the connectivity index, which when "correction" for the presence of methyl-methyl chains of length three was introduced correlation was improved significantly and could be compared with empirical schemes using dozen and more parameters³⁶. Another illustration of some "detective" work with "worst" cases has been outlined in a close view on correlation between the boiling points and the connectivity index, when the latter is associated with a sequence of contributing bond components³⁷. It was then possible to anticipate for which isomers the correlation may show larger departure. We have no answers for all variations presently observed, but it seems that their understanding may follow from the approach outlined. The graph invariants p_2 and p_3 clearly play the dominant role for an additivity or correlation, but they only count the number of nearest and next nearest neighbors. The bond types, the associated contributions to the connectivity index, reflects to some degree neighbor distribution, and higher connectivity indices generally will account for distributions of more distant neighbors. It seems therefore that a synthesis of the two kinds of approaches, based on (p_2, p_3) and based on the connectivity index and its higher analogues (or any graph theoretical quantity that plays a similar role)

in being sensitive also on the distribution of neighbors, may well provide a valid basis for discussion of isomeric variations and apparent deviations within them.

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Fig. 3

Table of Decades: $-\Delta H$

59.64											
61.28	60.70 60.75 60.73	60.15 60.19 60.24									
62.91	62.45 62.37 62.34	61.21 61.90 61.75 61.90 61.76	60.56 60.62 60.17 60.65 61.30	60.05 60.04	59.49						
63.79	64.16	62.56 62.67 62.85	62.35 62.25 62.27	61.25 61.38 61.96 59.26	60.24	60.03					
65.42	63.12 64.81	62.54 64.15 62.54	62.71 61.86	62.07 60.27 61.12	61.19 61.27 61.33 61.21	60.49 58.70	59.55	57.13			
		63.58	64.37	61.93	60.45 58.57	59.60	60.37	57.58			
67.83		61.46				61.73		59.37 59.59			58.27

Fig. 4

Table of Decones - Entropy

130.4										
128.5	129.9 128.2 129.5	128.2 129.1 125.0								
124.4	127.2 126.3 125.2	127.4 125.6 126.7 127.0 125.8 124.7	125.5 127.8 125.7 125.8 123.8	126.5 125.1	121.8					
122.1	119.7	123.7 122.5 123.6 124.2	124.2 123.6 121.6	121.4 120.0 122.9 121.4	122.9 121.0 123.5	115.2				
119.3	121.1 120.6	121.5 119.0 120.1	122.7 119.7	118.9 119.8 120.4	119.9 117.4 115.3 120.7	120.5 118.2	118.4	116.0		
			115.7	117.4	117.9 117.4	118.1	115.4	114.2		
112.3						112.5			112.8	
										109.8
					108.7					