striking effects in cyclopentadiene and particularly in benzene become less unusual when it is considered that in the direction from allene to tetramethylethylene other than conjugation effects have altered the heat of hydrogenation by some 14 Cal.

In conclusion we wish to thank Dr. J. B. Conant and Prof. E. P. Kohler for their advice and criticism which have materially helped the progress of this work, and Mr. M. A. Dolliver for his able assistance in the preparation of organic materials.

Summary

1. The following heats of hydrogenation have been obtained at 355°K.

	ΔH, cal./mole
Allene + 2H$_2$	−71,280 ± 103 (200)
1,3-Butadiene + 2H$_2$	−57,067 ± 28 (100)
1,4-Pentadiene + 2H$_2$	−60,790 ± 64 (150)
1,5-Hexadiene + 2H$_2$	−60,525 ± 43 (150)
1,3-Cyclohexadiene + 2H$_2$	−55,367 ± 56 (100)
Benzene + 3H$_2$	−49,802 ± 44 (150)
Cyclopentadiene + 2H$_2$	−50,865 ± 47 (200)

The uncertainties represent calorimetric precision, while the figures in parentheses are the crudely estimated all inclusive errors.

2. These data are discussed and it is pointed out that two double bonds, when placed close together in the molecule, exert an unstabilizing effect upon one another. The resonance predictions of Pauling are confirmed but qualitatively.

A Method of Comparison and Critical Analysis of the Physical Properties of Homologs and Isomers. The Molecular Volume of Alkanes*

BY GEORGE CALINGAERT AND JOHN W. HLADKY

Any simple and reasonably accurate method of correlating the physical properties of a compound with its structure is of obvious worth, both for the purpose of evaluating the reliability of the numerical values assigned to the property in question, and in studying the effects of molecular structure on physical properties in general.

There have been numerous attempts to develop correlations of this type, all of which, however, appear to suffer from the disadvantage that either they are not quantitative or that they depend on the calculation of some complex function involving two or more physical constants.

The present paper describes a correlation method involving a simple linear relation between the structure of the molecule and a single physical constant, and uses as illustration the application of the method to the molecular volumes of the straight and the branched-chain alkanes. The method is based on the fact that in an homologous series most of the properties are smooth functions of the molecular weights.

The usefulness of the method is enhanced by the simultaneous addition of 2 features: (a) by a suitable transformation of the ordinate scale, the lines for homologous series are made to plot as straight or nearly straight lines; (b) the properties of isomers are plotted against the number of carbon atoms in the longest chain, thus giving rise to a new set of curves (for isomers). These "homolog" and "isomer" lines form a lattice in which the position of individual compounds can be predicted with far greater accuracy than when family lines alone are used. In addition to permitting a critical evaluation of the data, the method throws considerable light on the effect of structure on the physical properties of homologs and isomers. The method appears to be applicable to a large number of physical properties, and as an illustration the molecular volume of the alkanes will be discussed below.

Molecular Volumes[1]

A. Preparation of Data and Plot.—All the data which can be found in the literature on the densities of all alkanes from C$_3$ to C$_{12}$, and on normal alkanes up to C$_{16}$, are collected and indexed. Whenever data by the same author are available at two or more temperatures the values of $\delta d/\delta t$ are calculated and plotted as a function of tem-

(1) The molecular volumes (M. V.) as used here are defined as: M. V. = Molecular Weight/$d^{20}{}_4$, using the atomic weights C, 12 and H, 1. This is used in preference to the densities which are usually reported in the literature, because M. V. are more nearly straight line functions of molecular weight in homologous series.

perature and molecular weight. In this manner, the most probable values are obtained for $\delta d/\delta t$, and these are used to correct all the literature data back to the common basis of $d^{20}{}_4$. Next, the data are examined for agreement among themselves, and for evidence of reliability (rigorous purification, sharp boiling or melting points, accurate methods of measurements).

In a preliminary plot, the best data for the normal alkanes are plotted as M. V. vs. length of chain, and a second curve is plotted of the increments in M. V. The increment curve is smoothed out empirically and the M. V. curve is corrected accordingly until the M. V. curve is as smooth as can be obtained while agreeing as closely as possible with the best published values for the densities. The figures finally adopted, which are given in Table I, constitute the standard of comparison for all other alkanes.

TABLE I

ACCEPTED VALUES OF PHYSICAL CONSTANTS FOR NORMAL ALKANES

Alkane	$d^{20}{}_4$	Molecular volume
Propane	0.5023	87.6
Butane	.5772	100.5
Pentane	.6261	115.0
Hexane	.6591	130.5
Heptane	.6836	146.3
Octane	.7025	162.3
Nonane	.7176	178.4
Decane	.7301	194.5
Undecane	.7404	210.7
Dodecane	.7492	226.9
Tridecane	.7567	243.1
Tetradecane	.7632	259.4
Pentadecane	.7689	275.7
Hexadecane	.7741	292.0

The final plot (Fig. 1) is then prepared as follows:

(1) The number of carbon atoms in the normal alkanes is reported on the y-axis (scale not labeled), and their M. V. along the x-axis (scale marked: "Auxiliary Molecular Volume Scale"). The curve of "carbon atoms" vs. M. V. is then plotted, using the values given in Table I. This curve is represented in Fig. 1 by the broken line marked "Interpolation curve."

(2) A 45° line is laid out, which will represent the M. V. of the normal alkanes on the arbitrary scale explained below.

(3) A new abscissa scale is laid out, marked "number of carbon atoms in the longest chain." This scale determines the position of the n-alkanes on the 45° line, and, in turn, the graduation of the final arbitrary M. V. scale on the y-axis.

(4) The M. V.'s of the isomeric alkanes are plotted on this arbitrary scale against the number of carbon atoms in the longest straight chain; thus 3-methylpentane, for instance, is plotted on the same vertical line as normal pentane. In order to locate its M. V. (128.9) on the ordinate scale, this figure is read off the "auxiliary M. V. scale" on the x-axis, a line is then drawn through this point first vertically to the "Interpolation curve," and horizontally from there to the y-axis, as shown by the dotted line.

In the case of the branched-chain alkanes, no attempt was made to choose a best value for the density beyond eliminating obviously unreliable data. In doubtful cases two or more values were retained.

The complete plot of these values is given in Fig. 1. The numbers identifying the compounds refer to the position of· the side chains. These are identified by subscripts, except in the case of methyl groups, when they are omitted. Thus, $23_{iPr}6$ on abscissa 7 represents 2,6-dimethyl-3-isopropylheptane.

B. **Analysis of Diagram.**—The original diagram reproduced in Fig. 1 is 70 × 70 cm. Reading the position of the points to 0.5 mm., this gives an accuracy of 0.0006 for the density near the C_3 end of the diagram and of 0.0003 at the other end (C_{12}).

There is a striking regularity in the diagram so obtained, the points tending to arrange themselves in a lattice of several groups of parallel lines. Some of these lines are shown on the diagram, and are labeled by a circled number identifying the type of substitution involved. Thus, 22 in a circle labels the line through all the 2,2-dimethyl homologs. The prime numbers refer to the count starting from the other end of the molecule, thus, 22′ in a circle means 2,4-dimethylpentane, 2,5-dimethylhexane, etc.

1. **Accuracy of Data.**—It will be noted that some of the points line up perfectly, while some others do not. In some cases, a comparison with the homologs suggests which of the values given in the literature is most likely to be correct. As an example, three values from the literature were retained for 3-methylheptane (see Table II). The second of these values could have been rejected immediately, because it is lower than that for n-octane, while it is known[2] that 3-methyl

(2) Graham Edgar and George Calingaert, THIS JOURNAL, 51, 1540 (1929).
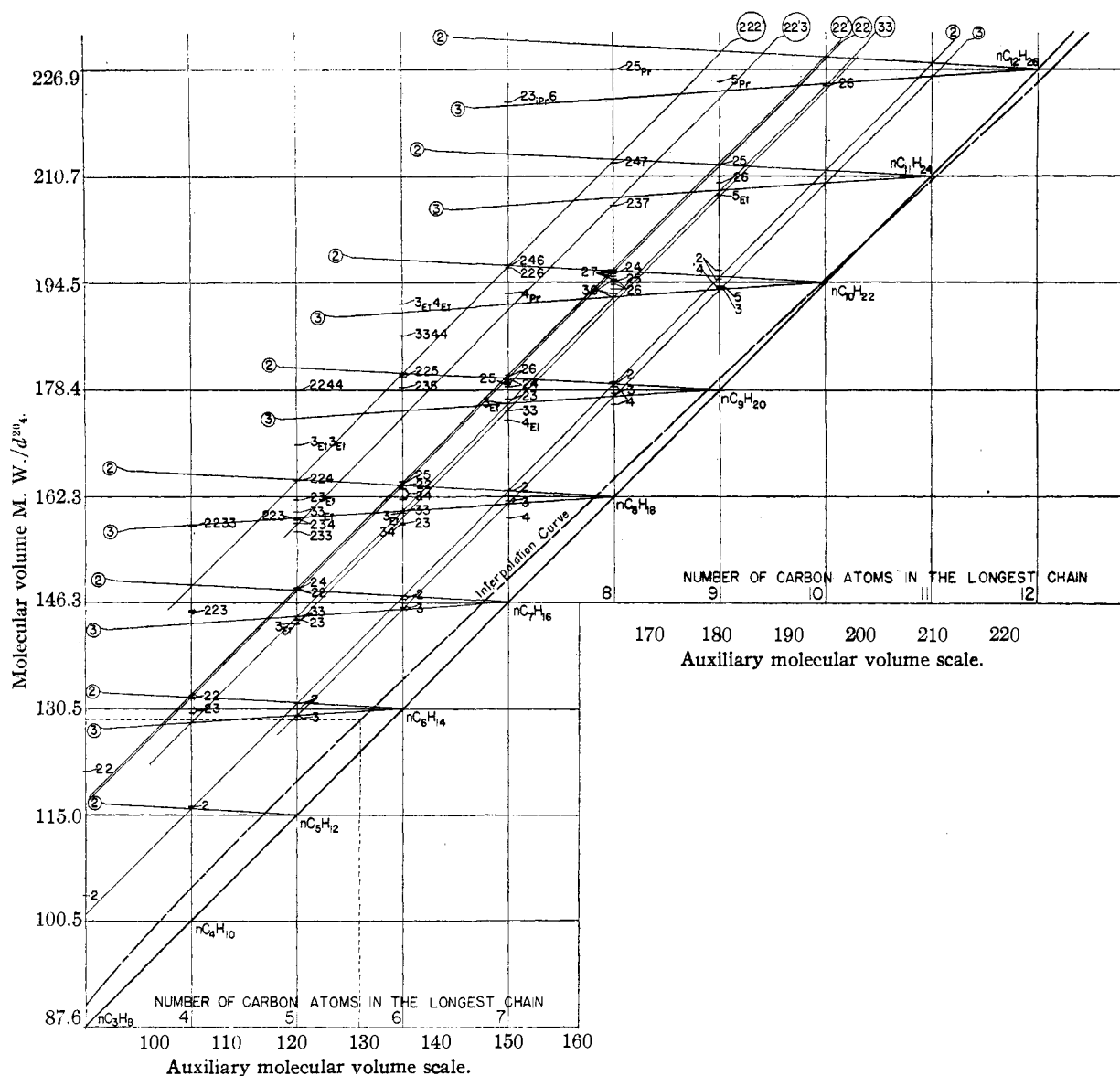
Fig. 1.—The molecular volume of the alkanes.

isomers invariably have a higher density than the corresponding normal alkanes. The other two, however, diverge from the value for n-octane in the right direction, but they differ by 0.0015. The plot indicates that the value of 0.7069 given by Levene and Taylor lines up best with the good values given by Van Risseghem[3] for 3-methyl-pentane and by Edgar and others[4] for 3-methyl-hexane, and this value is, therefore, to be preferred.

More discrepancies of this type will be revealed by a close examination of the plot. A few are

(3) H. Van Risseghem, *Bull. soc. chim. Belg.*, **30**, 8 (1921).
(4) Graham Edgar, George Calingaert and R. E. Marker, THIS JOURNAL, **51**, 1483 (1929).

listed in Table II, where the literature data are compared with the values suggested by the diagram.

One striking example is that of 2-methylnonane. "International Critical Tables" gives $d^{15.1}_4$ 0.728 which calculates to d^{20}_4 0.724.

The corresponding M. V. as shown on Fig. 1 (high value), fails to line up with the consistent data for 2-methylbutane to 2-methylheptane. The extrapolation of the data for these better known compounds suggested a value of 0.727 for the density of 2-methylnonane.

For several groups, too few isomers are known; predictions within these groups would be based

TABLE II

SUGGESTED VALUES FOR THE DENSITIES OF SOME ALKANES

	Original data As given	Corrected to d^{20}_4	d^{20}_4 from plot
2-Methylpentane			
d^0_4	0.6766^{5a}	0.6584	
d^{15}_4	$.6583^{5b}$	$.6541$	0.6547
d^{15}_4	$.6580^2$	$.6536$	
3-Methylpentane			
d^{15}_4	0.6681^{5c}	0.6672	
d^{15}_4	$.6687^3$	$.6643$	0.6643
2-Methylhexane			
d^{20}_4	0.6789^4	0.6789	
$d^{18.4}_{18.4}$	$.6833^{5d}$	$.6809$	0.6789
3-Methylhexane			
d^{20}_4	0.6865^{5e}	0.6865	
d^{20}_4	$.6870^4$	$.6870$	0.6882
d^{21}_4	$.687^{5f}$	$.688$	
3-Methylheptane			
d^{20}_4	0.7069^{5g}	0.7069	
d^{20}_{20}	$.7033^{5h}$	$.7021$	0.7069
d^{15}_4	$.7095^{5i}$	$.7054$	

on extrapolation only, with consequent doubt regarding their accuracy. As the amount and quality of the available data increases, the position of the family lines on the plot will be known with increasing certainty. Meanwhile, one of the great advantages of the method is to indicate on which points additional information is most urgently needed.

2. **The Effect of Structure.**—The plot illustrates the regular effect of structure on M. V., which has been mentioned by many authors, and which was discussed in the case of alkanes in a previous paper from this Laboratory.[2]

(a) Substitution in only the penultimate positions (2 and 4 in the pentanes, 2 and 5 in the hexanes, etc.), leads to a density lower than that of the normal isomer, except as stated in (e) below.

(b) Double penultimate substitution lowers the density still further, whether the substitutions are at each end or at the same end of the molecule.

(c) A straight line drawn through a normal alkane and its 2-methyl isomer also passes through the other isomers showing 2 or more methyl substituents in the penultimate positions. The corresponding lines for homologous groups, such as the

heptanes, octanes, etc., are parallel. For instance, the straight line through n-heptane, and 2-methylhexane passes through 2,2-dimethylhexane, and this line is parallel to a similar line passing through n-octane, 2-methylheptane, 2,2-dimethylhexane and 2,2,4-trimethylpentane.

(d) All other than exclusively penultimate substitutions raise the density, and the effect of further substitutions is substantially additive. This is illustrated by the position of the lines for the 3-methyl and 3,3-dimethyl isomers.

(e) Substitution on adjacent carbon atoms always raises the density, even though the positions occupied may be penultimate. Thus, 2,4-dimethylpentane has a lower density than n-heptane, but 2,3-dimethylbutane has a higher density than n-hexane. The additive effect of center or adjacent substitution is well illustrated by the fact that the line drawn through n-octane and 3-methylheptane, also passes through the value for liquid 2,2,3,3-tetramethylbutane (a solid), extrapolated from the densities of its solutions in n-octane.

(f) A marked deviation from the above rules is shown in the case of highly branched alkanes, such as dimethylpropane, tetramethylbutane, etc., which show usually values of M. V. lying above the line for the corresponding homologs. It may be that some form of steric hindrance causes this deviation.

(g) A close scrutiny of the diagram will reveal still other trends which will become more definite when the data become more reliable and when more isomers will have been prepared, particularly in the range C_9 to C_{12}.

Discussion

An important advantage of the method described here lies in the fact that only one property is used at a time, while many other methods of correlation necessitate using two or more physical constants, thus making it impossible to ascertain which property is responsible for any observed discrepancy. By using as abscissa the "longest chain" instead of the molecular weight, the effect of structure can be brought out more clearly, and the use of straight or nearly straight lines probably increases the accuracy with which points can be located.

The method illustrated above cannot be claimed to show as yet a perfect correlation between the physical properties of compounds and their struc-

(5) (a) Thorpe and Jones, *J. Chem. Soc. London*, **63**, 290 (1893); (b) Van Risseghem, *Bull. soc. chim. Belg.*, **31**, 83 (1922); (c) Zelinsky and Zelikov, *Ber.*, **34**, 2864 (1901); (d) Grimshaw, *Ann.*, **166**, 163 (1873); (e) Marckwald, *Ber.*, **37**, 1046 (1903); (f) Levene and Marker, *J. Biol. Chem.*, **91**, 77 (1931); (g) Levene and Taylor, *ibid.*, **54**, 351 (1923); (h) Tuot, *Compt. rend.*, **197**, 1434 (1933); (i) Van Risseghem, *Bull. soc. chim. Belg.*, **39**, 349 (1930).

ture. The good correlation which is obtained, however, in the case of those groups of compounds which are known with more certainty strongly suggests that equally good correlation may be expected for the other compounds when our knowledge of their properties is increased. On that basis the method appears to be decidedly worthy of consideration in the critical analysis of data reported in the literature.

It is fully appreciated that the correlation would perhaps be even more striking if the physical constants used were taken under more comparable conditions such, for instance, as vapor pressures at the same reduced temperatures or were given in more comparable units such as molecular volumes expressed as fractions of the respective critical volumes. This, however, could not be done because the necessary data are practically entirely lacking.

The method is not limited to the one group of compounds, nor to the property used here. A similar study has been made of the boiling points of alkanes and the plot obtained closely resembles that one given here for the molecular volumes.[6] A preliminary investigation has also

(6) Prints of Fig. 1 and of the corresponding plot of boiling points, 70 × 70 cm., will be furnished upon request, by the authors.

indicated that alkenes will plot in an orderly fashion on the diagram prepared from normal alkanes. Indeed, it would seem that the only requisite is to have available as a basis of comparison one series of compounds in any one class, such as normal alkanes, normal primary alcohols, etc., the data for which are known with a sufficient degree of accuracy. Of course, the accuracy obtainable on the branched chain isomers will always depend on the accuracy of the data on the homologous series which is used as a basis of comparison.

The authors wish to express to Prof. Frank C. Whitmore of Pennsylvania State College their appreciation for permission to include in the plot some unpublished data on several nonanes.

Summary

A graphical method is described for the critical comparison of data on any one of the physical properties of large groups of homologs and isomers. The illustration chosen covers the density (molecular volume) of the alkanes, and suggests the necessity of obtaining more and better data in the range C_9 to C_{12}.

The Decomposition of Di-ortho-tolyliodonium Iodide

BY H. J. LUCAS, E. R. KENNEDY AND C. A. WILMOT

Introduction

The belief that organic reactions may take place via the mechanism of a positive organic ion in which the carbon atom carries the positive charge is not new.[1] The important role which the positive ion plays in certain molecular rearrangements has been pointed out by others.[2] Recently, Whitmore[3] has interpreted molecular rearrangements on the basis of electron structures.

A reaction which may proceed via the mechanism of an intermediate, positively charged positive ion is the decomposition of di-*o*-tolyliodonium iodide. From the nature of the reaction product

(1) Euler, *Ber.*, **39**, 2726 (1906); Biilmann, *Ann.*, **388**, 330 (1912); Holmberg, *Ber.*, **59**, 1569 (1926).

(2) McKenzie, Rogers and Mills, *J. Chem. Soc.*, 778 (1926); Meerwein and Wortmann, *Ann.*, **435**, 190 (1924); Meerwein and Montfort, *ibid.*, **435**, 214 (1924); Meerwein, *ibid.*, **453**, 16 (1927).

(3) Whitmore, THIS JOURNAL, **54**, 3274 (1932).

one may draw conclusions in regard to the mechanism.

There are two possible mechanisms by which this decomposition might take place: (a) migration of the iodide iodine to one of the benzene rings in a position ortho or para to the C–I bond, followed by the scission of a C–I bond; (b) the scission of a C–I bond, followed by the attachment of the resulting positive organic ion to the negative iodide ion. These two mechanisms are pictured below.

On the assumption that the two iodine atoms are held together by a covalent bond (I), the migration of iodine to an ortho or para position on the benzene ring is quite plausible since atoms or radicals attached to other electronegative atoms (oxygen and nitrogen especially) readily migrate. If migration is the first step, then scission of a