7. Chandrasekaran, R., Lakshminarayanan, A. V., Pandya, U. V. and Ramachandran, G. N., *Biochim. Biophys. Acta*, 1973, 303, 14.
8. Wuthrich, K., In *NMR in Biological Research : Peptides and Proteins*, North Holland Publishing Company, Amsterdam.
9. Hruby, V. J., In *Chemistry and Biochemistry of Amino Acids, Peptides and Proteins* (B. Weinstein Ed.), 1974, 3, pp. 188 and related references therein.
10. Deslauriers, R. and Smith, I. C. P., In *Topics in Carbon-13 NMR Spectroscopy* (G. C. Levy Ed.), 1976, 2, 1. John Wiley and Sons, Inc.
11. Doddrell, D. M., *Pure and Appl. Chem.*, 1977, 94, 1385.
12. Horsley, W., Sternlicht, H. and Cohen, J. S., *Biochem. Biophys. Res. Commun.*, 1969, 37, 47.
13. Dorman, D. E. and Bovey, F. A., *J. Org. Chem.*, 1973, 38, 1719.
14. Torchia, D. A. and Lyerala, J. R. (Jr.), *Biopolymers*, 1974, 13, 97.
15. Deber, C. M., Madison, V. and Blout, E. R., *Acc. Chem. Res.*, 1976, 9, 106.
16. Wuthrich, K. and Grathwohl, Ch., *FEBS Letters*, 1974, 43, 337.
17. Dorman, D. E. and Bovey, F. A., *J. Org. Chem.*, 1973, 38, 2379.
18. Ramaprasad, S. and Chandrasekaran, R. (to be published).
19. Bystrov, V. F., Ivanov, V. T., Portnova, S. L., Balashova, T. A. and Ovchinnikov, Yu, A., *Tetrahedron*, 1973, 29, 873.
20. Ramachandran, G. N., Chandrasekaran, R. and Kopple, K. D., *Biopolymers*, 1971, 10, 2113.
21. "IUPAC–IUB Commission on Biochemical Nomenclature," *Biochemistry*, 1970, 9, 3471.

TOPOLOGY AND PHYSICAL PROPERTIES OF *n*-ALKANES

R. S. LALL
Chemistry Department, St. Andrew's College, Gorakhpur 273001, India

ABSTRACT

A relationship between the mean value of the Wiener Number and the physical properties of *n*-alkanes is presented. The root mean square value of the Wiener Number is defined. A good correlation between the topological index and physical properties has been obtained.

INTRODUCTION

MOLECULAR topology is a topic of current interest. This discipline of modern mathematics finds its various applications in chemistry. The term topology[1], in chemical literature, is generally used to represent the molecular graph[2], though both the terms are not synonymous. The molecular graph is a set of edges and vertices. The vertices are usually sp^2–C atoms and edges are C–C bonds, the bond lengths of which are topologically invariant. The molecular graph is therefore a topology with defined metric[3].

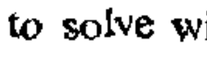
Considering the π-networks of conjugated hydrocarbons[4,5] and their C-skeleton molecular graphs, topological studies have been made both on simple[6] and heterocyclic systems[7,8]. The problems of aromaticity and resonance energies[9] based on the Hückel Molecular Orbital Theory, are now easy to solve with the help of topology.

Topological indices[10] have been introduced by various workers (e.g., Rouvray's index[11], Randic connectivity index[12], Platt index[13], and Hosoya index[14]). The Wiener number[15] is an important topological index, which is applied by Trinajstić and Bonchev[10,16] and Sondheimer[17] to monocyclic structures and the changes in the values are related to the structural features and the physical and chemical properties[17].

In this paper, it is shown that the topology can be equally applied to σ-bonded systems of sp^3–C skeleton graph, and that the mean value of the Wiener Number is directly related to the physical properties of *n*-alkanes.

THEORY

The molecular graph (*G*) is defined in terms of edges, the C–C bonds and vertices, the *C* atoms. A labelled graph of *n*-butane may be represented by



The topological distances[18] are defined as the elements of a real $N \times N$ matrix $D(G)$, which is known as the

distance matrix,[15,16] where N is the number of vertices in graph G. The elements of the distance matrix, $D_{i,j}(G)$, are integers, for i,j neighbours, the element

$$D_{ij}(G) = \left\{\begin{matrix} 1 \text{ for } i \neq j \\ 0 \text{ for } i = j \end{matrix}\right\}. \quad (1)$$

The distance matrix is symmetric in relation to the principal diagonal; the complete matrix can be divided into two triangular off-diagonal sub-matrices. The Wiener number is defined as half the sum of the off-diagonal elements of the distance matrix[16]

$$W(G) = \tfrac{1}{2} \sum_{i,j} D_{i,j}(G). \quad (2)$$

This is equal to the sum of the elements of the triangular off-diagonal sub-matrix. For example, *n*-butane $W(G) = 10$. The total number of elements in a triangular off-diagonal sub-matrix is equal to $\frac{1}{2} N(N-1)$. The mean value of the Wiener number $\bar{W}$ is defined as,

$$\bar{W}(G) = \frac{2W}{N(N-1)}. \quad (3)$$

The root mean square value of the Wiener number is defined as the square root of the mean of the square of the elements D_{ij} of the off-diagonal sub-matrix,

$$W_{rms} = \left\{\frac{1}{N(N-1)} \sum_{i,j} D_{ij}^2\right\}^{\frac{1}{2}}. \quad (4)$$

For *n*-alkanes' graphs, it can be shown that the Wiener number W[23], its mean value $\bar{W}$, and the r.m.s. values W_{rms} are given by the following equations,

$$W = 1/6\,(N^3 - N), \quad (5)$$

$$\bar{W} = 1/3\,(N+1), \quad (6)$$

and

$$W_{rms} = \left\{\frac{2}{N(N-1)} \sum_{j=1}^{N-1} (N-j)\,j^2\right\}^{\frac{1}{2}} \quad (7)$$

Comparing the values of $\bar{W}$ for *n*-alkanes and their physical properties, the following empirical equations were obtained for the heats of formation ΔH_f, density ρ and the boiling points B.P.,

$$\Delta H_f = -5{\cdot}0 - 15{\cdot}0\,\bar{W} \text{ k.cal.mole}^{-1} \quad (8)$$

$$\rho = 0{\cdot}48 + 0{\cdot}075\,\bar{W} \text{ gm.ml}^{-1} \quad (9)$$

$$\text{B.P.} = -150 + 93{\cdot}0\,\bar{W} \text{ °C}. \quad (10)$$

The values of the heats of formation are taken for gaseous states, while the density and boiling points for liquid states.

The *ionization potentials* (I.P.)[18] of *n*-alkanes were correlated with the corresponding $\bar{W}$ values and the following approximate relationship was found, to hold good:

$$\text{I.P.} = 13{\cdot}0 - 1{\cdot}5\,\bar{W} + 0{\cdot}0725\,\bar{W}^2 \text{ eV} \quad (11)$$

TABLE I

The values of the Wiener number $\bar{W}$, *mean* W, *and r.m.s. values.* W_{rms}

n-Alkanes	W	$\bar{W}$	W_{rms}
Ethane	1	1·00	..
Propane	4	1·33	1·414
Butane	10	1·66	1·826
Pentane	20	2·00	2·236
Hexane	35	2·33	2·645
Heptane	56	2·66	3·055
Octane	84	3·00	3·464
Nonane	120	3·33	3·872
Decane	165	3·66	4·282

TABLE II

Calculated and obsreved Heats of formation ΔH_f, *densities* ρ, *and boiling points B.P. of n-alkanes*

Compd.	ΔH_f K. cal mole^{-1}		ρ gm ml^{-1}		B.P. °C	
	Calcd.	Obsd. (*a*)	Calcd.	Obsd. (*b*)	Calcd.	Obsd. (*b*)
Ethane	−20·0	−20·20	..	..	..	..
Propane	−25·0	−24·80	0·580	0·507	26·0	−42·0
Butane	−30·0	−30·40	0·605	0·600	5·0	0·5
Pentane	−35·0	−35·10	0·630	0·626	36·0	36·1
Hexane	−40·0	..	0·655	0·659	67·0	68·7
Heptane	−45·0	..	0·680	0·684	98·0	98·4
Octane	−50·0	−49·82	0·705	0·708	129·0	125·7
Nonane	−55·0	−54·70	0·720	0·718	160·0	151·0

(*a*) Refs. 20 and 21, (*b*) Ref. 10 and Ref. 22.

TABLE III

Ionization Potentials I.P. of n-alkanes

Compound	Calcd. eV	Obsd. (Ref. 18, p. 198)
Ethane	11·573	11·630
Propane	11·084	11·080
Butane	10·710	10·630
Pentane	10·300	10·330
Hexane	9·910	10·170
Heptane	9·860	10·060

Results and Discussion

The mean and r.m.s. values of the Wiener number for *n*-alkanes upto $N = 10$, are reported in Table I. The values of ΔH_f, ρ and B.P.s calculated on the basis of equations 8, 9 and 10 are reported in Table II along with the experimental values. The I.Ps. calculated and observed are given in Table III. The calculated values are in good agreement with the observed values.

The physical properties of *n*-alkanes depend directly upon the size of the molecules and their relationship with the number of C atoms has already been discussed[19]. The molecular topology depends also on the number of vertices, i.e., C atoms. Therefore a relationship between the molecular topology and the physical properties can be thought. This presents a mapping of topology onto the physical properties. The structural or physical properties are reflected by the topological indices. The approach can further be extended to other σ-bonded systems.

Acknowledgement

The author is thankful to Prof. N. Trinajstic (Zegreb, Yugoslavia) for his recent papers in the preparation of this paper.

1. Blackett, D. W., *Elementary Topology : A Combinatorial and Algebraic Approach*, Academic Press, New York, 1967.
2. Harary, F., *Graph Theory*, Addison–Wesley, Reading, Mass, 1969.
3. Simmons, G. F., *Topology and Modern Analysis*, McGraw-Hill Book Co., New York, 1963.
4. Mallion, R. B., Schwenk, A. J. and Trinajstić, N., *Croat. Chem. Acta*, 1974, **43**, 171.
5. Graovac, A., Polanky, O. E., Trinajstic, N., and Tyutyulkov, N., *Z. Naturforsch*, 1975, **30a**, 1696.
6. Aihara, J., *J. Am. Chem. Soc.*, 1976, **98**, 2750.
7. —, *Ibid.*, 1976, **98**, 6840.
8. Graovac, A. and Trinajstic, N., *Croat. Chem. Acta*, 1975, **47**, 95.
9. Aihara, J., *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2010.
10. Bonchev, D., Mekenyan, Ov., Knop, J. V. and Trinajstić, N., *Croat. Chem. Acta*, 1979, **52**, 361.
11. Rouvray, D. H., *Math. Chem. (MATCH)*, 1975, **1**, 125.
12. Randic, M., *J. Am. Chem. Soc.*, 1975, **97**, 6609.
13. Platt, J. R., *J. Chem. Phys.*, 1947, **15**, 419.
14. Hosoya, H., *Bull. Chem. Soc. Jpn.*, 1971, **44**, 2332.
15. Wiener, H., *J. Am. Chem. Soc.*, 1947, **69**, 2636.
16. Bonchev, D., Mekenyan, Ov. and Trinajstić, N., *Int. J. Quant. Chem.*, 1980, **17**, 845.
17. Sondheimeri F., *Pure Appl. Chem.*, 1969, **7**, 303.
18. Streitwieser, A., Jr., *Molecular Orbital Theory for Organic Chemist*, John Wiley and Sons, New York, 1961, p. 188.
19. Brewsteri, R. Q. and McEwen, W. E., *Organic Chemistry*, Prentice Hall of India, New Delhi, 1969, p. 390.
20. Dewar, M. J. S. and Thiel, W., *J. Am. Chem. Soc.*, 1977, **99**, 4907, Table II.
21. Dean, J. A., ed., *Lange's Hand-Book of Chemistry*, McGraw-Hill Book Co., New York, 1973, Table 9–2.
22. Muller, W. E. and Babov, J. A., *General Chemistry*, Scientific Book Co., Calcutta, 1965, p. 421.
23. Bonchev, D. and Trinajstić, N., *J. Chem. Phys.*, 1977, **67**, 4517.