The Hosoya Index, Lucas Numbers, and QSPR

K. J. Dawson and T. M. Westerberg
Advisor: Dr. K.W. McLaughlin
University of Wisconsin-River Falls, River Falls, WI 54022

Introduction

The Hosoya index, Z, is known to correlate well with the normal boiling points of the small acyclic alkanes (see Figure 1).

As part of a study to extend quantitative structure-property relationships (QSPR) with this topological index to larger hydrocarbons which are allowed to have cyclic structures, we have identified three families of molecular graphs which possess identical values for Z.

An analysis of these results places limits on the application of this topological index for QSPR; limits which may apply to other topological indices and which have a significant bearing on the use of topological indices in QSPR for macromolecules.

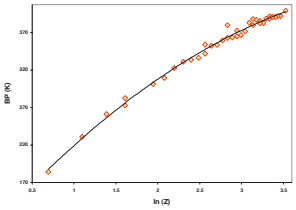
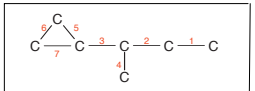


Figure 1. Normal boiling points plotted versus the natural logarithm of the Hosoya index (Z) for all 40 acyclic alkanes from C_2H_6 to C_8H_{18}.

The Hosoya Index

This topological index is defined as the number of ways to select non-adjacent bonds in a molecule.

Table 1 illustrates how to determine Z from its definition by direct enumeration for the hydrogen-depleted graph of 2-methyl cyclopropane.



Number of Edges Selected (t)	Number of Sets of t Non-adjacent Edges
0	1
1	7
2	12
3	4
≥ 4	0
Total	24 = Z

Table 1. Determination of the Hosoya index by direct enumeration for the hydrogen-depleted graph of 2-cyclopropyl butane

Hosoya Composition Theorem

Direct enumeration becomes overwhelming even for the fastest computers as molecules increase in size.

Therefore, it is convenient to calculate Z using a short-cut that produces a recurrence relation, as illustrated in Figure 2.

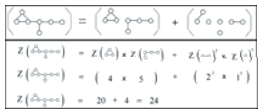


Figure 2. Application of the Hosoya Composition Theorem to 2-cyclopropyl butane.

Goal

Identify families of molecular structures which possess the same values for the Hosoya index, different numbers of cycles.

Then, using normal boiling point, analyze the relationship between the Hosoya index and this physical property for the various families possessing different numbers of cycles.

Ideally, if molecules have the same value of Z, they would have nearly identical boiling points. If the boiling point-Hosoya Index correlation is not nearly identical, identify the effect of cyclic structures on the QSPR relationship.

The 2-Methyl Alkanes

The values of the Hosoya index for the smallest members of this family of hydrocarbons are shown in Table 2.

Note that Z generates a sequence of integers which are the sum of the preceding two members in the series

$$Zn = Zn\text{-}1 + Zn\text{-}2$$

This integer sequence corresponds to something called Lucas numbers, which are also the sum of pairs of every other Fibonacci **number.**

Number of Carbon Atoms	Name	H-depleted Molecular Graph	Z
3	propane		3
4	2-methyl propane		4
5	2-methyl butane		7
6	2-methyl pentane		11
n	----		F_n+F_{n-2}

Table 2. The Hosoya index for the first four 2-methyl alkanes and the general case composed of n carbon atoms are shown. The vertices, representing carbon atoms, are designated by the letter C.

Cycloalkanes

The values of the Hosoya index for the smallest members of this family of molecules are shown in Table 3.
The cycloalkanes generate the same integer sequence as the 2-methyl alkanes, though the sequence is shifted up one member of the series relative to the number of carbons in the molecule.

n	Name	Structure of Molecule	Z
3	Cyclopropane		4
4	Cyclobutane		7
5	Cyclopentane		11
6	Cyclohexane		18
n	----		$F_{n+1}+F_{n-1}$

Table 3. The Hosoya index for the first four cyclic alkanes and the general case composed of n carbon atoms.

1-Methyl Bicyclo [X.1.0] Alkanes

As shown in Table 4, this family of molecules also generates values of the Hosoya index which are Lucas numbers.

Notice that the smallest member of this series has five carbon atoms and starts at a higher value in the Lucas number sequence than the previous examples.

This now gives us three families of molecules all producing the same sequence of values for the Hosoya index.

All three families of molecules are composed of molecules that exist and have physical properties in the NIST and Beilstein data bases.

1-Methyl Bicyclo[X.1.0] Alkanes

n	Name	Structure of Molecule	Z_n
5	1-methyl-[3.1.0] bicyclobutane		11
6	1-methyl-[4.1.0] bicyclopentane		18
7	1-methyl-[5.1.0] bicyclohexane		29
8	1-methyl-[6.1.0] bicycloheptane		47
n	---		$F_{n+1}+F_{n-1}$

Table 4. The Hosoya index for the first four 1-methyl bicyclo[X.1.0] alkanes and the general case composed of n carbon atoms.

Boiling Point Analysis

Since we have sets of three distinct molecular structures all having the same value of Z, it is possible to check if their normal boiling points re also nearly identical.

Table 5 shows the normal boiling points for the acyclic, monocyclic and bicyclic molecules possessing Lucas numbers for their Hosoya index.

As can be seen in this table, the boiling points can differ by as much as 50°C.

This implies that the use of the Hosoya index breaks down when comparing hydrocarbons with different numbers of cycles.

Boiling Points (K)						
Z	2-methyl alkane		cycloalkane		1-methyl bicyclo [x.1.0] alkane	
3	C_3H_8	231.1	---	---	---	---
4	C_4H_{10}	262	C_4H_8	240	---	---
7	C_5H_{12}	301.1	C_5H_{10}	284	---	---
11	C_6H_{14}	334	C_6H_{12}	322.4	C_6H_8	281.6
18	C_7H_{16}	363.2	C_7H_{14}	353.9	C_7H_{10}	353
29	C_8H_{18}	392	C_8H_{16}	392.0	C_8H_{12}	409
47	C_9H_{20}	416.1	C_9H_{18}	422	C_9H_{14}	463
76	$C_{10}H_{22}$	440.1	C_9H_{18}	448	---	---
123	$C_{11}H_{24}$	462.3	$C_{10}H_{20}$	474.4	---	---
199	$C_{12}H_{26}$	483.2	---	---	---	---

Table 5. The normal boiling points for the three families of alkanes discussed in this paper. The boiling points for the 2-methyl alkanes and the cycloalkanes were taken from the NIST database, while the boiling points for the bicycloalkanes were taken from Beilstein database.

As shown in Figure 4, within each family of molecules, a very well defined trend in exists between the boiling point and the Hosoya index.

However, between the families the boiling point increases much more sharply as a function of the number of cycles present.

Whether this is a general rule or not is unknown, but it represents an effect on this physical property that will have to be taken into account before a QSPR model can be developed involving the Hosoya index.

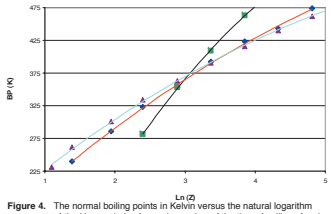


Figure 4. The normal boiling points in Kelvin versus the natural logarithm of the Hosoya index for each member of the three families of molecular graphs: purple triangles = acyclic alkanes, blue diamonds = monocyclic alkanes, and green squares = bicyclic alkanes.

Conclusions

The correlation between the normal boiling point and the Hosoya index clearly breaks when molecules with different numbers of cycles are permitted.

Though the data set is small, it does suggest as a working hypothesis that the boiling point increases faster as a function of Z for molecules with more cycles.

Therefore, when constructing QSPR models using the Hosoya index, it is important to confine the model to families of structures possessing the same number of cycles; at least until the correction for the effect of cyclic structures has been determined.