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Original article

Graph spectral analysis of nonane isomers

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ABSTRACT A group of substances known as alkanes is made up of carbon and hydrogen atoms bound together only by single covalent bond with the chemical formula C_nH_{2n+2}. Isomers are those molecules with identical chemical formula but different structural arrangement. Due to this, their corresponding molecular graphs differ in structure thereby leading to distinct spectral parameters. In this work, the spectral parameters of all isomers of nonane C_9H_{20} have been computed and its relationship with its eigenvalue-based entropy is established. The spectral results are then correlated with the density value of the nonane isomers and it is found that the "spectral gap" is closely associated to that of density.

KEYWORDS Alkane isomers, graph energy, spectrum, spectral gap, eigenvalue-based entropy

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1. Introduction

Organic chemistry deals with structures, compositions, properties, reactions, and preparation of carbon-containing compounds. The simplest organic compounds are hydrocarbons [1], which just have carbon and hydrogen atoms and can be either straight or branched chains with the same empirical formula but different characteristics. Alkanes are such kind of hydrocarbon. Alkanes are with identical empirical formula C_nH_{2n+2} and distinct arrangements of atoms joined only by single bonds. Alkanes with four or more carbon atoms can have more than one arrangement of atoms, thereby forming isomers. A linear alkane with the formula C_9H_{20} is nonane. It is a colourless, flammable liquid that is mostly extracted from crude oil and it is used in automobile fuels. The isomers of nonane have carbon chain branches at different locations in the chain leading to the compound having different IUPAC names. Altogether, nonane has 35 isomers, including the straight-chain compound n-nonane.

In chemical graph theory [2], the structural arrangement of molecules are depicted as chemical graphs. The organic chemical compounds are represented by their graph structure where the carbon atoms are represented by vertices and the relation between carbon atoms are represented by edges. This representation is widely used in cheminformatics. Predictions of structure-property relationships and (quantitative) structure activity are based on computed graph parameters. The physical characteristics of molecules can then be reflected in these graphs as graph-theoretical descriptors or indices. Spectrum of the graph is one such kind of descriptors. In quantum chemistry, the highest energy level of molecule is represented by the spectral radius of graph. Hence, it is advantageous to estimate the energy of molecules if the spectral radius has adequate upper bounds. The second-largest eigenvalue of the graph is closely related to the molecule stability and associated chemical characteristics. The spectral gap is the result obtained by subtracting the second-largest eigenvalue from that of the largest eigenvalue and is often used as a measure of the convergence rate in numerical methods in computational chemistry. A large spectral gap is associated with fast convergence, while a smaller spectral gap indicates slower convergence. Entropy is a measureable physical characteristics and a scientific notion that is frequently connected to a condition of disorder, unpredictability or uncertainty. The fundamental thermophysical quantities known as graph entropies [3] are used to quantify the heterogeneity and relative stabilities of molecules. They are defined for various graph invariants. Eigenvalue-based entropy is a kind of graph entropy that has been extensively studied which depends on the adjacency matrix of the graph. An indicator of a connection or statistical association between two variables is a correlation coefficient [4]. Note that the graphs considered in this paper are combinatorial graphs in which edges are relations between vertices only. In literature, there are also metric graphs in which certain differential operator is defined on the edges [5]. In this metric-model, the spectrum is not bounded above and the spectral gap is also defined differently as the difference between the last (smallest) and second smallest eigenvalues [6]. In the present work, the spectral parameters of all isomers of nonane have been computed and its relationship with the corresponding eigenvalue-based entropy is established. Then the spectral parameters are correlated with the density of nonane isomers in order to find which parameter has the best correlation with the density of nonane isomers.

2. Preliminaries

A graph denoted as $G = (V, E, \psi_G)$ consists of a collection of two sets: a set (necessarily nonempty) of vertices V, a set of edges E, and a relation $\psi_G : E \to V \times V$ termed as incidence relation. Adjacency matrix is a binary matrix which reflects whether two vertices v_i, v_j in the graph are adjacent or not. If they are adjacent then its entry in the matrix will be 1 and all the non-adjacent pairs are made 0. A characteristic polynomial can be derived from the matrix by using $P(A;\lambda) = det(A - \lambda I_n)$ where I_n is the identity matrix. Note that $n = |V|$. By solving the characteristic equation, eigenvalues of the matrix are obtained. The highest among all the eigenvalues is known as spectral radius. The sum of absolute eigenvalues is termed as graph energy [7]. The arrangement of distinct eigenvalues along with their algebraic multiplicities is called as spectrum. When arranged in a non-increasing order, the difference between the first two eigenvalues is known as the spectral gap.

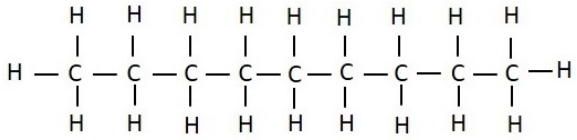
Two nonisomorphic graphs having same spectrum are called cospectral graphs and two non-cospectral graphs having same energy are called equienergetic graphs. If $\lambda_1, \lambda_2, .., \lambda_n$ denote the eigenvalues of $A(G)$ and $E(G)$ denote the energy of G, then the eigenvalue-based entropy [8] $\mathbf{I}$ of G is defined as $I(A) = -\sum_{j=1}^{n} \frac{|\lambda_j|}{E(G)} log \frac{|\lambda_j|}{E(G)}$. Spearman's rank correlation coefficient, also known as the Spearman coefficient correlation [9], is a statistical measure used to assess the strength and direction of the monotonic relationship between two variables. This coefficient is especially valuable when the relationship between the variables does not strictly adhere to a linear pattern, but rather exhibits a monotonic trend. The coefficient itself ranges between -1 and 1. A value of -1 indicates a perfect negative monotonic relationship. Conversely, a value of 1 represents a perfect positive monotonic relationship whereas, 0 suggests no monotonic relationship between the variables. The p-value indicates the likelihood of obtaining a result extreme (on both ends) than the observed result, assuming there is no relationship between variables. Covariance quantifies the extent to which variables vary together. The test statistic is a numerical summary used in hypothesis testing to compare the observed data to a distribution or critical values. It helps one to determine the statistical significance of the result and whether to reject the null hypothesis. Sample size is the number of observations in a sample which affects the reliability of estimates.

3. Literature Survey

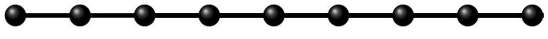
A. E. Brouwer and W. H. Haemers [10] cover a variety of topics in spectral graph theory and highlight the critical role that linear algebra plays in graph theory in their book Spectra of Graphs. R. Balakirshnan and K. Ranganathan [7] explain clearly the requisite for this study of chemical-graph and spectral basis. D. A. Spielman [11] gave an overview of certain spectrum applications and shed some light on the combinatorial relevance of the eigenvectors and eigenvalues. Ivan Gutman et al. [12] have put forth an innovative method for calculating the total pi-electron energy of a conjugated hydrocarbon using spectral moments along with coining certain outstanding problems. F. Harary and A. J. Schwenk [13] have developed a methodical approach for identifying graphs with integral spectra. O. Ahmadi et al. [14] have shown that only a small percentage of graphs contain an integral spectrum. G. Indulal et al. [15] have constucted numerous classes of integral graphs and by defining a new composition on three graphs. M. Dehmer and A. Mowshowitz [16] have done a survey on describing methods to measure graph entropy and to demonstrate its wide applicability. M. Dehmer [17] has introduced a general framework for defining the graph entropy based on a local-information graph and information-related functions derived from a graph's topology. Y. Sun and H. Zhao [8] have defined the eigenvalue-based entropy for the directed bipartite network.

4. Nonane and its Isomers

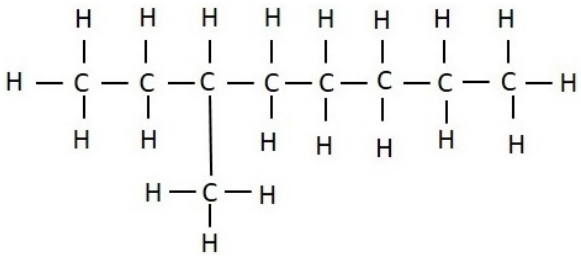
The nonane isomers having empirical formula C_9H_{20} are the subject of this study (refer Fig. 1). Nonane comes in 35 different isomers. Nonane naturally occurs in crude oil. One of the by-products of the fractional distillation of crude oil is kerosene fraction. Despite being insoluble in water, it is a good solvent for a variety of chemicals. Nonane is primarily used as an aviation and automotive fuel.



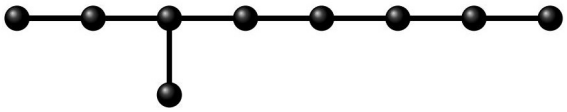
(a) n-Nonane (N_1)



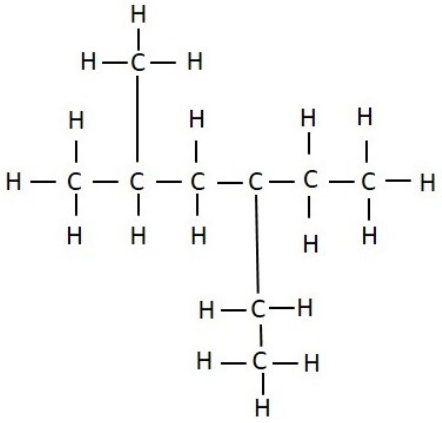
(b) molecular graph of n-Nonane (N_1)



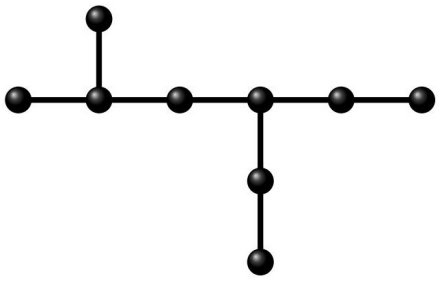
(c) 3-methyloctane (N_3)



(d) molecular graph of 3-methyloctane (N_3)



(e) 4-ethyl-2-methylhexane (N_{25})



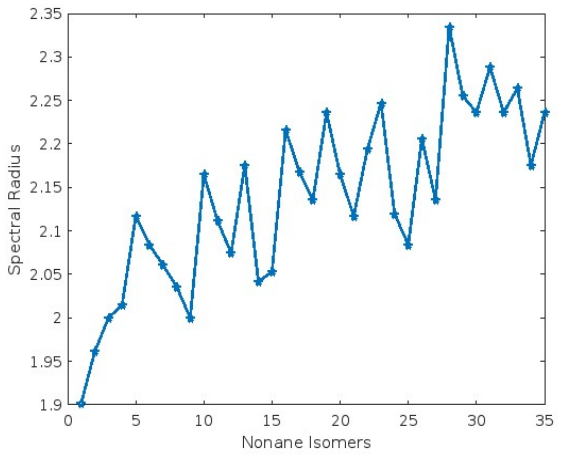
(f) molecular graph of 4-ethyl-2-methylhexane (N_{25})

FIG. 1. Some isomers of C_9H_{20} and their molecular graphs

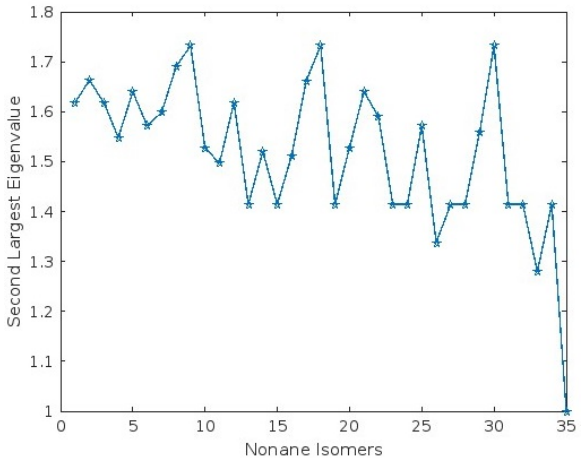
5. Main Results

From the IUPAC nomenclature, it is clear that the branching number and position vary among all the isomers of C_9H_{20}. Thus, it is observed that each molecular graph is nonisomorphic to one another. By using MATLAB, the spectrum, spectral radius, spectral gap, second largest eigenvalue, graph energy and eigenvalue-based graph entropy of all the isomers have been calculated.

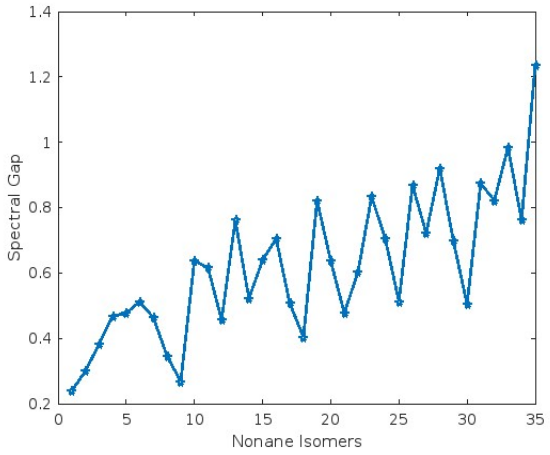
From the parameters given in Table 2, the following graphs (Fig 2) have been plotted to have a comparative view among the results obtained.



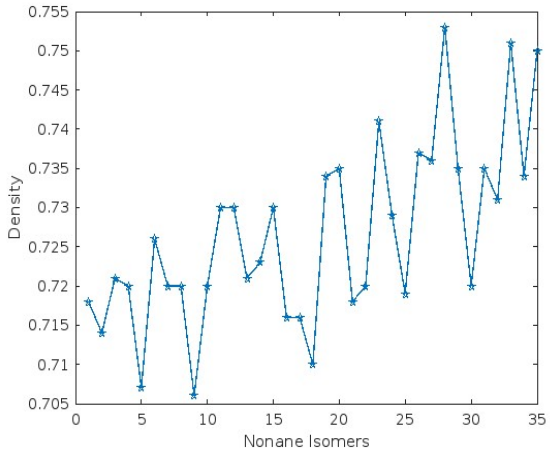
(a) Spectral Radius



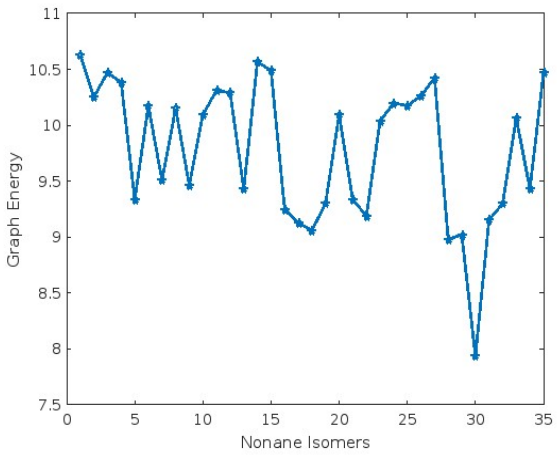
(b) Second Largest eigenvalue



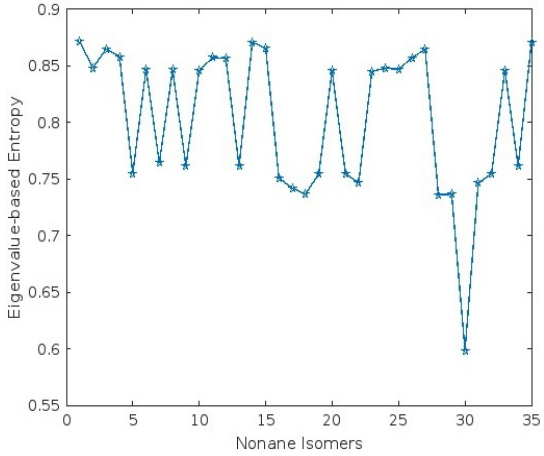
(c) Spectral Gap



(d) Density



(e) Graph Energy



(f) Eigenvalue-based Entropy

FIG. 2. 2D graph of spectral parameters

6. Observations

1. Isomers that have their third positioned carbon atoms in their spine to be branched are found to have an increase in their density values compared to their predecessors.
2. Except for N_5, it can be observed from Fig 2 that the second-largest eigenvalue is inversely proportional to the spectral radius.
3. Except for N_6, it can be noticed that the spectral gap is directly proportional to the spectral radius.
4. Fig. 2 (e and f) proves that the graph energy is directly proportional to the eigenvalue-based entropy.
5. The pairs of non-isomorphic graphs $(N_5, N_{21}), (N_6, N_{25}), (N_{10}, N_{20}), (N_{13}, N_{34})$ and (N_{19}, N_{32}) are having the same spectrum and thus, they are cospectral graphs.
6. The pairs of graphs $(N_3, N_9), (N_5, N_{21}), (N_6, N_{25}), (N_{10}, N_{20}), (N_{13}, N_{34}), (N_{18}, N_{27})$ and $(N_{19}, N_{30}, N_{32}, N_{35})$ have the same spectral radius.
7. The spectral radius increases based on the number of branches and their positions along the spine. Closer proximity between the branches leads to a higher spectral radius, indicating greater connectivity within the structure. This is due to the fact that branching affects the number of bonds and distance between atoms, which can result in different graph representations with distinct adjacency matrices.
8. The sets of graphs (N_5, N_{21}), (N_6, N_{25}), (N_{10}, N_{20}), (N_1, N_3, N_{12}), (N_9, N_{18}, N_{30}), $(N_{13}, N_{15}, N_{19}, N_{23}, N_{24}, N_{27}, N_{28}, N_{31}, N_{32}, N_{34})$ have the same second highest eigenvalues.
9. The pairs of non-isomorphic graphs $(N_5, N_{21}), (N_6, N_{25}), (N_{10}, N_{20}), (N_{13}, N_{34})$ and (N_{19}, N_{32}) are having the same spectral gap.

10. The pair of graphs (N_3, N_{35}), (N_5, N_{21}), (N_6, N_{25}), (N_{13}, N_{34}), (N_{18}, N_{29}) and (N_{19}, N_{32}) have the same energy, thus, they are equienergetic graphs.
11. The pair of graphs (N_5, N_{21}), (N_6, N_{25}), (N_{10}, N_{20}), (N_{13}, N_{34}), (N_{18}, N_{29}) and (N_{19}, N_{32}) have the same eigenvalue-based entropy.
12. The pair of graphs (N_{18}, N_{29}) have the same entropy though they are not equienergetic whereas the graphs (N_3, N_{35}) have different entropies though they have the same graph energy.
13. The isomer pairs (N_1, N_{21}), (N_3, N_{13}), (N_7, N_8, N_{10},N_{22}, N_{30}), (N_{11}, N_{12}, N_{15}), (N_{16}, N_{17}), (N_{19}, N_{34}), (N_{20}, N_{29}, N_{31}) have the same density.

TABLE 1. Extremal graphs of nonane

Parameters	**Density**	**Spectral Radius**	**Second Largest Eigenvalue**	**Spectral gap**	**Graph energy**	**Eigenvalue-based entropy**
Highest valued isomer	N_{28}	N_{28}	(N_9, N_{18}, N_{30})	N_{35}	N_1	N_1
Least valued isomer	N_9	N_1	N_{35}	N_1	N_{30}	N_{30}

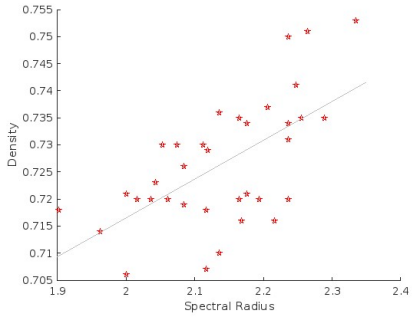
7. Correlation Coefficient of nonane density

The correlation coefficient between the density and the spectral parameters of 35 nonane isomers has been calculated and presented in the following table 2. In this analysis, the density values of all 35 nonane isomers are fixed as variables of Y, and they are correlated with spectral parameters as variables of X. The correlation coefficients provide insights into the strength and direction of the linear relationships between the density and the spectral parameters. Additionally, a graphical representation of the correlations is provided. This analysis utilizes the entire sample size of 35 nonane isomers to explore the relationships between the density and the spectral parameters.

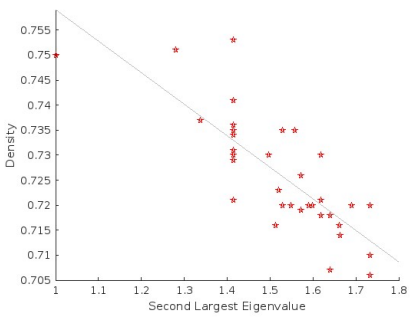
TABLE 2. Correlation coefficient between the density and the spectral parameters of nonane

Correlation	**Spectral Radius**	**Second Largest Eigenvalue**	**Spectral gap**	**Graph energy**	**Eigenvalue-based entropy**
Correlation Coefficient	0.59499	-0.81322	0.80398	0.11307	0.12701
P value	6.96e-5	5.613e-9	4.3332e-10	0.3794	0.2161
Covariance	7.296e-4	-1.4e-3	2.13e-3	1.123e-3	1.598e-4
Sample Size	35	35	35	35	35
Test statistic	4.5471	-7.7908	8.7296	0.891	1.2612

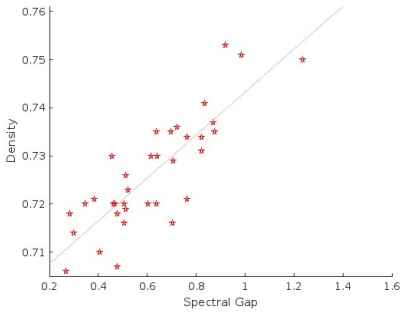
From the above parameters, the following graphs (Fig 3) have been plotted to have a comparative view among the results obtained.



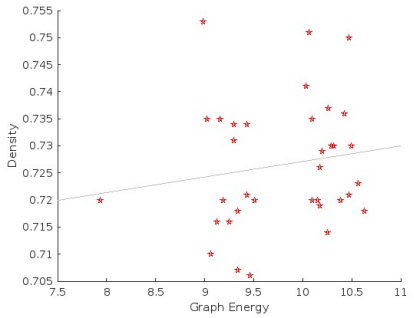
(a) Spectral Radius



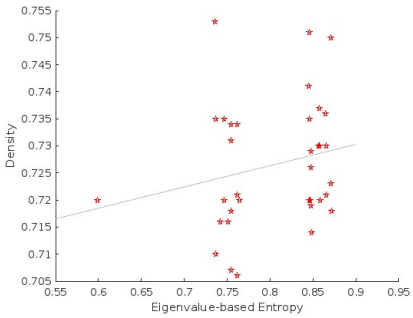
(b) Second Largest eigenvalue



(c) Spectral Gap



(d) Graph Energy



(e) Eigenvalue-based Entropy

FIG. 3. Graphical representation of Correlation Coefficient between density and spectral parameters of nonane isomers

8. Observation

1. From the above table 2 we can notice that the spectral gap has maximum correlation with the density of nonane.
2. A correlation coefficient of 0.80398 suggests a strong positive correlation between the variables in the sample of 35 observations(isomers). It indicates that there is a strong tendency for the variables to increase or decrease together.
3. The extremely small p-value 4.3332e-10 indicates that the observed data is highly unlikely to occur by chance if the null hypothesis is true based on sample of 35 observations. This suggests strong evidence against the null hypothesis and supports the presence of a significant effect or relationship in your data.
4. The covariance measures the extent to which two variables vary together. With a covariance of 2.13e-3 in the sample of 35 observations, it suggests a positive covariance between the variables, indicating that they tend to vary in a similar direction.
5. The correlation coefficient of -0.81322 indicates a strong negative monotonic relationship between the two variables. This means that as one variable increases, the other variable tends to decrease. The negative sign indicates the direction of the relationship.

6. The p-value of 5.613e-9 is extremely small, suggesting strong evidence against the null hypothesis. In this case, it indicates that the observed correlation coefficient is significantly different from zero. Thus, we can conclude that there is a statistically significant correlation between the two variables.
7. The covariance of -1.4e-3 indicates a negative relationship between the variables.
8. The sample size of 35 indicates the number of data points used to calculate the correlation coefficient. A larger sample size generally provides more reliable estimates of the correlation between variables.
9. The test statistic of -7.7908 is likely associated with a significance test for the correlation coefficient. The exact interpretation of this value depends on the specific test employed.
10. Except the second largest eigenvalue, all other spectral parameters has positive correlation with the density of nonane.

9. Conclusion

To extend this further, we could try to investigate the relationship between graph energy and graph entropy in detail for different classes of molecular graphs beyond the isomers of nonane. By analyzing a larger and more diverse set of molecular graphs, we would be able to draw more general conclusions about the relationship between graph energy and graph entropy, and identify any patterns or trends across different classes of molecules. We could also explore some of the underlying chemical and physical factors that contribute to these properties, such as bond strength, electronic interactions, and molecular shape. This type of research could have potential applications in fields such as drug discovery, materials science, and catalysis.

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Conflict of interest: the authors declare no conflict of interest.