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QSPR Study of Coumarins Based on the Hyper Neighbourhood Stress Index

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ABSTRACT: In this paper, we introduce a novel molecular descriptor called the Hyper neighbourhood stress index $HNS(G)$, which is based on the neighbourhood stresses of individual vertices. We explore the $HNS(G)$ values for well-known graphs. Further, we perform QSPR (Quantitative Structure-Property Relationship) analysis to study the intercorrelation between the $HNS(G)$ of molecular graph structures and the structural properties of coumarins. Our findings reveal a better correlation between the physicochemical properties of coumarins and the $HNS(G)$ of their molecular graph structures. Finally, we establish quadratic regression models to relate these molecular descriptors with the physicochemical properties of coumarins.

Key Words: Graph, geodesic, topological index, stress of a vertex, neighbourhood stress of a vertex.

Contents

1. Introduction

Cancer cells are abnormal cells, and they can divide uncontrollably and can attack surrounding tissues. These can destroy the normal cell growth and regulation called mutations. Cancer cells may also develop resistance to programmed cell death and these cells are having longer life span than the normal cells. They can create their own blood supply through an angiogenesis process. This process can support to growth and spread of the cancer cell. Long term health condition disease like cancer, diabetes mellitus respiratory related diseases and cardiovascular sickness have encounter large portion of population. These diseases are parament and slowly progressive in the organs of human body. Due to this rigorous research has been performed to develop potent drugs to cure these diseases.

Coumarins and derivatives of coumarins are mainly used for the treatment of cancer. They can occur in any organ of the body and also have ability to fight against the side effect caused by the radio therapy. Both natural and syntactic derivatives of coumarins drawn attention due to their photochemotherapy and therapeutic applications in cancer. They can expose to a wide range of biological activities like warfarin and dicoumaral are well known for their ability to hinder the blood clothing. Warfarin is mainly used as an oral anti-coagulant to prevent and treat thromboembolic disorders such as deep vein thrombosis and stroke. Coumarins are the class of aromatic compounds contains benzene ring(C_6) and pyrone rings(C_3O). In this benzene ring is fused with lactone structure. The molecular formula of coumarin is $C_9H_6O_2$. Majority of the natural coumarins originate from the vascular plants such as novobiocin, coumermycin and uflatoxin are produced by the microbial sources. Recent research in chemical graph theory has led to the introduction of many new parameters in topological indices. By motivation on the work of topological indices an attempt is made to define a new parameter in topological index and called as Hyper neighbourhood stress index $HNS(G)$. We placed explicit formulae for $HNS(G)$ of standard graph along with QSPR analysis of coumarins.

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2. Preliminary results

Harary's textbook ([4]) provides standard vocabulary and principles in graph theory. This article will provide nonstandard information when needed.

Let $G = (V, E)$ be a graph (finite, simple, connected, undirected). The degree of a node v in G is represented by $\deg(v)$. The shortest path (graph geodesic) between two nodes u and v in G is the path with the fewest number of edges. A graph geodesic P passes through a node v in G if v is an internal node of P.

Shimbel proposed the notion of stress as a centrality metric for nodes in networks (graphs) in 1953 [23]. This centrality metric has applications in biology, sociology, psychology, and other fields (see [8,21]). The stress of a node v in a graph G, denoted by $\mathrm{str}_G(v)$ $str(v)$, is the number of geodesics traveling through. Bhargava et al.'s study [3] examines the notions of stress number and stress regular graphs. A graph G is considered k-stress regular if $str(v) = k$ for every $v \in V(G)$. neighbourhood of a vertex v is defined as

$$N_G(v) = \{u \in V(G) \mid uv \in E(G)\}.$$

The neighbourhood stress of a vertex v, denoted by $N_s(v)$. This index is defined as the sum of the stresses of the adjacent vertices of v, formally expressed as:

$$N_s(v) = \sum_{u \in N_G(v)} str(u)$$

. The first neighbourhood stress index of a graph G [1] is defined as

$$NS_1(G) = \sum_{v \in V(G)} N_s(v)^2.$$

The second neighbourhood stress index [6] of a graph G is defined as

$$NS_2(G) = \sum_{uv \in E(G)} N_s(u)N_s(v).$$

Within the scope of this investigation, we investigate finite simple connected graphs, which are also referred to as graphs. A particular graph is denoted by the letter G, and the letter N is used to denote the number of geodesics in G that have a length of at least two. In response to the neighbourhood stress on vertices and the related indices, we come up with a novel topological metric that we call the Hyper neighbourhood stress index. In addition to constructing several inequalities, proving fundamental facts, and calculating this index for a range of conventional graphs, Furthermore, we examine the chemical significance of the Hyper neighbourhood stress index through regression analysis applied to anti-cancer drugs, investigating its correlation with several physicochemical properties. Many stress related concepts in graphs and topological indices have been defined and studied by several authors [1,2,5-7,9-20,22,24-26].

3. Hyper neighbourhood stress index

Definition 3.1 The Hyper neighbourhood stress index of a graph G is defined as

$$HNS(G) = \sum_{uv \in E(G)} [N_s(u) + N_s(v)]^2. \tag{3.1}$$

Definition 3.2 A graph G is called k- neighbourhood stress regular if $N_s(v) = k$ for all $v \in V(G)$

Corollary 3.1 *If there is no geodesic of length ≥ 2 in a graph G, then $HNS(G) = 0$. Moreover, for a complete graph K_n, $HNS(K_n) = 0$.*

Proof: If there is no geodesic of length ≥ 2 in a graph G, then $N_s(v) = 0$. Hence we have $HNS(G) = 0$. In K_n, there is no geodesic of length ≥ 2 and so $HNS(K_n) = 0$. □

Proposition 3.1 *For the complete bipartite $K_{m,n}$,*

$$HNS(K_{m,n}) = \frac{m^3n^3}{4}\left[m+n-2\right]^2.$$

Proof: Let $V_1 = \{v_1, \ldots, v_m\}$ and $V_2 = \{u_1, \ldots, u_n\}$ be the partite sets of $K_{m,n}$. We have,

$$N_s(v_i) = \frac{n.m(m-1)}{2} \text{ for } 1 \leq i \leq m \tag{3.2}$$

and

$$N_s(u_j) = \frac{m.n(n-1)}{2} \text{ for } 1 \leq j \leq n. \tag{3.3}$$

Using (3.2) and (3.3) in the Definition 3.1, we have

$$\begin{aligned} HNS(K_{m,n}) &= \sum_{uv \in E(G)} [N_s(u) + N_s(v)]^2 \\ &= \sum_{1\leq i\leq m,\ 1\leq j\leq m} [N_s(v_i) + N_s(u_j)]^2 \\ &= \sum_{1\leq i\leq m,\ 1\leq j\leq m} \left[\frac{nm(m-1)}{2} + \frac{mn(n-1)}{2}\right]^2 \\ &= mn\left[\frac{m^2n^2}{4}(m+n-2)^2\right] \\ &= \frac{m^3n^3}{4}\left[m+n-2\right]^2. \end{aligned}$$

□

Proposition 3.2 *For the star graph $K_{1,n}$ on $n+1$ vertices*

$$HNS(K_{1,n}) = \frac{n^2(n-1)}{2}.$$

Proof: In a star graph $K_{1,n}$, internal vertex has neighbourhood stress zero and remaining n have neighbourhood stress $\frac{n(n-1)}{2}$ By the Definition 3.1, we have

$$\begin{aligned} HNS(G) &= \sum_{uv \in E(G)} [N_s(u) + N_s(v)]^2 \\ &= \frac{n^3(n-1)^2}{4}. \end{aligned}$$

□

Proposition 3.3 *If $G = (V, E)$ is a k-neighbourhood stress regular graph, then*

$$HNS(G) = 4k^2|E|.$$

Proof: Suppose that G is a k-neighbourhood stress regular graph. Then

$$N_s(v) = k \text{ for all } v \in V(G).$$

By the Definition 3.1, we have

$$\begin{aligned} HNS(G) &= \sum_{uv \in E(G)} [N_s(u) + N_s(v)]^2 \\ &= \sum_{uv \in E(G)} [k+k]^2 \\ &= 4k^2|E|. \end{aligned}$$

□

Corollary 3.2 *For a cycle C_n,*

$$HNS(C_n) = \begin{cases} \dfrac{n(n-1)^2(n-3)^2}{4}, & \text{if } n \text{ is odd;} \\ \dfrac{n^3(n-2)^2}{4}, & \text{if } n \text{ is even.} \end{cases}$$

Proof: For any node v in C_n, we have,

$$N_s(v) = \begin{cases} \dfrac{(n-1)(n-3)}{4}, & \text{if } n \text{ is odd;} \\ \dfrac{n(n-2)}{4}, & \text{if } n \text{ is even.} \end{cases}$$

Hence C_n is

$$\begin{cases} \dfrac{(n-1)(n-3)}{4}\text{-neighbourhood stress regular}, & \text{if } n \text{ is odd;} \\ \dfrac{n(n-2)}{4}\text{-neighbourhood stress regular}, & \text{if } n \text{ is even.} \end{cases}$$

Since C_n has n edges, by Proposition 3.3, we have

$$\begin{aligned} HNS(C_n) &= 4n \times \begin{cases} \dfrac{(n-1)^2(n-3)^2}{16}, & \text{if } n \text{ is odd;} \\ \dfrac{n^2(n-2)^2}{16}, & \text{if } n \text{ is even.} \end{cases} \\ &= \begin{cases} \dfrac{n(n-1)^2(n-3)^2}{4}, & \text{if } n \text{ is odd;} \\ \dfrac{n^3(n-2)^2}{4}, & \text{if } n \text{ is even.} \end{cases} \end{aligned}$$

□

Proposition 3.4 *For the path P_n on n nodes $HNS(P_n)$*

$$= 2(3n-8)^2 + \sum_{i=2}^{n-2} \left[(i-2)(n+1-i) + i(n-1-i) + (i-1)(n-i) + (i+1)(n-i-2)\right]^2.$$

Proof: Let P_n be the path with node sequence $v_1, v_2, \ldots, v_n$
We have ,

$$N_s(v_i) = \begin{cases} (i-2)(n+1-i) + i(n-1-i), & \text{if } 1<\text{i} < n \text{ ;} \\ (n-2), & \text{if } i\text{=1 or } i\text{=}n. \end{cases}$$

Thus by the Definition 3.1, we have

$$\begin{aligned} HNS(P_n) &= \sum_{uv \in E(G)} \left[N_s(u) + N_s(v)\right]^2 \\ &= \sum_{i=1}^{n-1} \left[N_s(v_i) + N_s(v_{i+1})\right]^2 \\ &= \left[N_s(v_1) + N_s(v_2)\right]^2 + \left[N_s(v_{n-1}) + N_s(v_n)\right]^2 + \sum_{i=2}^{n-2} \left[N_s(v_i) + N_s(v_{i+1})\right]^2. \end{aligned}$$

Thus we have $HNS(P_n)$

$$= 2(3n-8)^2 + \sum_{i=2}^{n-2} \left[(i-2)(n+1-i) + i(n-1-i) + (i-1)(n-i) + (i+1)(n-i-2)\right]^2.$$

□

Proposition 3.5 *Let $Wd(n,m)$ denotes the windmill graph constructed for $n \geq 2$ and $m \geq 2$ by joining m copies of the complete graph K_n at a shared universal node v. Then*

$$HNS(Wd(n,m)) = \frac{m^3(m-1)^2(n-1)^5(2n-3)}{4}.$$

Hence, for the friendship graph F_k on $2k+1$ nodes,

$$HNS(F_k) = 24k^3(k-1)^2.$$

Proof: In the windmill graph $W_d(n,m)$, the stress of any node v_i other than the universal node v is zero. This is because the neighbors of each non-universal node induce a complete subgraph within $W_d(n,m)$. Since there are m copies of K_n (the complete graph on n vertices) in $W_d(n,m)$, and each node v_i within these copies is adjacent to the universal node v, it follows that all geodesics passing through v have length 2. Thus, the stress of v is given by $str(v) = \frac{m(m-1)(n-1)^2}{2}$. Additionally, note that v has $m(n-1)$ incident edges, and all edges not incident to v connect nodes whose stress is zero. Therefore, the neighbourhood stress of the universal node v is zero, while the neighbourhood stress of each remaining vertex v_i is $\frac{m(m-1)(n-1)^2}{2}$. By Definition 3.1, we obtain

$$\begin{aligned}
HNS(Wd(n,m)) &= m(n-1)\left[\frac{m^2(m-1)^2(n-1)^4}{4}\right] + \frac{m(n-1)(n-2)}{2}\left[\frac{2m(m-1)(n-1)^2}{2}\right]^2 \\
&= \frac{m^3(m-1)^2(n-1)^5}{4} + \frac{m^3(m-1)^2(n-1)^5(n-2)}{2} \\
&= \frac{m^3(m-1)^2(n-1)^5(2n-3)}{4}.
\end{aligned}$$

Since the friendship graph F_k on $2k+1$ nodes is nothing but $Wd(3,k)$, it follows that

$$HNSS(F_k) = 24k^3(k-1)^2.$$

□

Proposition 3.6 *Let W_n denotes the wheel graph constructed on $n \geq 4$ nodes. Then*

$$HNS(W_n) = (n-1)\left[\frac{n^2-3n+6}{2}\right]^2 + (n-1)(n^2-5n+8).$$

Proof: In W_n with $n \geq 4$, there are $(n-1)$ peripheral nodes and one central node, say v. It is easy to see that

$$str(v) = \frac{(n-1)(n-4)}{2} \tag{3.4}$$

Let p be a peripheral node. Since v is adjacent to all the peripheral nodes in W_n, there is no geodesic passing through p and containing v. Hence we have

$$\begin{aligned}
str_{W_n}(p) &= str_{W_n - v}(p) \\
&= str_{C_{n-1}}(p) \\
&= 1.
\end{aligned} \tag{3.5}$$

Thus we have ,

$$N_s(v) = (n-1)$$

and

$$N_s(p) = \frac{(n-1)(n-4)}{2} + 2.$$

Let us denote the set of all the radial edges in W_n by R and the set of all peripheral edges by Q. Note that there are $(n-1)$ radial edges and $(n-1)$ perpheral edges in W_n
Thus by the Definition 3.1, we have

$$\begin{aligned} HNS(W_n) =& (n-1)\sum_{vp \in E(G)} [N_s(v) + N_s(p)]^2 + 4(n-1)\sum_{p \in P(G)} N_s(p)^2 \\ =& (n-1)\left[(n-1) + \frac{n^2-5n+8}{2}\right]^2 + 4(n-1)\frac{(n^2-5n+8)^2}{4} \\ =& (n-1)\left[\frac{n^2-3n+6}{2}\right]^2 + (n-1)(n^2-5n+8). \end{aligned}$$

□

4. A QSPR Analysis

We investigated the physical characteristics of coumarins and coumarin-related compounds used in cancer pharmacotherapy using QSPR. The Hyper neighbourhood stress index in molecular graphs was used in this investigation. The Hyper neighbourhood stress index $HNS(G)$ of molecular graphs is shown in Table 1. The study also takes into account the experimental values for the following physical properties: boiling point (BP) in °C at 760 mmHg, enthalpy of vaporization (E) in kJ/mol, flash point (FP) in °C, molar refractivity (MR) in A^2, polar surface area (PSA) in cm^3, polarizability (P) in dyne/cm, and molar volume (MV) in cm^3. The source of these physical characteristics is http://www.chemspider. com/.

Table 1: Hyper neighbourhood stress index ($HNS(G)$), boiling point (BP) , enthalpy of vaporization (E) , flash point (FP) , molar refractivity (MR) , polar surface area (PSA) , polarizability (P) , and molar volume (MV) of anti-cancer drugs.

Drugs	HNS(G)	BP	E	FP	MR	PSA	P	MV
Coumestrol	6028117	406.0	68.3	199.3	69.4	80	27.5	167.4
Daphnetin	164240	430.4	71.2	184.5	43.5	67	17.3	114.0
Daphnin	5242130	670.0	103.4	252.4	77.4	146	30.7	202.6
Dicumarol	9603345	620.7	96.7	231.9	85.4	93	33.9	213.8
Esculetin	188781	469.7	76.0	201.5	43.5	67	17.3	114.0
Esculin	5727966	697.7	107.3	262.8	77.4	146	30.7	202.6
Gravelliferone	3379093	454.3	74.1	184.9	87.5	47	34.7	267.1
Herniarin	5248733	335.3	57.8	138.6	46.4	36	18.4	141.1
Imperatorin	1004938	448.3	70.7	224.9	75.0	49	29.7	217.5
Isobergapten	449605	412.4	66.5	203.2	56.6	49	22.4	158.0
Isopimpinellin	828179	448.7	70.7	225.1	63.3	58	25.1	182.0
Limettin	358438	388.1	63.7	176.3	53.1	45	21.1	165.1
Novobiocin	459749666	876.2	133.4	483.7	155.3	196	61.6	431.0
Pimpinellin	916350	441.0	69.8	220.5	63.3	58	25.1	182.0
Psoralen	235768	362.6	60.9	173.1	49.9	39	19.8	134.0
Seselin	720832	403.0	65.4	170.5	62.5	36	24.8	186.7
Skimmin	5248733	632.0	98.2	239.3	75.5	126	29.9	204.2
Umbelliferon	109165	382.1	65.5	181.2	41.6	47	16.5	115.5
Visnadin	9475176	477.7	74.2	206.9	99.3	88	39.4	307.2
Warfarin	4388626	515.2	82.9	188.8	84.4	64	33.5	235.8
Xanthotoxin	447292	414.8	66.8	204.7	56.6	49	22.4	158.0
Xanthyletin	1037870	340.0	58.4	159.5	45.4	29	18.0	133.9
Angelicin	192767	362.6	60.9	173.1	49.9	39	19.8	134.0

Bergapten	447636	412.4	66.5	203.2	56.6	49	22.4	158.0
Alternariol	1201680	384.6	63.3	161.9	62.5	36	24.8	186.7

Regression Models

Using Table 1, a study was carried out with a quadratic regression model

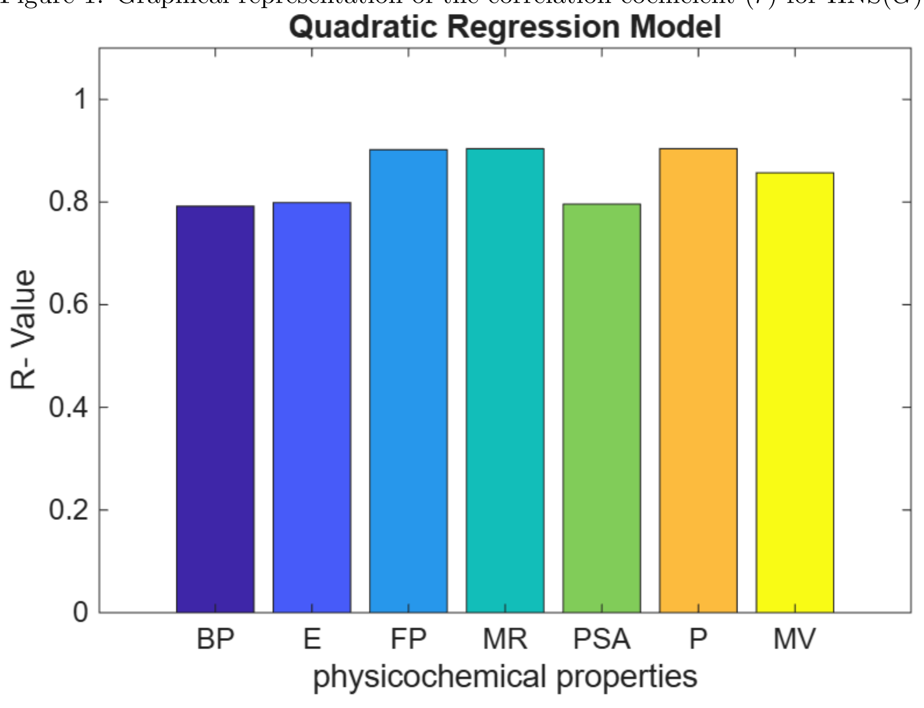
$$P = A \cdot (HNS(G))^2 + B \cdot (HNS(G)) + C,$$

where P = Physical property and $HNS(G)$ = Hyper neighbourhood stress index.

Table 2: The correlation coefficient r from quadratic regression model between Hyper neighbourhood stress index and physicochemical properties (BP, E, FP, MR, PSA, P, MV) of coumarins.

BP	E	FP	MR	PSA	P	MV
0.829	0.832	0.918	0.952	0.817	0.952	0.898

Figure 1: Graphical representation of the correlation coefficient (r) for HNS(G).



The quadratic regression models for boiling point (BP), enthalpy of vaporization (E), flash point (FP), molar refractivity (MR), polar surface area (PSA), polarizability (P), and molar volume (MV) of anti-cancer drugs are as follows:

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Table 3: Statical parameters for the quadratic QSPR model for Hyper neighbourhood stress index $HNS(G)$ of lower alkanes.

Physiochemical properties	R^2	Adjusted R^2	F	Sig
boiling point (BP)	0.627	0.594	18.522	0.000
enthalpy of vaporization (E)	0.638	0.606	19.421	0.000
flash point (FP)	0.814	0.797	48.155	0.000
molar refractivity (MR)	0.817	0.8	48.946	0.000
polar surface area (PSA)	0.633	0.6	19.002	0.000
polarizability (P)	0.817	0.8	49.725	0.000
molar volume (MV)	0.734	0.71	30.352	0.000

$$BP = -1.429 \times 10^{-13} \cdot (HNS(G))^2 + 2.076 \times 10^{-5} \cdot HNSS(G) + 401.045 \quad (4.1)$$
$$E = -1.060 \times 10^{-13} \cdot (HNS(G))^2 + 2.902 \times 10^{-6} \cdot HNS(G) + 65.817 \quad (4.2)$$
$$FP = -1.072 \times 10^{-13} \cdot (HNS(G))^2 + 3.946 \times 10^{-6} \cdot NSS(G) + 188.483 \quad (4.3)$$
$$MR = -1.085 \times 10^{-13} \cdot (NSS(G))^2 + 4.12 \times 10^{-6} \cdot NSS(G) + 52.94 \quad (4.4)$$
$$PSA = -1.148 \times 10^{-13} \cdot (NSS(G))^2 + 7.132 \times 10^{-6} \cdot NSS(G) + 45.904 \quad (4.5)$$
$$P = -1.034 \times 10^{-13} \cdot (NSS(G))^2 + 1.638 \times 10^{-6} \cdot NSS(G) + 20.993 \quad (4.6)$$
$$MV = -1.22 \times 10^{-13} \cdot (NSS(G))^2 + 1.073 \times 10^{-5} \cdot NSS(G) + 150.704 \quad (4.7)$$

Figure 2: Graphical representation of the scattered points and its quadratic fit using HNS(G) for boiling point.

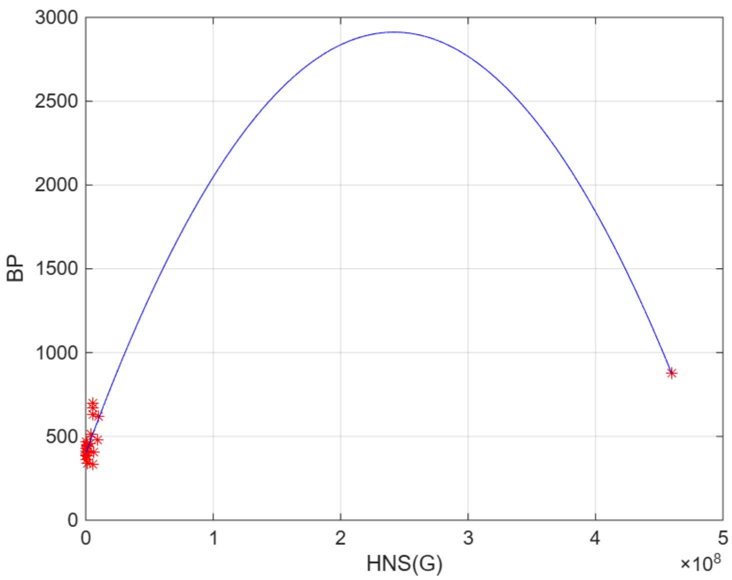


Figure 3: Graphical representation of the scattered points and its quadratic fit using HNS(G) for enthalpy of vaporization.

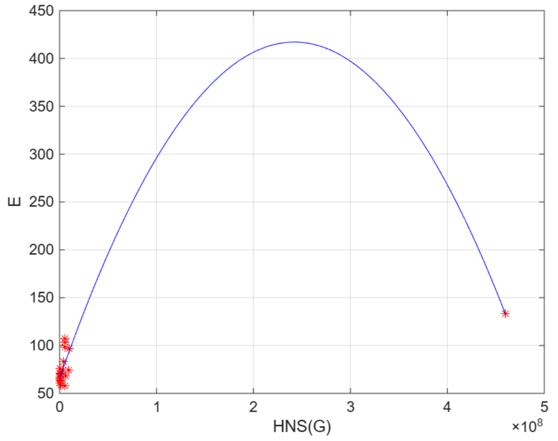


Figure 4: Graphical representation of the scattered points and its quadratic fit using HNS(G) for flash point.

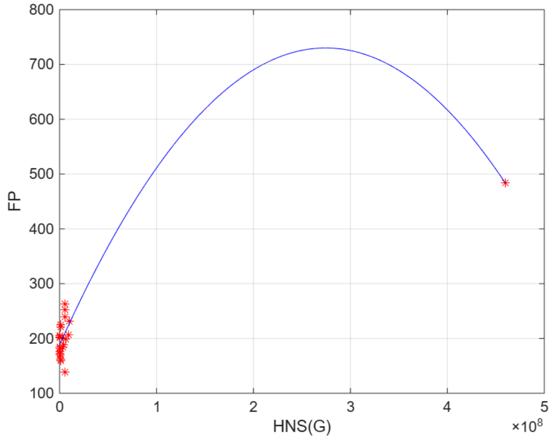


Figure 5: Graphical representation of the scattered points and its quadratic fit using HNS(G) for molar refractivity.

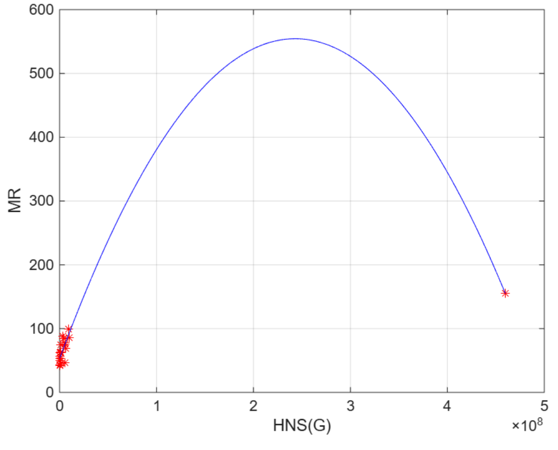


Figure 6: Graphical representation of the scattered points and its quadratic fit using HNS(G) for polar surface area.

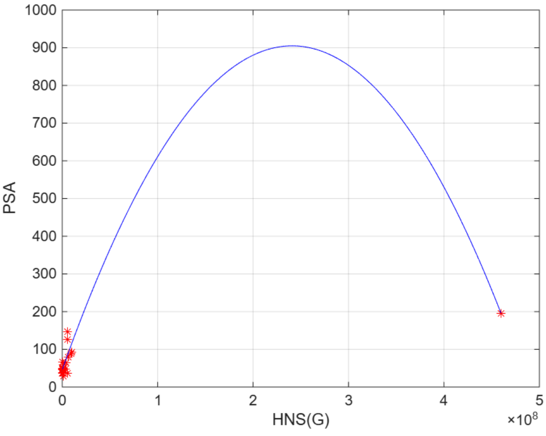


Figure 7: Graphical representation of the scattered points and its quadratic fit using HNS(G) for polarizability.

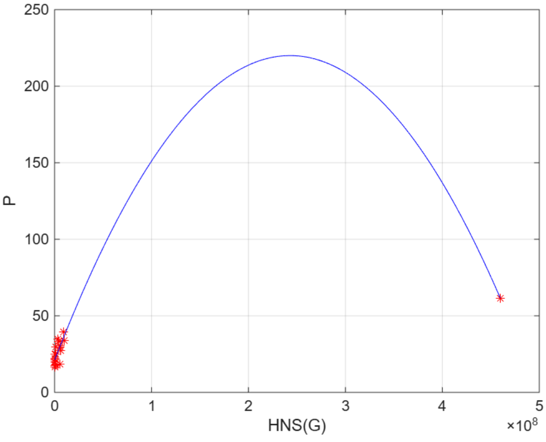
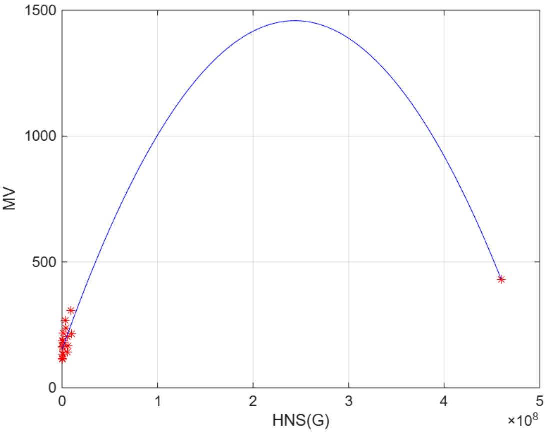


Figure 8: Graphical representation of the scattered points and its quadratic fit using HNS(G) for molar volume.



5. Conclusion

In this exploration we proposed explicit formulae for $HNS(G)$ of some standard graphs. And table 2 shows that the quadratic regression models (4.1)-(4.2)-(4.3)-(4.4)-(4.5)-(4.6)-(4.7) are effective in predicting the physical properties of anti-cancer drugs. It demonstrates that the Hyper neighbourhood stress index may be utilized as a forecasting tool in QSPR research.

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