



Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Environmental friendly promoted synthesis of N-hydroxy-2,6-bis(p-hydroxy phenyl)-3-isopropyl piperdin-4-one-thiosemicarbazone and analysis through complete tripartite graph, complete bipartite graph and complete split graph analysis from the spectral data

J. B. Veeramalini¹, V. Narayanan² and G. Baskar^{3*}

¹Department of Chemical Engineering, Sri Ram Engineering College, Anna University Affiliated, Chennai, Tamilnadu, India

²Department of Mathematics, Sri Ram Engineering College, Anna University Affiliated, Chennai, Tamilnadu, India

³Department of Applied Chemistry, Sri Venkateswara College of Engineering, Anna University Affiliated, Chennai, Tamilnadu, India

ABSTRACT

A new approach for synthesis of N-hydroxy-2, 6-bis (p-hydroxyphenyl)-3 isopropyl piperdin-4-one-thiosemicarbazone has been developed from the Graph theory. A key step to access the characterization of the synthesized compound was achieved, by the elemental analysis IR, ¹H NMR and ¹³C NMR and Raman spectral data. This Graph theory has developed a great target of interest for synthetic organic chemistry because of its structural simplicity, efficient methods and convenient roots are still being sought after. This strategy involves the in situ classification of Graph theory and further it has been discussed mathematically in terms of p – vertices and q – cliques. In order to illustrate the efficiency of our method, we are interested in extending this methodology to privileged structures of Graph theory. The good functional group compatibility renders the synthesized compound into four sub groups. Each subset of a group has been defined, such as dialkyl by complete Tripartite Graph, thiosemicarbazone by Complete Bipartite Graph, N-hydroxy ring and halo aromatic compounds are represented by Complete Split Graph analysis. This work has been taken up with an idea of a complete picturization of the compound by combining all the subgroups together and it also been schematically represented.

Keywords: Thiosemicarbazone, Complete Tripartite Graph, Complete Bipartite Graph and Complete Split Graph, NMR, IR.

INTRODUCTION

A graph labeling is an assignment of integers to the p – vertices or e – edges or both edges to certain q – cliques' representations. An extensive survey on graph labeling can be found in Gallian [1-9]. Graph labeling is one of the potential research areas due to its diversified applications in analytical conditions. Recently there is a fast development in graph labeling problem which appears in graph theory. This work has been carried out is not only due to its mathematical importance but also due to its wide range of applications arising from the chemistry dictionary. Further an enormous body of literature has grown around the subject of Radar astronomy, DFT studies and commercial design. This journal has given birth to families of graphs with different attractive names such as dialkyl by complete Tripartite Graph, thiosemicarbazone by Complete Bipartite Graph and N-hydroxy ring and hydroxy aromatic compounds which are represented by Complete Split Graph analysis. All graphs considered are finite, simple, and undirected and further it has also provided a useful survey to know about the numerous graph labeling methods in chemistry dictionary.

EXPERIMENTAL SECTION

All the reagents and solvents purchased were reagent grade and were used without further purifications. Completion of reactions was monitored by TLC on silica gel coated aluminium sheet (Type 60 GF254, Merck). Noller and Balliah [2-11] have synthesized several substituted 2, 6-diaryl-4-one compound. The melting points were measured in open capillaries and are uncorrected. FT-IR spectra were recorded on an AVATAR-300 FT-IR spectrometer (Thermo Nicolet) using KBr (pellet form). The spectral features are reported in wave number (cm⁻¹). ¹H-NMR and ¹³C-NMR were recorded on Bruker 400 MHz and 100MHz spectrometer. ¹H-NMR and ¹³C-NMR chemical shifts values are reported in parts per million (ppm) from Tetramethylsilane (TMS) with solvent resonance as the integral standard (CDCl₃). Peak multiplicities are designated by: s-singlet, bs-broad singlet, d-doublet, dd-double doublet, t-triplet, q-quartet, and m-multiplet in Hz.

II.1.Preparation of N-hydroxy-2, 6-bis (p-hydroxyphenyl)-3 isopropyl piperdin-4-one:

The respective piperdone [1] and m-chloro per benzoic acid (1:1) were mixed in 20 ml chloroform at 0°C. The mixture was extracted and washed with 10 % Sodium bicarbonate solution. The chloroform layer was dried with anhydrous sodium sulphate and evaporated. The separated solid was subjected to Column chromatography. The column was packed with silica gel (100-200 mesh) in hexane. The eluting solvents are benzene, and benzene pet ether (40:60) (8:2). The compound was found to be separated in benzene pet ether (8:2) and it is enlisted in table 1.

TABLE 1: Physical data of N-hydroxy-2, 6-bis (p-hydroxyphenyl)-3 isopropyl piperdin-4-one

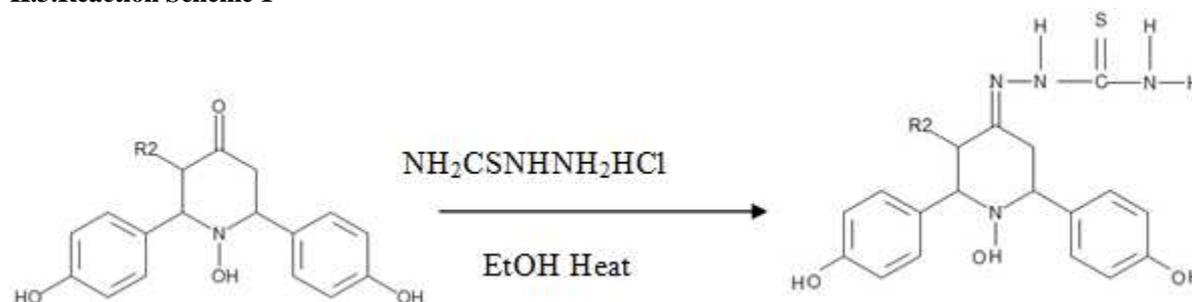
Molecular Formula	Molecular Weight	Melting Point	Yield
C ₁₉ H ₂₁ NO ₃	304	176	82

II.2. Preparation of N-hydroxy-2, 6-bis (p-hydroxyphenyl)-3 isopropyl piperdin-4-one-thiosemicarbazone

A mixture of N-hydroxypiperdin-4-one (1gm, 0.0027mol), thio hydrochloride (0.316, 0.0027mol), and sodium acetate (0.75 gm) were dissolved in ethanol (40 ml) and refluxed for two hours on a steam bath and cooled. The separated solid was filtered and washed with water and recrystallised from ethanol. The physical data of N-hydroxy-2, 6-bis (p-hydroxyphenyl)-3 isopropyl piperdin-4-one thiosemicarbazone is indicated in table 2.

TABLE 2: Physical data of N-hydroxy-2, 6-bis (p-hydroxyphenyl)-3 isopropyl piperdin-4-one thiosemicarbazone

Molecular Formula	Molecular Weight	Melting Point	Yield
C ₂₀ H ₂₄ N ₄ O ₃ S	386	187	88

II.3.Reaction Scheme 1**III. Definition of Complete Tripartite Graph:**

In the Complete Tripartite Graph (CTG) with the blue colour as an assembly of main vertex or parent vertex p_1 . It would branch into three similar partitions of sub vertex namely p_3 , p_4 , and p_5 with grey colour representation. Thus the trisection of branch vertices p_3 , p_4 , and p_5 were made conjecture attack of another main vertex p_2 [13-15]. The study of new graph labeling method has been initialized, by stating that all the main vertex or root vertex or parent vertex and corresponding sub vertex can be arranged in the dual concept of cliques' representation of CTG of variable position as CTG (1,3,1). CTG follows the special kind of colour notations and representations with particular set of rules.

Rule 1: A graph can be CTG, if it is branched into three desired sub vertex.

Rule 2: If a root vertex or a main vertex should not be connected to some other sub vertex, then the assembly is a CTG.

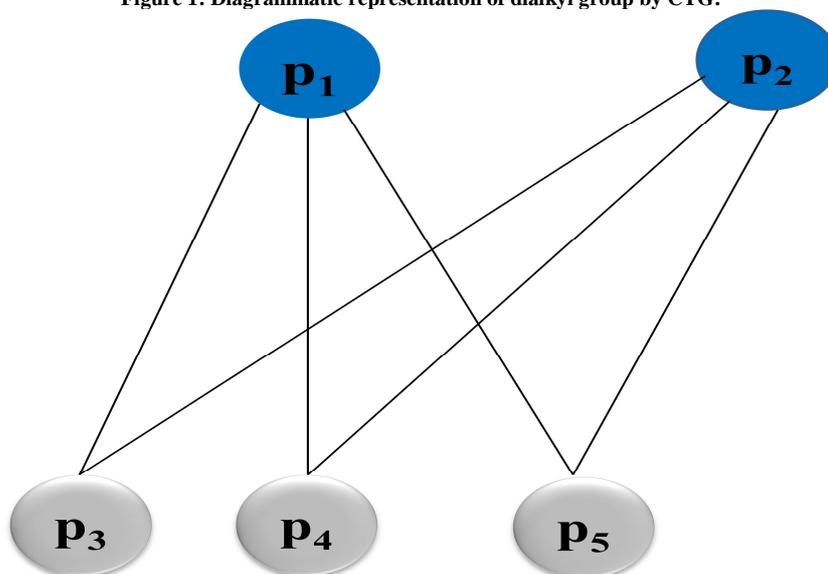
Rule 3: If a main vertex is connected to some other embedded vertex, then assembly is not a CTG.

Rule 4: The CTG need to be in specified direction.

III.1. Complete Tripartite Graph representation of dialkyl group:

In the CTG we have two parent vertex or root vertex or main vertex namely represented as primary main vertex p_1 and secondary main vertex p_2 which holds goods by the same elemental carbon with blue colour representation. The primary main vertex of carbon element is being identified by the position 1 as p_1 vertex. The path of primary main vertex is branched into three desired sub vertex of similar elements. The variable positions of sub vertex p_3 , p_4 , and p_5 holds with same elemental group of Hydrogen atom with grey color representations are depicted in figure 1. Thus we introduced a new concept of convergence of Complete Tripartite Graph, only if we have same element of parent vertex. Thus the branched sub vertex of variable position p_3 , p_4 , and p_5 are connected or linked to the secondary main vertex p_2 by mapping concept. Such that the one to many mapping (p_1-p_3, p_4, p_5) and again p_3, p_4, p_5 sub vertexes mapping into secondary main vertex p_2 by many to one mapping concept. The order of mapping for dialkyl groups of CTG has been represented as CTG (1,3,1). In such a way that there is no linked line between primary vertex and secondary vertex thus dialkyl group representation of CTG has been introduced and also picturised in graphical labeling method.

Figure 1: Diagrammatic representation of dialkyl group by CTG:



IV. Definition of Complete Bipartite Graph (CBG):

In the CBG we introduced some basic properties and coloring of graphs to the p – vertex, by assigning one colour to each vertex. So those sub vertexes are assigned in different colors simply they are denoted by chromatic number of graph (G). Such a graph is called a Complete Bipartite Graph. The q – cliques of a graph G is the maximum number of order among the CBG depends upon the structural formula of functional groups of the compound exist. We followed some basic notations and terminologies for the graph theory. Each vertex and disjoint sets belong to a single edge. The middle disjoint will be advantageous and represented by darker edge. There is a natural one to one correspondence between perfect matching of CBG. These set of vertex – disjoint sets are delineated by additional requirements, such that for the study of properties can be pretense through various color attentions and notations. The main vertex set exists as blue cliques and center in the form of darker representations with yellow cliques [14, 16-17]. The upper and lower disjoint sets of cliques act as green and grey color. Here we have presented and covered in simplified and undirected method by correlation data enlisted in table 2 and color notations in table 3.

TABLE 2: Correlations Data:

Graph Theory	Chemistry Dictionary
Graph	Structural formula
Vertex	Atom
Edge	Chemical bond
Tree	Acyclic structure
Bipartite graph	Alternant structure
Adjacency matrix	Huckel matrix

TABLE 3: Nomenclature

Symbols	Meaning
	Carbon Hydrogen Atom
	Nitrogen Atom
	Carbon Atom
	Oxygen Atom
	Hydrogen Atom
	Sulphur Atom
	Oxygen Hydrogen Atom

IV.1. Representation of thiosemicarbazone by Complete Bipartite Graph (CBG):

The parent vertex has been fixed as elemental carbon and it is linked to these different disjoint sets of sub vertex of distinguishable elements namely Nitrogen and Sulphur. The top and bottom disjoint sets are labeled through similar elemental groups and conceptually the center disjoint sets are occupied by Sulphur element as shown in figure 2. We extended their colour notations and corresponding figure representations for CBG are done through Carbon by blue colour, Nitrogen by green colour, Hydrogen by grey colour and finally Sulphur by yellow colour, they are depicted in figure 3. The sub vertex of nitrogen element is again partitioned into two subsets of vertices, (N&H), the lower sub vertex of nitrogen element is bifurcated into two similar subsets of hydrogen. The vertex and the sub vertex are connected by lines called edge. These edges are connected and it is depicted as chemical bonds. The single bond is given by thin line edge, and the double bond by thicker line.

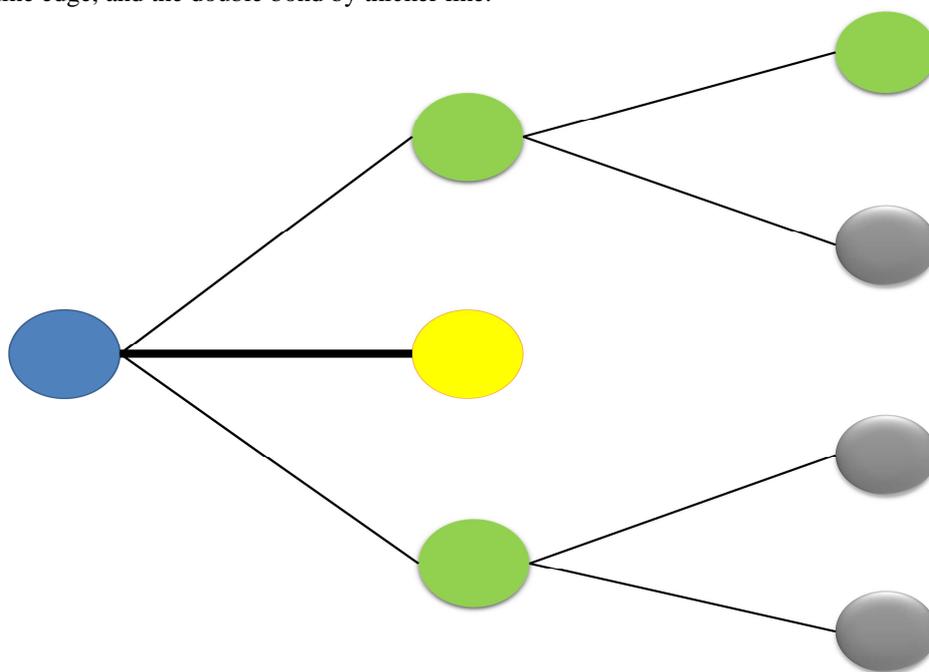


Figure 2: Diagrammatic representation of thiosemicarbazone by Complete Bipartite Graph

V. Definition of Complete Split Graph:

The cycle paths of every vertex are joined together with various - q cliques. Among the main vertex some of them were suspended in the path of sub vertex of variable position 2, 4 and 6 respectively. A close look at graphical representation of these graphs showed that among the known main vertex, some of them were suspended in the path of the sub vertex [6, 15, 17, and 18]. By tradition we shall let the colors as Blue (B), Red (R), Grey (GY), Green (G) for various terminologies used [18-20]. It is well known that the "CSG" is quite easy in some cases.

V.1. N-hydroxy ring compound and hydroxy aromatic compound representation by Complete Split Graph:

We shall argue that with cyclic structure, there is a classification of vertex in all six positions. The vertex, sub vertex, embedded vertex and the link or edge are chosen with proper colors and represented respectively. Having done so vertex and sub vertex 2,3,4,5,6 holds with same elemental group, where blue color argue for carbon atom as the outer ring and Grey color for hydrogen atom of sub vertex position. The first position of ring structure is indicated by nitrogen atom with green in color mode and significantly it splits into sub vertex and embedded vertex. In that case it follows, Red color indication for oxygen element of outer envelope, so that it holds good for grey color for hydrogen atom of inner envelope that is embedded vertex. Certainly let's proceed with spanned of various vertices, sub vertex and embedded vertex of aromatic compounds. We wish to extend complete Split Graph to an N-hydroxy ring compound, with several cases in which such a strategy will be successful. We have seen that within the vertex of the bottom ring in the position 1, it is branched into desired sub vertex, which further bonded to embedded vertex as shown in figure 3. Consequently there is a positive probability that all the vertices are good, when analysis is successful through elemental cyclic structure of CSG [20-23]. Except for every special case, it can be improved, by two or more vertex to the cyclic structure, which also binds to the Complete Split graph rule which gives rise to the hydroxy functional groups in the para position.

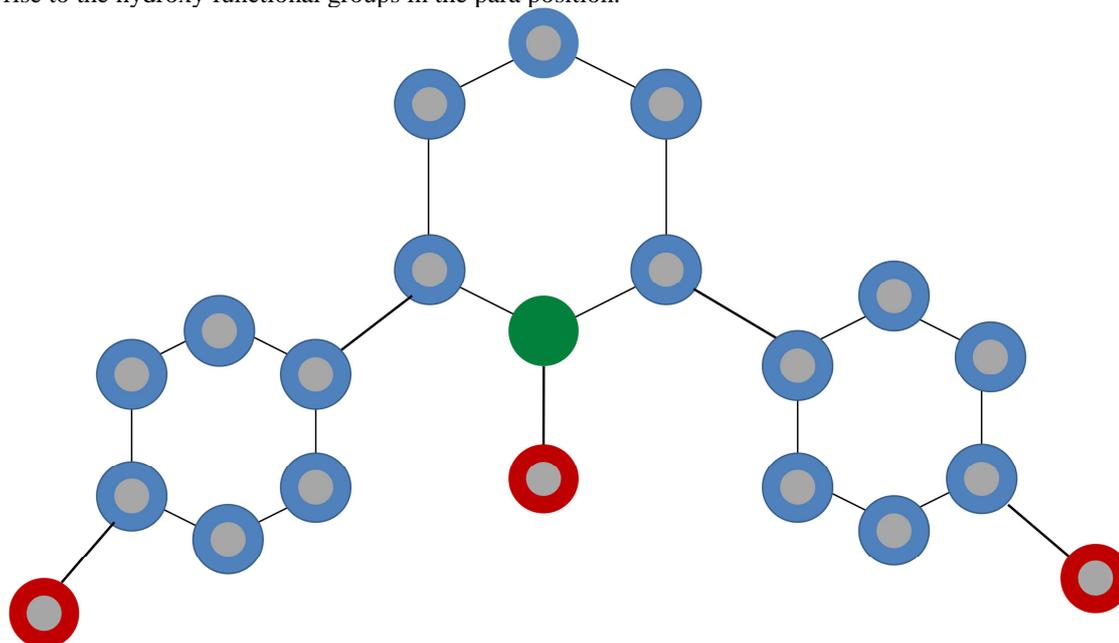


Figure 3: N-hydroxy ring compound and hydroxy aromatic compound pictorial representation by Complete Split Graph

V.2. Schematic identification of N-hydroxy-2, 6-bis (p-hydroxyphenyl)-3 isopropyl piperdin-4-one-thiosemicarbazone

The compound synthesized has been induced and the complex structure of the compound N-hydroxy-2, 6-bis (p-hydroxyphenyl)-3 isopropyl piperidine-4-one-thiosemicarbazone has been represented in the simplified way by various subsets analysis. The subset are illustrated by the functional group of thiosemicarbazone, dialkyl, N-hydroxy ring compound and hydroxy aromatic compound can be picturised in figure 4 through simple workup method [15-16]. Thus the identification of synthesized compound is done by Complete Tripartite Graph, Complete Bipartite Graph and Complete Split Graph analysis.

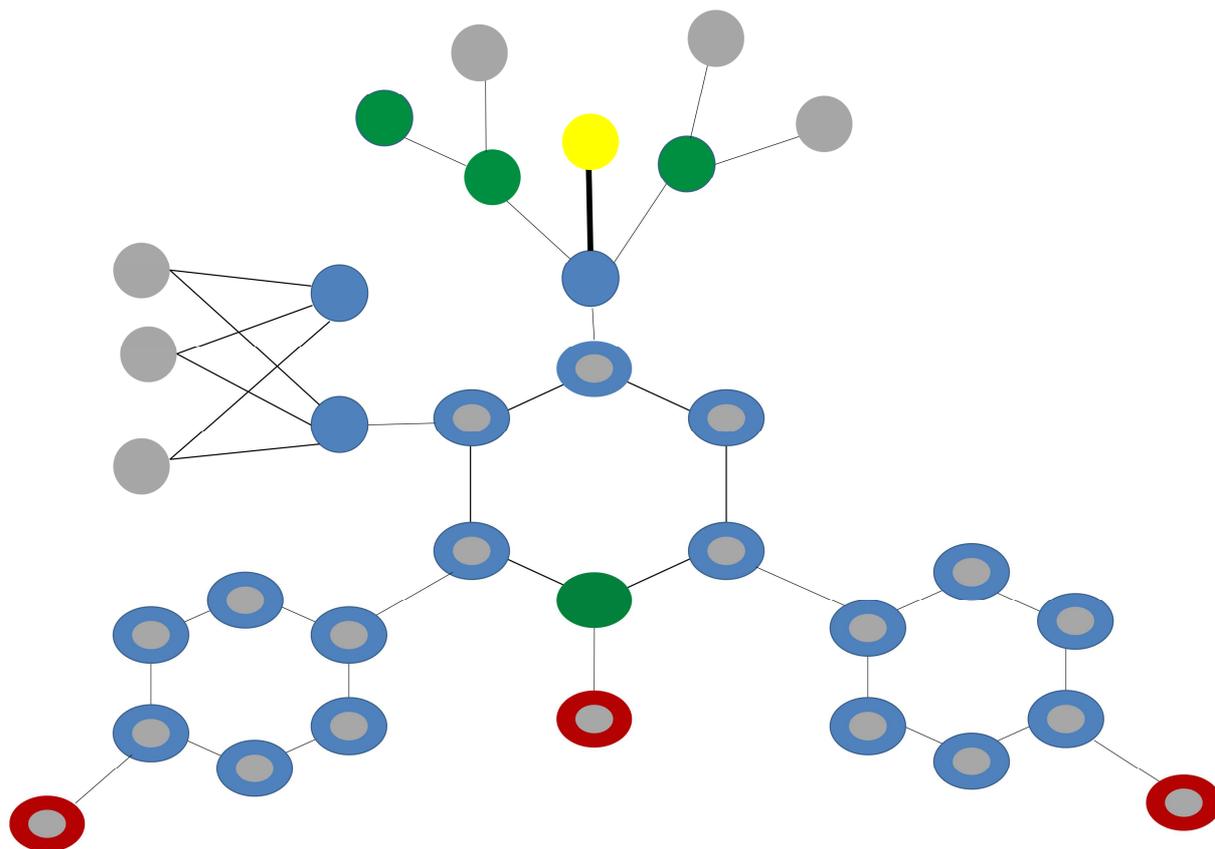


Figure 4: Representation of N-hydroxy-2, 6-bis (p-hydroxyphenyl)-3 isopropyl piperidin-4-one-thiosemicarbazone through connectivity

RESULTS AND DISCUSSION

In the present study N-hydroxy-2, 6-bis (p-hydroxyphenyl)-3 isopropyl piperidin-4-one-thiosemicarbazone have prepared and analyzed through ^1H and ^{13}C NMR data. In all cases the position H15 – H19 are assigned for respective carbons and observed a quartet methylene protons in the region 3.01 – 3.76 ppm. A multiplet between 6.71 – 9.07 ppm is due to the aromatic protons of the phenyl rings. Similarly two signals appear in the region of 4.26 – 4.37 ppm due to the hydroxy protons in the para position of the phenyl rings. This is due to the different orientation of the phenyl rings. The signal analysis of ^{13}C NMR data for synthesized compounds in the range of 23.60 – 24.79 ppm is assigned to methylene carbon. The signals at 152.28 – 153.32 ppm and 156.25 – 158.78 ppm are due to C-5 and C-7 Carbons. The absorption in the range of 135.86 – 138.14 ppm is assigned to C-8 Carbon atom and the signal between 164.45 – 167.93 ppm is obviously due to C-9 Carbon [20,24-25]. The absorption in the range of 132.31 – 134.92 ppm is due to C-4 Carbon. The chemical shifts in the range of 141.25 – 143.46 ppm and 139.34 – 142.57 ppm are due to ipso Carbons of the phenyl rings carbons. The chemical shift values between 125.87 – 133.07 ppm are due to aromatic carbons of the phenyl rings. The two signals are obtained at 21.54 and 21.59 ppm for methyl group in the aromatic ring. Similarly two peaks appear 55.10 and 55.12 ppm which corresponds to the orientation of phenyl rings. Thus the molecular structure of the synthesized compound is confirmed through the theoretical behavior of Density Functional Theory studies and is represented in figure 5 through Raman data spectrum.

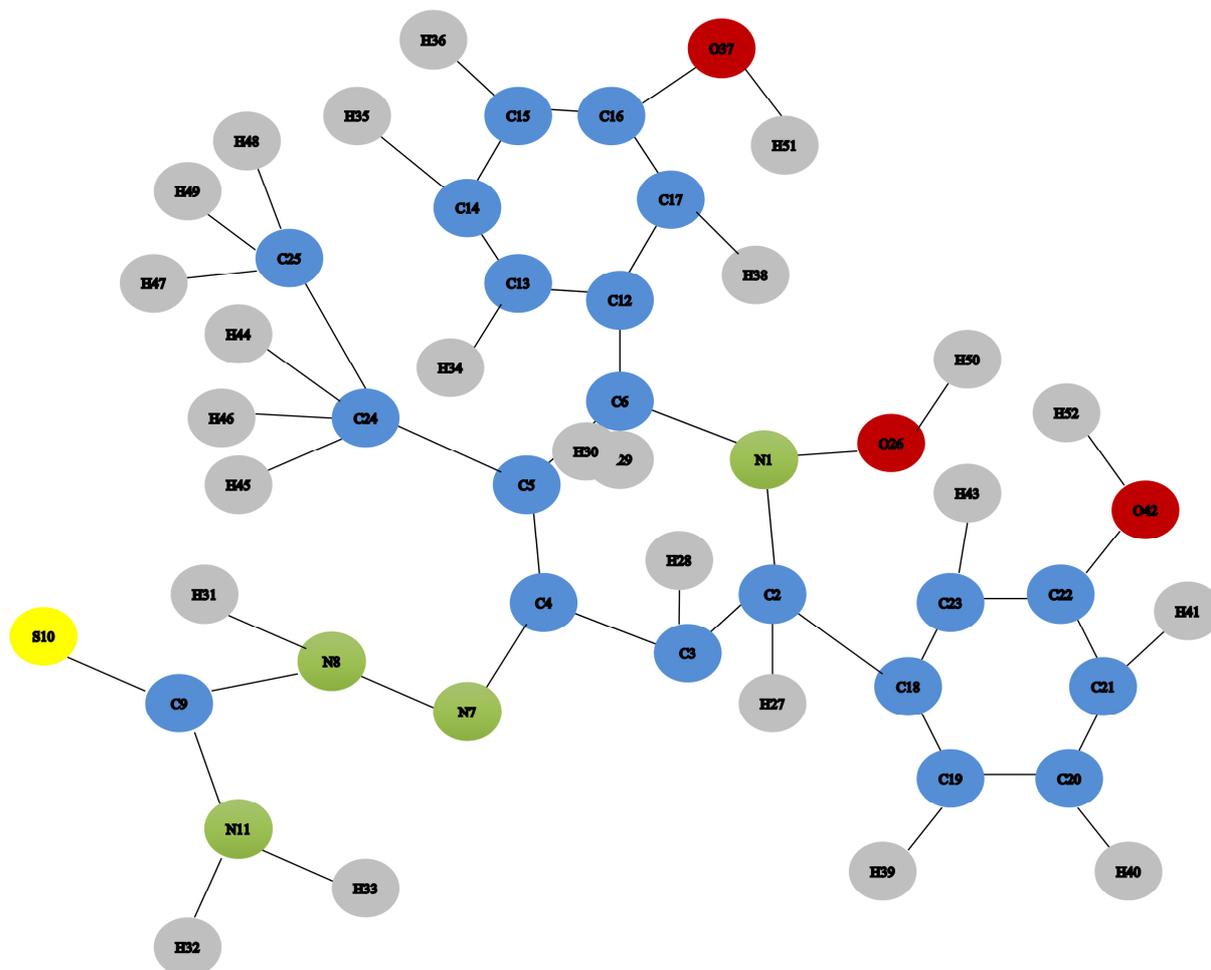


Figure 5: Diagrammatic representation of N-hydroxy-2, 6-bis (p-hydroxyphenyl)-3 isopropyl piperidine-4-one-thiosemicarbazone from the Raman spectral data through Density Functional Theory

CONCLUSION

We have described in this paper a new methodology for synthesis of “N-hydroxy-2, 6-bis (p-hydroxyphenyl)-3 isopropyl piperidine-4-one-thiosemicarbazone” from the spectral data. It constructed the key step in the organic synthesis and promote chemistry dictionary is equal to graph theory. Thus the compound is justified by graphical labeling method. An efficient analysis of mathematical model to chemistry dictionary is carried over in a simple, effective and undirected way. This graph theory methodology has many advantages over conventional method that includes high yield, simple workup, short analysis time, no cross view analysis, no expensive Column Chromatography and finally quick compound identification analysis is done through picturised way. The present method is practically convenient, economic and environmental friendly process for the synthesis of thiosemicarbazone derivatives.

REFERENCES

- [1] J A Gallian; A dynamic survey of graph labelling, *The Electronic Journal of Combinatorics*, **2011**, 18, #DS6.
- [2] Noller; C R Baliah. *J. Am. Chem. Soc.*, **1948**, 70, 3853-3855.
- [3] K Pandiarajan; R T Sabapathy Mohan; M U Hasan, *Magn. Reson. Chem.* **1986**, 24, 312-316.
- [4] G Xu; A Kannan; T L Hartman; H Wargo; K Watson; J A Turpin; R W Buckheit Jr; A A Johnson; Y Pommier; M Cushman, *Bioorg. Med. Chem.* **2002**, 10, 2807-2816.
- [5] D Cheng; S Valente; S Castellano; G Sbardella; R D Santo; R Costi; M T Bedford; A Mai, *Enzyme Selectivity and Cellular Activity. J. Med. Chem.* **2011**, 54, 4928-4932.
- [6] U Heinelt; D Schultheis; S Jager; M Lindenmaier; A Pollex; H S G A Beckmann, *Tetrahedron*, **2004**, 60, 9883-9888.
- [7] S Sharma. *Thiophosgene in Organic Synthesis*, **1978**, 803-820.

- [8] (a) The Chemistry of Cyanates and Their Thioderivatives; Patai, S., Ed.; Wiley: Chichester, **1977**; (b) A K Mukerjee; R Ashare, *Chem. Rev.* **1991**, *91*, 1-24; (c) A R Katritzky; S Ledoux; R M Witek; S K Nair, *J. Org. Chem.* **2004**, *69*, 2976-2982.
- [9] K Selvaraj; P Nanjappan; K Ramalingam; K Ramarajan, *J Chem Soc, Perkin Trans, 11.* **1983**, 49.
- [10] K Ramalingam; K D Berlin; N Satyamurthy; R Sivakumar, *J Org Chem* **44**, **1979**, 471.
- [11] M U Hasan; M Arab; K Pandiarajan; R Sekar; Dale Marko, *Magn Res Chem*, **23.**, **1985**, 292.
- [12] S Foldes; P L Hammer. *Split graphs, in: Proceedings of the 8th South-Eastern Conference on Combinatorics, Graph Theory and Computing.*, **1977**, 311–315.
- [13] E Ruch; I Gutman, *J. Combin. Inform. System Sci.* **4**, **1979**, 285–295.
- [14] R Merris, *Graph Theory*, Wiley Interscience, New York. **2001**.
- [15] D Clark; J Chalmers; P R Griffiths (Eds.), *Handbook of Vibrational Spectroscopy*, Vol. 5, Wiley & Sons, Chichester, **2001**; 3576–3589.
- [16] T Threlfall; J Chalmers, P R Griffiths (Eds.), *Handbook of Vibrational Spectroscopy*, Vol. 5, Wiley & Sons, Chichester, **2001**; 3557–3573.
- [17] J Gross; J Yellen. *Graph theory and its applications*, CRC Press, Baco Raton, **1999**.
- [18] A Kelmans. *On homotopy of connected graphs having the same degree function*, *Discrete Math* **230**. **2001**, 167–187.
- [19] P L Hammer; B Simeone, *Combinatorica* **1**, **1981**, 275–284.
- [20] D J Kleitman; S Y Li. *Stud. Appl. Math.* **54**. **1975**, 283–287.
- [21] S Y Li. *J. Combin. Theory Ser. B* **19**, **1975**, 42–68. [22] A W Marshall; I Olkin. *Inequalities: Theory of Majorization and Its Applications*, Academic Press, Newyork, **1979**.
- [23] J L Gersting; W H Freeman and Company, *Mathematical Structures for Computer Science*, **2007**.
- [24] S R Arikati; U N Peled, Degree sequences and majorization, *Linear Algebra Appl.* **199**, **1994**; 179–211.
- [25] S R Arikati; U N Peled. The realization graph of a degree sequence with majorization gap 1 is Hamiltonian, *Linear Algebra Appl.* **290**, **1999**; 213–235.
- [26] J B Veeramalini; V Narayanan; G Baskar, *Journal of Chemical and Pharmaceutical Research*, **2015**, 7(9):882-888.