On Molecular Graphs with Valencies 1, 2 and 4 with Prescribed Numbers of Bonds*

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In this paper, necessary and sufficient conditions are given for the existence of molecular graph(s) with the prescribed sequence \(m_{11}, m_{12}, m_{14}, m_{22}, m_{24}, m_{44}\), where \(m_{ij}\) denotes the number of edges (bonds) connecting vertices (atoms) of degree \(i\) with vertices of degree \(j\). The main result expressed as Theorem 1 covers the great variety of molecules with valencies 1, 2 and 4.

Key words
molecular graphs
prescribed sequence
molecules with valencies 1, 2, 4

INTRODUCTION

Molecules are conveniently described by graph(s)1–3 and there is an intuitive correspondence between chemical and graph-theoretical notions: atoms are represented by vertices and chemical bonds by edges. The ability of atoms to make chemical bonds, i.e., their valencies, are equivalent to the notion of vertex degrees in a graph.

Regarding the vertex degrees, all \(n\) vertices of \(G\) could be partitioned in \(n_1\) of those having degree 1, \(n_2\) having degree 2, etc., and obviously \(n = n_1 + n_2 + \ldots\). In this way, a unique sequence \(n_1, n_2, \ldots\) is ascribed to each graph. The inverse problem, namely whether there are graph(s) with a prescribed \(n_1, n_2, \ldots\) sequence is a well known and already solved problem in chemistry and graph theory.4,5

Besides the vertex degrees, one could further characterize the connectivity in the graph by specifying how many edges \(m_{ij}\) connect vertices of degree \(i\) with vertices of degree \(j\). Here again an inverse problem could be posed, namely whether there are graph(s) with a prescribed \(m_{ij}\) sequence. Such a question was raised by Gutman6 and was declared to be a difficult one. Here, we answer the question, but only for those graphs whose vertex degrees are 1, 2, and 4, i.e., we offer an answer to whether there are graph(s) with a prescribed sequence \(m_{11}, m_{12}, m_{14}, m_{22}, m_{24}, m_{44}\). This paper gives the necessary and sufficient conditions for \(m_{11}, m_{12}, m_{14}, m_{22}, m_{24}, m_{44}\) to ensure the existence of graph(s) having that sequence, and it reads as:

Theorem 1.
\begin{align}
\{ f(m_{11}, m_{12}, m_{14}, m_{22}, m_{24}, m_{44}) = 1 \} \iff \\
\left( \left[ (m_{11} = 1) \land (m_{12} = 0) \land (m_{14} = 0) \land (m_{22} = 0) \land (m_{24} = 0) \land (m_{44} = 0) \right] \lor \\
\left[ (m_{11} = 0) \land (m_{12} = 0) \land (m_{14} = 0) \land (m_{22} \geq 3) \land (m_{24} = 0) \land (m_{44} = 0) \right] \lor \\
\left[ (m_{11} = 0) \land (m_{12} = 2) \land (m_{14} = 0) \land (m_{24} = 0) \land (m_{44} = 0) \right] \lor \\
\left[ (m_{11} = 0) \land \left( (m_{23} = 0) \lor (m_{12} > 0) \right) \land (m_{14} + m_{24} = 4) \lor \\
\left( m_{22} \land m_{44} = 0 \right) \lor \\
\left( m_{12} + m_{24} \in N_{0} \right) \land (m_{24} - m_{12} \in N_{0}) \land \\
\left( m_{14} + m_{24} + 2m_{44} \leq \frac{4}{2} \right) \land \\
\left( m_{14} + m_{24} + 2m_{44} \geq 2 \right) \right) \right) 
\end{align}

**THE MAIN RESULT**

Let \( m_{11}, m_{12}, m_{14}, m_{22}, m_{24}, m_{44} \in N_{0} \). The aim of this paper is to determine if there is a simple connected graph \( G \) such that each vertex in \( G \) has degree 1, 2 or 4, and such that there are \( m_{ij} \) edges that connect vertices of degree \( i \) with vertices of degree \( j \).

Formally, the existence could be described by function \( f \) defined by:

\[
\begin{align}
\text{if and only if } f(m_{11}, m_{12}, m_{14}, m_{22}, m_{24}, m_{44}) &= 1 \quad (2) \\
\text{if and only if } f(m_{11}, m_{12}, m_{14}, m_{22}, m_{24}, m_{44}) &= 0 \quad (3)
\end{align}
\]

We need the following notation. Let \( G \) be a graph. By \( d_{G}(x) \) we denote the degree of vertex \( x \) in \( G \) and by \( N_{G}(x) \) the set of neighbors of vertex \( x \) in \( G \). Let \( V(G) \) denote the set of vertices of \( G \). For \( V' \subseteq V \) a subgraph of \( G \) induced by \( V' \) is graph \( G' \) such that \( V(G') = V' \) and edges of \( G' \) are the edges of \( G \) with their both endvertices in \( V' \).

Let \( i, j \) be any natural numbers such that \( i \leq j \). Denote by \( \mu_{ij} \) the number of edges in a given \( G \) that connect vertices of degree \( i \) and \( j \). The basic problem to be answered in this paper is to find whether \( \mu_{ij} \)'s coincide with a prescribed sequence \( m_{11}, m_{12}, m_{14}, m_{22}, m_{24}, m_{44} \). The answer is given by Theorem 1.

**PROOF OF THEOREM 1**

We start with a few Lemmas:

**Lemma 1.** – Suppose that \( m_{11} > 0 \). Then:

\[
\begin{align}
f(m_{11}, m_{12}, m_{14}, m_{22}, m_{24}, m_{44}) &= 1 \quad (4) \\
\text{if and only if } m_{11} = 1, m_{12} = 0, m_{14} = 0, m_{22} = 0, m_{24} = 0, m_{44} = 0.
\end{align}
\]

**Proof:** The condition that the graph must be connected implies the claim.

Obviously, this Lemma reflects the fact that there is only one connected graph with adjacent vertices of degree 1, which graph is called the complete graph \( K_{2} \) or path \( P_{2} \).

**Lemma 2.** – Suppose that \( m_{22} > 0 \) and \( m_{11} = 0 \). Then:

\[
\begin{align}
f(m_{11}, m_{12}, m_{14}, m_{22}, m_{24}, m_{44}) &= 1 \quad (5) \\
\text{if and only if } m_{11} = 0, m_{12} = 0, m_{14} = 0, m_{22} = 0, m_{24} = 0, m_{44} = 0.
\end{align}
\]

**Proof:** Suppose that we have \( m_{12} + m_{24} \neq 0 \) and \( f(0, m_{12}, m_{14}, m_{22}, m_{24}, m_{44}) = 1 \).

\[
\begin{align}
\text{if and only if } m_{11}(m_{11} = 1) \lor & \\
\left[ \left( (m_{12} + m_{24} > 0) \land (m_{12} = 0) \land (m_{24} = 0) \land (m_{44} = 0) \land (m_{22} = 0) \land (m_{22} = 3) \right) \right] & \\
& \lor \\
\left[ \left( (m_{12} = 0) \land (m_{24} = 0) \land (m_{22} = 0) \land (m_{44} = 0) \land (m_{22} = 0) \land (m_{22} = 3) \right) \right].
\end{align}
\]

Then there is a simple connected graph \( G \) such that each vertex in \( G \) has one of the following degrees 1, 2, 4, and such that \( \mu_{11}(G) = m_{11}, \mu_{12}(G) = m_{12}, \mu_{14}(G) = m_{14}, \mu_{22}(G) = m_{22}, \mu_{24}(G) = m_{24}, \mu_{44}(G) = m_{44} \). Note that there is a vertex \( x \) such that \( d_{G}(x) = 2 \), because \( m_{12} + m_{24} \neq 0 \).
Let denote \( N_0(x) = \{y, z\} \) and let \( G \) be the following graph:

\[
V(G') = (V(G) \setminus \{x\}) \cup \{v_0, v_1, v_2, ..., v_{m_{22} - 1}, v_{m_{22}}\}
\]

\[
E(G') = (E(G) \setminus \{xy, xz\}) \cup \{[v_0, v_1, v_2, ..., v_{m_{22} - 1}, v_{m_{22}}] \}.
\]

Note that the edge with endpoints \( u \) and \( v \) is denoted by \( uv \). Note further that \( G' \) is obtained from \( G \) by replacing the path \( xyz \) by path \( v_0v_1v_2 \). Also, we have \( m = 22 \).

**Lemma 3.** We have:

\[
E(G') = \left( \bigcup_{i=1}^{k} V(p_i) \right) \cup \{z_1, z_2, ..., z_k \}
\]

**Proof:** Suppose that

\[
f(0, m_{12}, m_{14}, 0, m_{24}, m_{44}) = 1,
\]

holds and that

\[
(m_{12} = 2) \land (m_{14} = 0) \land (m_{24} = 0) \land (m_{44} = 0)
\]

does not hold.

Then, there is a simple connected graph \( G \) such that each vertex in \( G \) has degrees 1, 2, and 4, such that \( \mu_{11}(G) = 0, \mu_{12}(G) = m_{12}, \mu_{14}(G) = m_{14}, \mu_{22}(G) = 0, \mu_{24}(G) = m_{24}, \) and \( \mu_{44}(G) = m_{44}. \) Denote by \( x_1, x_2, ..., x_{m_{12}} \) vertices of degree 1, each of which is adjacent with a vertex of degree 2 and denote by \( y_1, y_2, ..., y_{m_{14}} \) vertices of degree 2, each of which is adjacent with a vertex of degree 1. Also, denote \( N_0(y_i) = \{x_i, z_i\} \) for each \( i = 1, ..., m_{12} \). Note that \( d_G(z_i) = 4 \) for each \( i = 1, ..., m_{12} \).

Let graph \( G' \) be the graph such that:

\[
V(G') = (V(G) \setminus \{y_1, y_2, ..., y_{m_{14}}\}) \cup \{z_1, z_2, ..., z_{m_{12}}\}.
\]

\[
E(G') = (E(G) \setminus \{y_1z_1, ..., y_{m_{14}}z_{m_{14}}\}) \cup \{y_1z_1, ..., y_{m_{14}}z_{m_{14}}\}.
\]

Note that \( G' \) is a simple connected graph such that each vertex of \( G' \) has degree 1, 2, or 4, and \( \mu_{11}(G') = 0, \mu_{12}(G') = m_{12}, \mu_{14}(G') = m_{14}, \mu_{22}(G') = 0, \mu_{24}(G') = m_{24} - m_{12}, \) and \( \mu_{44}(G') = m_{44}. \) Let pick up arbitrary \( m_{12} \) vertices of degree 1 that are adjacent to vertices of degree 4 and denote them by \( x_1, ..., x_{m_{12}} \). Also, denote \( N_0(x_i) = y_i, i = 1, ..., m_{12} \). Let \( G' \) be a graph such that:

\[
V(G') = V(G) \cup \{z_1, z_2, ..., z_{m_{12}}\}.
\]

\[
E(G') = (E(G) \setminus \{y_1z_1, ..., y_{m_{14}}z_{m_{14}}\}) \cup \{y_1z_1, ..., y_{m_{14}}z_{m_{14}}\}.
\]

Note that \( G' \) is a simple connected graph such that each vertex of \( G' \) has degree 1, 2, or 4, and \( \mu_{11}(G') = 0, \mu_{12}(G') = m_{12}, \mu_{14}(G') = m_{14}, \mu_{22}(G') = 0, \mu_{24}(G') = m_{24} - m_{12}, \) and \( \mu_{44}(G') = m_{44}. \) Let

\[
E(C) = E(G) \cup \{y_1z_1, ..., y_{m_{14}}z_{m_{14}}\} \cup \{y_1z_1, ..., y_{m_{14}}z_{m_{14}}\}.
\]
\[ f(0, m_{12}, m_{14}, 0, m_{24} - m_{12}, m_{44}) = 1. \]  

(20)

**Lemma 4.** Let \( k \geq 2 \) and let \( p_1, ..., p_k \in \{0,1,2,3,4\} \), such that \( p_1 \leq p_2 \leq ... \leq p_k \). Let \( q \in \mathbb{N} \) such that \( 2q \leq \sum_{i=1}^k (4 - p_i) \).

If \( p_1 - p_2 \leq 1 \), then there are numbers \( i_1, i_2, ..., i_q, j_1, j_2, ..., j_q \in \{1, ..., k\} \), such that \( i_l \neq j_l \), \( l = 1, ..., q \), and

\[
p_i + \operatorname{card}(i_0 : 1 \leq i_0 \leq q, i_0 = i) + \operatorname{card}(j_0 : 1 \leq j_0 \leq q, j_0 = i) \leq 4, 1 \leq i \leq k. \quad \text{(21)}
\]

Note that \( \operatorname{card} X \) stands for the number of elements in set \( X \).

**Proof:** We prove the claim by induction on \( q \). Suppose that \( q = 1 \). Note that \( p_1, p_2 \leq 3 \), so it is sufficient to take \( i_1 = 1 \) and \( j_1 = 2 \). Now, suppose that the claim holds for \( q \) and let us prove it for \( q + 1 \). Take \( i_{q+1} = 1 \) and \( j_{q+1} = 2 \). Denote \( p_1' = p_1 - 1 \), \( p_2' = p_2 - 1 \) and \( p_i' = p_i \) for each \( 3 \leq i \leq k \). Denote by \( p_1'' \), \( p_2'' \), ..., \( p_k'' \) numbers \( p_1', p_2', ..., p_k' \) sorted in the ascending order. More formally, collections \( \{p_1', p_2', ..., p_k'\} \) and \( \{p_1'', p_2'', ..., p_k''\} \) are equal and \( p_1'' \leq p_2'' \leq ... \leq p_k'' \). Denote by \( \phi \) a bijection such that

\[
p_k'' = p_{\phi(k)}'' .
\]

(22)

Note that \( p_1'' - p_k'' \leq 1 \). So, by the inductive hypothesis, there are numbers \( i_1', i_2', ..., i_q', j_1', j_2', ..., j_q' \in \{1, ..., k\} \) such that \( i_l \neq j_l \), \( l = 1, ..., k \), and

\[
p_i'' + \operatorname{card}(i_0' : 1 \leq i_0' \leq q, i_0' = i) + \operatorname{card}(j_0' : 1 \leq j_0' \leq q, j_0' = i) \leq 4, 1 \leq i \leq k. 
\]

(23)

So, it is sufficient to take numbers

\[
\begin{align*}
i_l &= \phi(i_l'), 1 \leq l \leq q, \\
j_l &= \phi(j_l'), 1 \leq l \leq q,
\end{align*}
\]

and \( i_{q+1} \) and \( j_{q+1} \).

**Lemma 5.** We have

\[
[f(0, 0, m_{14}, 0, m_{24}, m_{44}) = 1] \iff \left[ \left( \left( n_4 \in \mathbb{N} \right) \wedge \left( \frac{m_{44}}{2} \in \mathbb{N} \right) \right) \wedge \left( n_4 - 1 - \frac{n_{44}}{2} \leq m_{44} \leq \frac{n_4}{2} \right) \right] \wedge (n_4 \geq 2) \end{equation}
\]

(26)

where \( n_4 = \frac{1}{4} (m_{14} + m_{24} + 2m_{44}) \).

**Proof:** First, let us prove

\[
\begin{align*}
\left[ \left( \left( n_4 \in \mathbb{N} \right) \wedge \left( \frac{m_{44}}{2} \in \mathbb{N} \right) \right) \wedge \\
\left( n_4 - 1 - \frac{n_{44}}{2} \leq m_{44} \leq \frac{n_4}{2} \right) \right] \wedge (n_4 \geq 2) \end{align*}
\]

(27)

If \( n_4 = 1 \) and \( m_{44} = 4 \), the claim is trivial, so it remains to prove

\[
\begin{align*}
\left[ \left( n_4 \in \mathbb{N} \right) \wedge \left( \frac{m_{44}}{2} \in \mathbb{N} \right) \wedge \\
\left( n_4 - 1 - \frac{n_{44}}{2} \leq m_{44} \leq \frac{n_4}{2} \right) \right] \wedge (n_4 \geq 2) \end{align*}
\]

(28)

It follows from the previous Lemma that it is sufficient to construct graph \( G_0 \) with \( n_4 \) vertices and \( m_{44} \) edges such that its maximal degree \( \Delta(G_0) \) is less or equal to 4 and that there are vertices \( x \) and \( y \) such that the minimal degree \( \delta(G_0) \) equals \( d_{G_0}(x) \) and \( d_{G_0}(y) - d_{G_0}(x) \leq 1 \).

If \( n_4 = 2 \), the claim is trivial, so suppose that \( n_4 \geq 2 \). Denote vertices of \( G_0 \) by \( x, y, z_1, z_2, ..., z_{n_4-2} \). Distinguish two cases:

**Case 1:** \( m_{44} \geq n_4 - 1 \)

Let \( E(G_0) \supseteq \{x z_1, z_1 z_2, ..., z_{n_4-2} z_{n_4-2}, z_{n_4-2} y\} \). Since \( m_{44} \geq n_4 - 1 \), \( G_0 \) can consist of these edges. If \( m_{44} \leq \frac{n_4 - 2}{2} + 2 \), then form arbitrary \( m_{44} - (n_4 - 1) \) edges between vertices \( z_1, z_2, ..., z_{n_4-2} \) and we are done. Otherwise, let \( G_0[z_1, z_2, ..., z_{n_4-2}] \) be a complete graph. Add \( \frac{n_4 - 2}{2} + 2 \) vertices of the form \( x z_i \) and \( \frac{n_4 - 2}{2} + 2 \) vertices of the form \( y z_i \) and the claim is proven in this case. Note that \( [x] \) and \( [y] \) stand for lower and upper integer parts of \( x \), respectively.

**Case 2:** \( m_{44} \leq n_4 - 1 \)

By using the construction of the previous case, we can construct graph \( G' \) such that \( \mu_1(G') = 0, \mu_2(G') = 0, \mu_3(G') = m_{14}, \mu_2(G') = 0, \mu_2(G') = m_{44} - 2(n_4 - 1 - m_{44}) \). Let us take \( n_4 - 1 - m_{44} \) edges that connect vertices
of degree 4 and replace each of them by the path of length 2. This proves Case 2. Let us illustrate this for the case \(m_{14} = 8, m_{24} = 2\) and \(m_{44} = 1\).

Let us prove the claim in the opposite direction. Suppose that:

\[
f(0, 0, m_{14}, 0, m_{24}, m_{44}) = 1. \quad (29)
\]

Then there is a simple connected graph \(G\) such that each vertex in \(G\) has degree 1, 2 or 4 and such that

\[
\mu_1(G) = 0, \mu_2(G) = 0, \mu_4(G) = m_{14}, \mu_8(G) = m_{24}, \mu_9(G) = m_{44}. \quad (30)
\]

If there is only one vertex of degree 4 in \(G\), it can be easily checked that \(m_{14} = 4, m_{24} = 0,\) and that \(m_{44} = 4\) or equivalently \(n_4 = 4\) and \(m_{14} = 4\).

Thus, it remains to prove the claim when there are at least two vertices of degree 4 in \(G\). Note that the number of vertices of degree 4 in \(G\) is:

\[
(m_{14} + m_{24} + 2m_{44}) / 4 = n_4.
\]

So, indeed \(n_4 \in \mathbb{N}\) and \(n_4 \geq 2\). Also, note that the number of vertices of degree 2 in \(G\) is \(m_{24} / 2\) and so this has to be a natural number or zero.

Since \(G\) is connected, it follows that:

\[
n_4 - 1 - m_{24} / 2 \leq m_{44},
\]

and since \(G\) is simple, it follows that

\[
m_{44} \leq \binom{n_4}{2}. \quad (32)
\]

Thus, the Lemma is proven.

By combining the results of Lemmas 1–5, one obtains:
and this finally proves Theorem 1.

CONCLUSIONS

The difficult problem of determining whether there are graph(s) with a prescribed $m_{ij}$ sequence, where $m_{ij}$ denotes how many edges connect vertices of degree $i$ with vertices of degree $j$, is tackled in this paper. We have been able to solve the problem for the case of graphs with degrees 1, 2 and 4 and the findings are given by Theorem 1, which gives the necessary and sufficient conditions for the existence of graph(s) with the prescribed sequence $m_{11}, m_{12}, m_{14}, m_{22}, m_{24}, m_{44}$. Although there is a multitude of chemical moieties covered by our special consideration, it will be of the utmost importance for chemistry to allow also vertices of degree 3, i.e., to consider the existence of molecular graph(s) with prescribed sequences of $m_{ij}$’s, $i, j = 1, 2, 3, 4$.

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REFERENCES

SAŽETAK

O molekularnim grafovima valencije 1, 2 i 4 sa zadanim brojevima veza

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U radu su dani nužni i dovoljni uvjeti za egzistenciju molekularnoga grafa(ova) sa zadanim slijedom $m_{11}$, $m_{12}$, $m_{14}$, $m_{22}$, $m_{24}$, $m_{44}$, gdje $m_{ij}$ označava broj bridova (veza) što povezuju vrhove (atome) stupnjeva $i$ i $j$. Osnovni rezultat iskazan je Teoremom 1 koji je primjenljiv na vrlo široku klasu molekula sa valencijama 1, 2 i 4.