APPLICATION OF BURNSIDE'S LEMMA AND POLYA'S ENUMERATION THEOREM IN THE ENUMERATION OF DISTINCT SUBSTITUTED NAPHTHALENE AND ANTHRACENE COMPOUNDS

Kumsa Guluma Bonsa

A Thesis Submitted to the Department of Applied Mathematics,

College of Applied Natural Science

Presented in Partial Fulfillment of the Requirement for the Degree of Master's in Applied Mathematics (Algebra)

Office of Graduate Studies

Adama Science and Technology University

June, 2025

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Declaration

I hereby declare that this Master Thesis entitled " ***Application of Burnside's lemma and Polya's Enumeration Theorem in the enumeration of distinct substituted naphthalene and anthracene compounds***" is my original work. That is, it has not been submitted for the award of any academic degree, diploma or certificate in any other university. All sources of materials that are used for this thesis have been duly acknowledged through citation.

Name of Student	Signature	Date

Recommendation of Advisors

We, the advisors of this thesis, hereby certify that we have read the revised version of the thesis entitled ***"Application of Burnside's lemma and Polya's Enumeration Theorem in the enumeration of distinct substituted naphthalene and anthracene compounds "*** prepared under our guidance by **Kumsa Guluma Bonsa** submitted in partial fulfillment of the requirements for the degree of Master's of Science in Applied Mathematics. Therefore, we recommend that the submission of revised version of the thesis to the department following the applicable procedures.

Major Advisor	Signature	Date
Co-advisor	Signature	Date

Approval Page

We, the advisors of the thesis entitled ***"Application of Burnside's lemma and Polya's Enumeration Theorem in the enumeration of distinct substituted naphthalene and anthracene compounds"*** and developed by **Kumsa Guluma Bonsa**, hereby certify that the recommendation and suggestion made by the board of examiners are appropriately incorporated into the final version of the thesis.

Major Advisor	Signature	Date
Co-advisor	Signature	Date

Approval of Board of Examiners

We, the undersigned, members of the Board of Examiners of the thesis by **Kumsa Guluma Bonsa**, have read and evaluated the thesis entitled ***"Application of Burnside's lemma and Polya's Enumeration Theorem in the enumeration of distinct substituted naphthalene and anthracene compounds"*** and examined the candidate during the open defense. This is, therefore, to certify that the thesis is accepted for partial fulfilment of the requirement of the degree of Master of Science in Applied Mathematics.

Chairperson	Signature	Date
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Finally, approval and acceptance of the thesis are contingent upon submission of its final copy to the Office of Postgraduate Studies (OPGS) through the Department Graduate committee (DGC) and School Graduate Committee (SGC).

Department Head	Signature	Date
School Dean	Signature	Date
Office of Postgraduate Studies,Dean	Signature	Date

Acknowledgment

I sincerely express my deepest gratitude to my advisor, Dr. Dawit Cherinat, for his generous provision of essential resources and his invaluable guidance and suggestions throughout the preparation and successful completion of my master's thesis. I am also thankful to Dr. Dinkayehu Mengesha for his insightful advice on the analysis. My heartfelt thanks go to my friends for their support and collaboration, which greatly contributed to the timely completion of this work. I would also like to acknowledge, with profound appreciation, the authors of the references and other literature cited in this thesis. Lastly, I am eternally grateful to my parents, whose unwavering support and encouragement have been my guiding light at every step of this journey.

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List of Abbreviations

PET Polya's Enumeration Theorem

PAHs Polycyclic aromatic hydrocarbons

PNAs Polynuclear aromatic hydrocarbons

Abstract

In this thesis, we have used Burnside's lemma and Polya's Enumeration Theorem. Both Burnside's lemma and Polya's Enumeration Theorem are the results of group theory used to solve counting or enumeration problems. While Burnside's lemma counts distinct (non-equivalent) objects under symmetry, Polya's Enumeration Theorem generalizes this by enumerating all possible configurations, tracking both the unique orbits and the multiplicity of each pattern. One of their most well-known uses is in chemical combinatorics, particularly for the enumeration of chemical isomer(substituted) compounds. So, by using them, we have enumerated the distinct substituted naphthalene compounds through substitution of one or more hydrogen atoms with chlorine (Cl) atoms and the number of distinct substituted anthracene compounds by substituting one or more hydrogen atoms with bromine (Br) atoms.

Keywords: *Anthracene compounds, Burnside's lemma, Cycle index, Naphthalene compounds, Polya's Enumeration Theorem.*

CHAPTER ONE

INTRODUCTION

1.1 Background of the study

Burnside's lemma and Polya's Enumeration Theorem are powerful outcomes of group theory that provide systematic methods for counting distinct configurations of objects under symmetry operations (e.g. rotations, reflections) and enumerating all possible patterns along with their frequencies.

Group theory, a branch of Mathematics discovered by Évariste Galois in the 19th century, has been a powerful tool in mathematics. In the beginning, it was used to investigate the solvability of quintic polynomials. Later, group theory has proved its power in many different fields, including combinatorics(Hao, 2023). In combinatorics, group theory plays a pivotal role in simplifying object counting, especially through the use of permutation groups and the concept of group actions.

These tools allow mathematicians to account for symmetries and reduce the complexity of enumerative coloring problems and the necklace problem, both involving rotational or reflectional symmetry (Hao, 2023). As group theory is especially helpful when applied to problems involving symmetry, it is natural to believe that it can be used on two major types of problem in combinatorics. Among a vast number of counting problems, one of the most popular is a necklace enumeration. A cyclic necklace is a coloring in m colors of the vertices of a regular n-gon, where two colorings are equivalent if one can be obtained from the other by a cyclic symmetry (Fel & Zimmels, 2009).

A symmetry of an object is a structure-preserving transformation (like a rotation or reflection) that maps the object onto itself, and the collection of all such symmetries forms a group under composition called its symmetry group. This framework applies universally because any object can be modeled as a structured set, where symmetries are bijections preserving that structure, making symmetry groups a powerful tool across mathematics, chemistry, and physics for analyzing invariant properties under transformations.

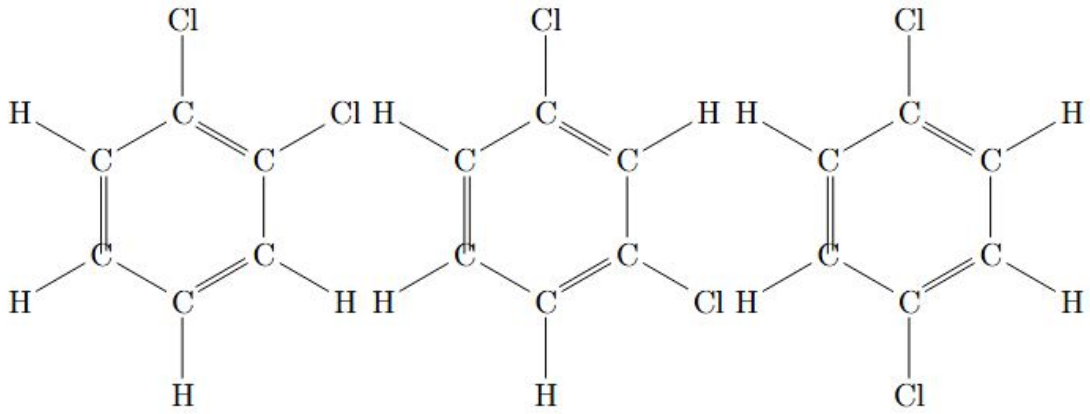
In order to count the number of distinct colorings of an object, we can apply the results of group theory: Burnside's lemma and Polya's Enumeration Theorem. Burnside's lemma, sometimes also called Burnside's counting theorem, the Cauchy-Frobenius lemma or the

orbit-counting theorem (Nasseef, 2016). It provides a formula to count the number of objects, where two objects that are symmetric by rotation or reflection are not categorized as distinct. The theorem was further generalized with the discovery of the Polya's Enumeration Theorem, which expands the theorem to include all numbers of orbits on a set. This theorem not only enumerates the number of distinct objects but also the configurations of each object and its frequency. The result from Polya's enumeration theorem has been extensively used, in particular in the enumeration of chemical isomer compounds (Jin, 2018). Generally, the theorem combines group theory and generating functions to count the number of inequivalent combinatorial objects that form equivalence classes under the action of an algebraic group (Beekman, 2020).

Burnside's lemma and Polya's Enumeration Theorem have interesting applications in chemistry, particularly in understanding the symmetry properties of molecules. In chemistry, a chemical formula can represent more than one molecules due to varying arrangements of the compounds in space. The molecules that have the same chemical formula but different chemical structures are called isomers, and we can use Polya's Enumeration Theorem to enumerate these types of isomers (Jin, 2018).

Let us consider at an example of a chemical compound that exhibits multiple isomers. From the Derivatives of benzene (which formed by replacing the hydrogen atoms by other atoms which is chlorine (Cl)) Dichlorobenzene, formed by four hydrogen and two chlorine atoms, represented by the chemical formula $C_6H_4Cl_2$.

Using Burnside's lemma, we can calculate the number of distinct isomers depending on a given choice of n atoms. But what if we want to impose further restrictions? For instance, how can we determine the number of possible derivatives with a specific number of atoms? Specifically, how many isomers are possible with four hydrogen atoms and two chlorine atoms? To address such problems, we can use Polya's Enumeration Theorem because, in chemistry, Polya's Enumeration Theorem can be used to find isomers(the molecules that have the same chemical formula but different chemical structures) of a given molecule (Bjørge, 2009). Dichlorobenzene has the following isomeric forms (von Bell, 2015):



1,2-Dichlorobenzene **1,3-Dichlorobenzene** **1,4-Dichlorobenzene**

Likewise, in this thesis the problems of enumerating distinct substituted naphthalene and anthracene compounds are discussed. By determining the distinct number of ways of attaching 1 chlorine atom and 7 hydrogen atoms, 2 chlorine atoms and 6 hydrogen atoms, 3 chlorine atoms and 5 hydrogen atoms, ..., and 8 chlorine atoms and no hydrogen atom on the naphthalene compound, and we enumerated them. To do this, we assign numbers 1-8 for the eight carbons as shown in the Figure 1.2 below to obtain its symmetry group.

And also, by determining the distinct number of ways of attaching 1 bromine atom and 9 hydrogen atoms, 2 bromine atoms and 8 hydrogen atoms, 3 bromine atoms and 7 hydrogen atoms, ..., and 10 bromine atoms and no hydrogen atom onto the anthracene compound. To do this, we assign numbers 1-10 for the ten carbons as shown in Figure 1.4 below.

Naphthalene and anthracene belong to a class of organic compounds known as polycyclic aromatic hydrocarbons (PAHs). Also called polynuclear aromatic hydrocarbons (PNAs), condensed ring aromatics, or fused ring systems, these compounds are characterized by having two or more interconnected aromatic rings (Boehm, 1964).

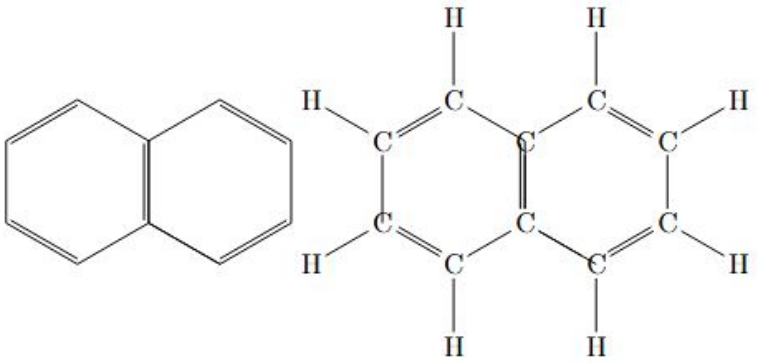


Figure 1.1: Naphthalene structure

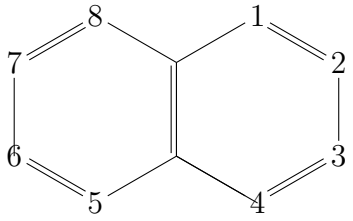


Figure 1.2: Numbering of Naphthalene

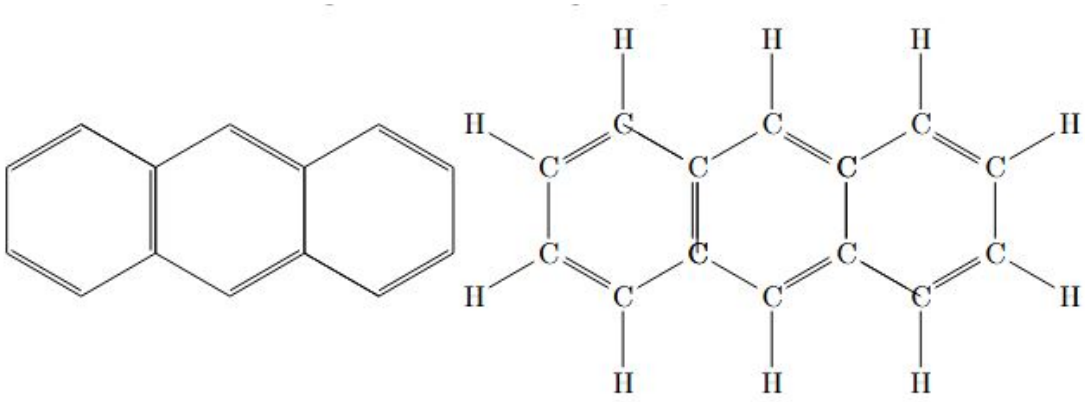


Figure 1.3: Anthracene structure

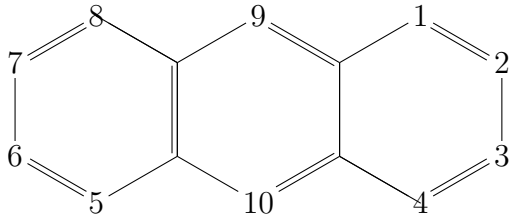


Figure 1.4: Numbering of Anthracene

1.2 Statement of the problem

Numerous mathematical and combinatorial methods have been employed to address enumeration problems in chemistry, particularly concerning molecular structures that exhibit symmetry. Symmetry-based enumeration techniques, such as those utilizing Burnside's lemma and Polya's Enumeration Theorem, have shown significant effectiveness in tackling combinatorial challenges within molecular chemistry. These methods have successfully enumerated various substitution patterns in benzene derivatives, as demonstrated in different journal articles.

However, their application has predominantly been focused on simpler compounds such as listing benzene derivatives, thereby leaving a considerable gap in the analysis of polycyclic aromatic hydrocarbons, such as enumerating distnict substituted naphthalene and anthracene. In comparison to benzene, naphthalene and anthracene present more intricate substitution patterns due to their multi-ring fused structures. The complexity of naphthalene and anthracene substitution patterns poses a formidable combinatorial challenge, particularly regarding questions such as:

- How many distinct substituted naphthalene compounds are there, by substituting one or more hydrogen atoms with 1, 2, 3, ..., and 8 chlorine (Cl) atoms?
- How many distinct substituted anthracene compounds are there, by substituting one or more hydrogen atoms with 1, 2, 3, ..., and 10 bromine (Br) atoms?

To the best of our knowledge, a comprehensive enumeration of distinct substituted naphthalene and anthracene has not yet been systematically documented. Addressing this gap, this thesis develops a rigorous framework using Burnside's lemma and Polya's Enumeration Theorem to classify and count all unique substitution patterns for these polycyclic aromatic hydrocarbons.

1.3 Objectives

1.3.1 General Objective

The general Objective of this study is to use Burnside's lemma and Polya's Enumeration Theorem in the enumeration of distinct substituted naphthalene and anthracene compounds.

1.3.2 Specific Objectives

The specific objectives of this study are to:

- identify the symmetry groups of the Naphthalene and Anthracene.
- compute the fixed points (attachments) across all elements of the symmetry group and apply Burnside's lemma to determine the number of distinct substitutions.
- apply Polya's Enumeration Theorem (PET) to systematically analyze substitution cases.
- listing all distinct substituted naphthalene compounds with $1, 2, 3, \ldots$ and 8 chlorine (Cl) atoms and all distinct substituted anthracene compounds with $1, 2, 3, \ldots$, and 10 bromine (Br) atoms.

1.4 Significance of the Study

The significance of this study are to:

- serve as reference material for scholars working on this area.
- help the researchers as they motivate in the applications of Burnside's lemma and Polya's Enumeration Theorem in chemistry.
- inspire further studies on the enumeration of substituted aromatic compounds and the development of computational tools for symmetry analysis.

1.5 Scope of the study

This thesis focuses on the exhaustive enumeration of all unique substituted Naphthalene and Anthracene using Burnside's lemma and Polya's Enumeration Theorem where their symmetry groups are analyzed, different substitution patterns of common atoms (Cl, Br) are considered, as well as both positional isomerism and symmetry-equivalent positions to avoid over counting, and ultimately provide complete lists of non identical structures classified by degree of substitution.

CHAPTER TWO
LITERATURE REVIEW

Group theory's theoretical importance is underscored by Burnside's lemma and Polya's Enumeration Theorem as fundamental tools for solving symmetry-related enumeration problems. The foundational aspects of Burnside's lemma are explored in Hao (2023) and Hernandez (2013), which analyze orbits, stabilizers, and fixed points in relation to the Orbit-Stabilizer Theorem. Huisinga (2012) further develops this framework by introducing Polya's Enumeration Theorem, including advanced concepts like the cycle index polynomial for symmetry group analysis. These collective works establish group theory as a versatile approach for addressing diverse symmetry challenges.

Burnside's lemma consistently appears in combinatorial studies: Hao (2023) applies it to count unique necklace arrangements and cube face colorings under rotational symmetry, employing Euler's totient function to prevent overcounting; Hernandez (2013) similarly uses the lemma to examine geometric shape colorings, necklace patterns, and even Escher's artwork; while Jin (2018) extends these principles to musical chord structures. Collectively, they demonstrate how Burnside's lemma systematically simplifies enumeration through symmetry operations.

The connection between group theory and chemistry emerges clearly in studies of aromatic compounds. Jin (2018) and Zaka & Çullhaj (2011) highlight how Burnside's lemma and Polya's counting theory enable precise isomer enumeration, particularly for dichlorobenzene configurations and carbon ring derivatives. Tang et al. (2022) broadens this perspective by showing the relevance of group theory to quantum mechanics and crystallography, emphasizing its cross-disciplinary value. These applications reveal the natural alignment between group-theoretic methods and molecular symmetry patterns.

The applications of group theory span beyond chemistry and mathematics into physics, computer science, and the arts. Tang et al. (2022) demonstrates its critical role in physics, especially for quantum mechanics and molecular symmetry analysis. Zaka & Çullhaj (2011) investigates computational applications, particularly algorithm optimization through cyclic groups and the Chinese Remainder Theorem. Parallel work by Hernandez (2013) and Jin (2018) explores creative implementations in music theory and artistic pattern analysis, showcasing the theory's remarkable adaptability across disciplines.

While all these studies share a group theory foundation, their focuses differ significantly. Hao (2023) and Hernandez (2013) emphasize pedagogical examples illustrating Burnside's lemma, while Huisinga (2012) concentrates on advanced mathematical constructs like the cycle index polynomial. Conversely, Tang et al. (2022) and Zaka & Çullhaj (2011) prioritize practical implementations in physics and computer science. This diversity underscores group theory's remarkable flexibility in addressing both theoretical and applied challenges.

Despite these advances, significant gaps persist in applying these methods to complex molecular structures like substituted naphthalene and anthracene. Current research, including Huisinga (2012), Jin (2018), and Zaka & Çullhaj (2011), primarily examines simpler benzene derivatives, leaving more intricate aromatic systems largely unexplored.

Our comprehensive literature review reveals no existing studies that enumerate or catalog distinct substituted naphthalene and anthracene compounds. This thesis therefore addresses this critical gap through systematic application of Burnside's lemma and Polya's Enumeration Theorem.

CHAPTER THREE

PRELIMINARIES

Group Theory

In this chapter, we start by introducing and reviewing several concepts from group theory.

Definition 3.1. *(von Bell, 2015) A group, represented as $(G, *)$, is defined as a non-empty set G that is equipped with a binary operation $*$, which satisfies the following properties:*

(i) ***(Closure)****. For any elements a and b in G, it follows that $a * b \in G$.*

(ii) ***(Associativity)****. For any elements a, b, and c in G, then $a * (b * c) = (a * b) * c$.*

(iii) ***(Identity element)****. There exists an element $e \in G$ such that for every $a \in G$,*

$$e * a = a = a * e.$$

This element e is referred to as the identity element.

(iv) ***(Inverse elements)****. For any element $a \in G$, there exists an element $a^{-1} \in G$ such that*

$$a * a^{-1} = e = a^{-1} * a.$$

The element a^{-1} is known as the inverse element of a.

The group $(G, *)$ is classified as abelian or commutative if it also fulfills the condition:

(v) ***(Commutativity)****. For all elements a and b in G, then $a * b = b * a$ is satisfied.*

The order of the group $(G, *)$ refers to the cardinality of the set G, denoted as $|G|$.

Definition 3.2. *(von Bell, 2015) Let G be a group. A subset H of G is referred to as a subgroup if H, equipped with the same operation as G, satisfies the group axioms. This is typically denoted by $H \leq G$.*

Definition 3.3. *(Huisinga, 2012)* ***Coset of*** H ***in*** G*:Consider* G *as a group and* H *as a subset of* G*. For any element* $a \in G$*, the set* $\{ah \mid h \in H\}$ *is represented as* aH*. Similarly,* Ha *is defined as* $\{ha \mid h \in H\}$*, and* aHa^{-1} *is expressed as* $\{aha^{-1} \mid h \in H\}$*. When* H *qualifies as a subgroup of* G*, the set* aH *is referred to as the left coset of* H *in* G *that includes* a*, while* Ha *is identified as the right coset of* H *in* G *that includes* a*.*

Theorem 3.1. *(Judson, 2020)* ***Lagrange's Theorem*** *: Let* G *be a finite group with* H *as one of its subgroups. The ratio of the order of* G *to the order of* H*, denoted as*

$$\frac{|G|}{|H|} = [G : H],$$

represents the count of distinct left cosets of H *within* G*. This indicates that the number of elements in* H *is a divisor of the number of elements in* G*.*

Proof. (Huisinga, 2012) Let $a_1H, a_2H, \ldots, a_rH$ denote the distinct left cosets of H in G. For each $a \in G$, we have $aH = a_iH$ for some i and $a \in aH$. Thus, each member of G belongs to one of the cosets a_iH. In symbols,

$$G = a_1H \cup \cdots \cup a_rH.$$

Because, the left cosets of H in G partition G Judson (2020), Since these cosets are disjoint,

$$|G| = |a_1H| + |a_2H| + \cdots + |a_rH|.$$

Because $|a_iH| = |H|$ for each i, we have

$$|G| = r|H|.$$

□

Definition 3.4. *(von Bell, 2015) The* ***cyclic group*** C_n *is the group of rotational symmetries of the regular* n*-gon. The* ***dihedral group*** D_n *is the group of rotational and reflective symmetries of a regular* n*-gon.*

Definition 3.5. *(von Bell, 2015) Take a set* X *and a bijective function* $f : X \to X$*. Another name for the function* f *is a* permutation *of* X*. If* $\circ$ *represents the composition of functions and*

$$S_X = \{f : X \to X \mid f \text{ is a permutation of } X\},$$

then $(S_X, \circ)$ *forms a group known as the* symmetric group *of* X*. We call a* **group of permutations** *a subgroup of* $(S_X, \circ)$*. The symmetric group of* X *is represented by* S_n

if $X = \{1, 2, \ldots, n\}$.

There are two conventional ways to encode a permutation $\sigma \in S_n$. *In the first notation, the elements* $1, 2, \ldots, n$ *are listed in parenthesis, and the image they represent is placed beneath them under the permutation* σ *as follows: Let*

$$\sigma = \begin{pmatrix} 1 & 2 & \cdots & n \\ \sigma(1) & \sigma(2) & \cdots & \sigma(n) \end{pmatrix}.$$

For a permutation, the second standard notation is called cycle notation. *Because it is smaller, it will be utilized. A* k*-cycle is a sequence* $(j_1 j_2 \ldots j_k)$ *of elements from* $\{1, 2, \ldots, n\}$ *for which*

$$\sigma(j_1) = j_2, \quad \sigma(j_2) = j_3, \quad \ldots, \quad \sigma(j_{k-1}) = j_k, \quad \sigma(j_k) = j_1$$

Example 1. *(Bjørge, 2009) Let* $X = \{1, 2, 3, 4, 5, 6\}$ *and define a permutation* σ *such that:*

$$\sigma(1) = 4, \quad \sigma(2) = 3, \quad \sigma(3) = 5, \quad \sigma(4) = 1, \quad \sigma(5) = 2, \quad \sigma(6) = 6,$$

hence,

$$1 \to 4 \to 1, \quad 2 \to 3 \to 5 \to 2, \quad 6 \to 6.$$

Thus, we can write σ *as follows:*

$$\sigma = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 4 & 3 & 5 & 1 & 2 & 6 \end{pmatrix} = (1\ 4)(2\ 3\ 5)(6).$$

Group Actions

The notion of group multiplication generalizes to group actions. If G is a group and X is any set, an action of an element $g \in G$ and an element $x \in X$ produces an element $gx \in X$. Many problems in algebra are best understood via group actions. For example, the proofs of Burnside's Counting Theorem are most naturally understood when framed in the language of group actions

Definition 3.6. *(Judson, 2020)* ***Group Action on set****: Let* X *be a set and* G *be a group. A (left) action of* G *on* X *is a map* $G \times X \to X$ *given by* $(g, x) \mapsto gx$*, where:*

1. $ex = x$ *for all* $x \in X$*, and*

2. $(g_1g_2)x = g_1(g_2x)$ *for all* $x \in X$ *and all* $g_1, g_2 \in G$.

Definition 3.7. *(Huisinga, 2012)* ***Stabilizer of a Point****: Let* G *be a group of permutations of a set* X*. For each* $x \in X$*, the stabilizer of* x *in* G *is defined as*

$$stab_G(x) = \{g \in G \mid gx = x\}.$$

The set $\text{stab}_G(x)$*, which consists of elements in* G *that fix the element* $x \in X$*, is not only a subset of* G *but also forms a subgroup. It is guaranteed to be nonempty, since the identity element of* G *always fixes* x*. Moreover, if* g *and* h *are elements of* $\text{stab}_G(x)$*, then both satisfy* $gx = x$ *and* $hx = x$*.*

$$(gh^{-1})x = g(h^{-1}x) = gx = x,$$

which confirms that $gh^{-1} \in stab_G(x)$*.*

Definition 3.8. *(Huisinga, 2012)* ***Orbit of a Point****: Let* G *be a group of permutations of a set* X*. For each* $x \in X$*, let*

$$orb_G(x) = \{gx \mid g \in G\}.$$

Definition 3.9. *(Huisinga, 2012)* ***Elements Fixed by*** g*: For any group* G *of permutations on a set* X *and any* $g \in G$*, we let*

$$fix(g) = \{x \in X \mid gx = x\}.$$

This set is called the elements fixed by g*.*

Theorem 3.2. *(Huisinga, 2012)* ***Orbit-Stabilizer Theorem****: Let* G *be a finite group of permutations of a set* X*. Then, for any* $x \in X$*,*

$$|G| = |orb_G(x)||stab_G(x)|.$$

Proof. We know that $|G|/|\text{stab}_G(x)|$ is the number of distinct left cosets of $\text{stab}_G(x)$ in G by Lagrange's Theorem. Define a correspondence

$$T : G \times X \to X$$

by $T((g, x)) = gx$. If there is a one-to-one correspondence between the left cosets of $\text{stab}_G(x)$ and the elements in the orbit of x, we are done.

To show that T is well-defined, we must show that if $\alpha\text{stab}_G(x) = \beta\text{stab}_G(x)$, then

$\alpha x = \beta x$. But $\alpha \text{stab}_G(x) = \beta \text{stab}_G(x)$ implies $\alpha^{-1}\beta \in \text{stab}_G(x)$, so that $(\alpha^{-1}\beta)x = x$ and, therefore, $\beta x = \alpha x$.

Because these arguments can be reversed from the last step to the first step, T is one-to-one. To show T is onto $\text{orb}_G(x)$, let $j \in \text{orb}_G(x)$. Then $\alpha x = j$ for some $\alpha \in G$, and $T(\alpha \text{stab}_G(x)) = \alpha x = j$. Thus, T is onto. □

Burnside's lemma

Burnside's lemma (named in honour of William Burnside), also known as the cauchy-frobenius lemma, the lemma of Burnside or the orbit-counting theorem, is a result in group theory which is sometimes useful in counting orbits of a group action. It gives a formula for counting the number of objects in which two objects that are symmetric through rotation or reflection are not considered as different object (Jin, 2018).

Theorem 3.3. *(Huisinga, 2012)* ***(Burnside's lemma)****:If G is a finite group of permutations on a set X, then the number of orbits of G on X is:*

$$\frac{1}{|G|} \sum_{g \in G} |\mathit{fix}(g)|.$$

Burnside's Lemma can be described as finding the number of distinct orbits by taking the average size of the fixed sets.

Proof. Let n denote the number of pairs (g, x), with $g \in G$, $x \in X$, and $gx = x$. We begin by counting these pairs in two ways. First, for each particular $g \in G$, the number of such pairs is exactly $|\text{fix}(g)|$, as x runs over X. So,

$$n = \sum_{g \in G} |\text{fix}(g)|. \tag{1}$$

Second, for each particular $x \in X$, observe that $|\text{stab}_G(x)|$ is exactly the number of pairs of the form (g, x), as g runs over G. So,

$$n = \sum_{x \in X} |\text{stab}_G(x)|. \tag{2}$$

We know that if x and t are in the same orbit of G, then $\text{orb}_G(x) = \text{orb}_G(t)$ and $|\text{stab}_G(x)| = |\text{stab}_G(t)|$. So if we choose $t \in X$, sum over $\text{orb}_G(x)$, and appeal to

Theorem (3.2), we have

$$\sum_{t \in \text{orb}_G(x)} |\text{stab}_G(t)| = |\text{orb}_G(x)||\text{stab}_G(x)| = |G|. \tag{3}$$

Finally, by summing over all the elements of G, one orbit at a time, it follows from Equations (1), (2), and (3) that

$$\sum_{g \in G} |\text{fix}(g)| = \sum_{x \in X} |\text{stab}_G(x)| = |G| \times (\text{number of orbits}),$$

and then we are done. □

Polya's Enumeration Theorem

Polya's Enumeration Theorem, also known as Redfield–Polya's Theorem, is a powerful generalization of Burnside's lemma which takes symmetry into account when counting mathematical objects (Bjørge, 2009). For the example of Necklace colorings, Burnside's lemma will tell us how many distinct colorings exist, while Polya's theorem will provide details on each color configuration within each coloring.

Definition 3.10. ***Cycle Index****: Let G be a group whose elements are permutations of X, where $|X| = k$. We will define a polynomial with k variables $x_1, x_2 ... x_k$ with non-negative coefficients to create a product $x_1^{b1}, x_2^{b2}, ... x_k^{bk}$ (Jin, 2018) for each $g \in G$*
If $\{b_1, b_2, b_3, \dots\}$ is the type of g then the polynomial:

$$P_G(x_1, x_2, ...x_k) = \frac{1}{|G|} \sum_{g \in G} x_1^{b_1} x_2^{b_2} \cdots x_k^{b_k}$$

is called the cycle index *of G (Huisinga, 2012). This formula is very similar to Burnside's Lemma, but now we specify how many of each cycle there are as we differentiate between the cycles of different length (Jin, 2018).*

Theorem 3.4. *(Huisinga, 2012)* ***Polya's Enumeration Formula.*** *Let X be a non-empty set and G be a group of permutations of X that acts to induce an equivalence relation on the colorings of X. The inventory of nonequivalent colorings of X using colors $c_1, c_2, \dots, c_m$ is given by the generating function*

$$P_G\left(\sum_{j=1}^{m} c_j, \sum_{j=1}^{m} c_j^2, \dots, \sum_{j=1}^{m} c_j^k\right),$$

where k corresponds to the largest cycle length.

So the inventory of colorings of X using three colors, A, B, and C, is given by

$$P_G\Big((A+B+C),(A^2+B^2+C^2),\ldots,(A^k+B^k+C^k)\Big).$$

Example 2. *(Huisinga, 2012) Figure 3.1 shows the benzene molecule. A hydrogen atom is joined to each of the six carbon atoms that make up its ring. The same approach that we would use to count different six-bead necklaces may be used to this one because of its "flat" structure. Benzene derivatives are created by substituting additional atoms or groups of atoms for the hydrogen atoms.*

Dichlorobenzenes, where hydrogens can be replaced by chlorines, will be our initial topic of discussion. We shall consider the dihedral group D_6 as group G since the molecule remains unchanged whether rotated or flipped. It has the following components:

$$R_0, R_{60}, R_{120}, R_{180}, R_{240}, R_{300}, F_0, F_{30}, F_{60}, F_{90}, F_{120}, \text{and } F_{150}$$

where:

$$R_0 = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 1 & 2 & 3 & 4 & 5 & 6 \end{pmatrix} = (1)(2)(3)(4)(5)(6)$$

$$R_{60} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 2 & 3 & 4 & 5 & 6 & 1 \end{pmatrix} = (1\ 2\ 3\ 4\ 5\ 6)$$

$$R_{120} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 3 & 4 & 5 & 6 & 1 & 2 \end{pmatrix} = (1\ 3\ 5)(2\ 4\ 6)$$

$$R_{180} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 4 & 5 & 6 & 1 & 2 & 3 \end{pmatrix} = (1\ 4)(2\ 5)(3\ 6)$$

$$R_{240} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 5 & 6 & 1 & 2 & 3 & 4 \end{pmatrix} = (1\ 5\ 3)(2\ 6\ 4)$$

$$R_{300} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 6 & 1 & 2 & 3 & 4 & 5 \end{pmatrix} = (1\ 6\ 5\ 4\ 3\ 2)$$

$$F_0 = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 1 & 6 & 5 & 4 & 3 & 2 \end{pmatrix} = (2\ 6)(3\ 5)$$

$$F_{30} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 2 & 1 & 6 & 5 & 4 & 3 \end{pmatrix} = (1\ 2)(3\ 6)(4\ 5)$$

$$F_{60} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 3 & 2 & 1 & 6 & 5 & 4 \end{pmatrix} = (1\ 3)(4\ 6)$$

$$F_{90} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 4 & 3 & 2 & 1 & 6 & 5 \end{pmatrix} = (1\ 4)(2\ 3)(5\ 6)$$

$$F_{120} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 5 & 4 & 3 & 2 & 1 & 6 \end{pmatrix} = (1\ 5)(2\ 4)$$

$$F_{150} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 6 & 5 & 4 & 3 & 2 & 1 \end{pmatrix} = (1\ 6)(2\ 5)(3\ 4)$$

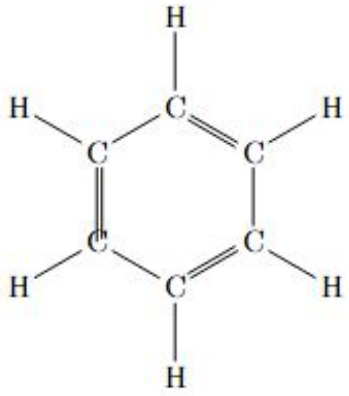


Figure 3.1: The benzene molecule

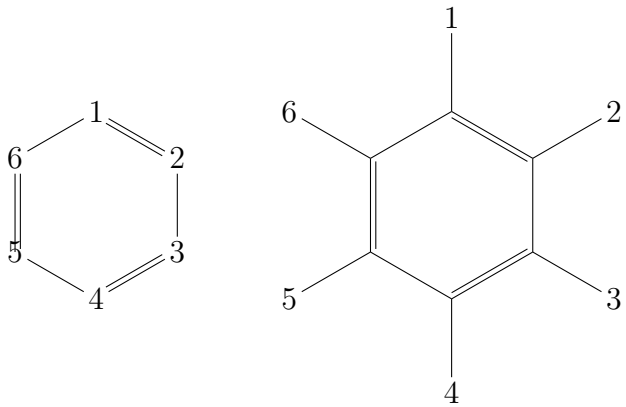


Figure 3.2: Numbering of benzene and Numbered substitution positions

Table 3.1: Number of cycles of g (cyc(g)), values of |fix(g)|, types of g and cycle index of $g \in D_6$

$g \in D_6$	cyc(g)	$\lvert fix(g)\rvert$	type of g	cycle index
(1)(2)(3)(4)(5)(6)	6	n^6	(6,0,0,0,0,0)	x_1^6
(1 2 3 4 5 6)	1	n^1	(0,0,0,0,0,1)	x_6^1
(1 3 5)(2 4 6)	2	n^2	(0,0,2,0,0,0)	x_3^2
(1 4)(2 5)(3 6)	3	n^3	(0,3,0,0,0,0)	x_2^3
(1 5 3)(2 6 4)	2	n^2	(0,0,2,0,0,0)	x_3^2
(1 6 5 4 3 2)	1	n^1	(0,0,0,0,0,1)	x_6^1
(1)(2 6)(3 5)(4)	4	n^4	(2,2,0,0,0,0)	$x_1^2x_2^2$
(1 4)(2 3)(5 6)	3	n^3	(0,3,0,0,0,0)	x_2^3
(1 6)(2 5)(3 4)	3	n^3	(0,3,0,0,0,0)	x_2^3
(1 2)(3 6)(4 5)	3	n^3	(0,3,0,0,0,0)	x_2^3
(1 3)(4 6)(2)(5)	4	n^4	(2,2,0,0,0,0)	$x_1^2x_2^2$
(1 5)(2 4)(3)(6)	4	n^4	(2,2,0,0,0,0)	$x_1^2x_2^2$

Now by using Burnside's lemma ($n = 2$) we obtain the total number of distinct isomers:

$$\frac{1}{|D_6|}\sum_{g\in D_6}|fix(g)| = \frac{1}{12}\left[2^6 + 3(2^4) + 4(2^3) + 2(2^2) + 2(2)\right] = \frac{156}{12} = 13$$

Thus, there are 13 unique molecules.

And, we then have the cycle index of D_6 is:

$$P_{D_6}(x_1, x_2, ...x_6) = \frac{1}{12}\left(x_1^6 + 4x_2^3 + 2x_3^2 + 3x_1^2x_2^2 + 2x_6\right). \tag{3.1}$$

When n distinct atoms are used, the total number of unique isomers can be calculated by substituting all x_i by n as:

$$P_{D_6}(n, n, \ldots, n) = \frac{1}{12}\left(n^6 + 2n^2 + 4n^3 + 3n^4 + 2n\right)$$

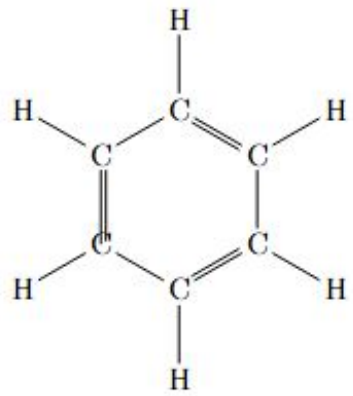
However, it is helpful to substitute the specific weights of interest if we wish to find the number of isomers of a given type.

To obtain the desired enumeration in the case of *dichlorobenzenes*, we substitute $x_i =$

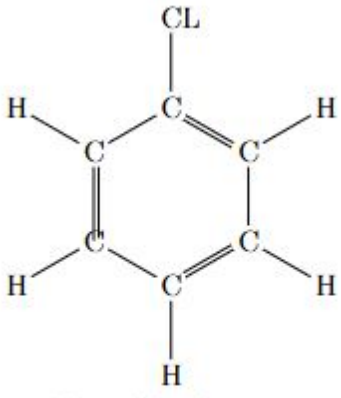
$(H^i + \mathrm{Cl}^i)$ for each $i \in \{1, 2, \ldots, 6\}$.

$$
\begin{aligned}
&P_{D_6}((H + \mathrm{Cl}), (H^2 + \mathrm{Cl}^2), (H^3 + \mathrm{Cl}^3), \ldots, (H^6 + \mathrm{Cl}^6)) \\
&\quad = \frac{1}{12}\Big((H + \mathrm{Cl})^6 + 4(H^2 + \mathrm{Cl}^2)^3 + 2(H^3 + \mathrm{Cl}^3)^2 \\
&\qquad + \ 3(H + \mathrm{Cl})^2(H^2 + \mathrm{Cl}^2)^2 + 2(H^6 + \mathrm{Cl}^6)\Big) \\
&\quad = H^6 + H^5\mathrm{Cl} + 3H^4\mathrm{Cl}^2 + 3H^3\mathrm{Cl}^3 + \ 3H^2\mathrm{Cl}^4 + H\mathrm{Cl}^5 + \mathrm{Cl}^6 \qquad (3.2)
\end{aligned}
$$

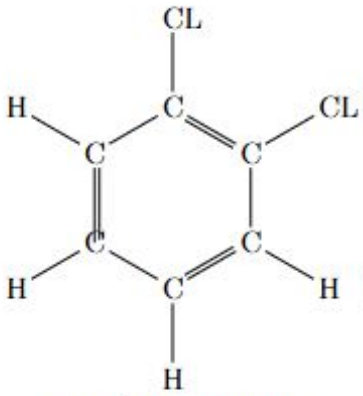
The coefficients in equation 3.2 represent how many isomers exist for that chemical formula. In this case, the coefficient of H^5Cl, H^4Cl^2, H^3Cl^3, H^2Cl^4, and HCl^5 means that there is only one monochlorobenzene it self, there are three isomers of dichlorobenzene, there are three isomers of trichlorobenzene, there are three isomers of tetrachlorobenzene, and there is only one pentachlorobenzene, respectively.



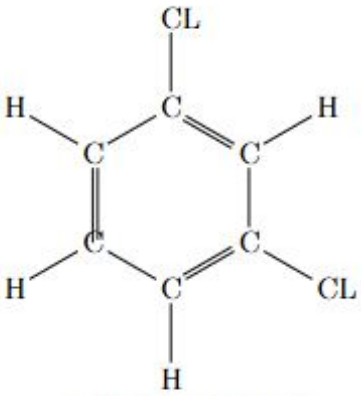
Benzene



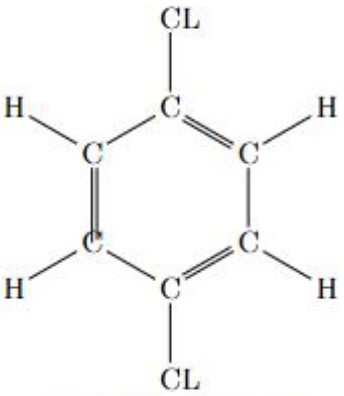
Monochlorobenzene



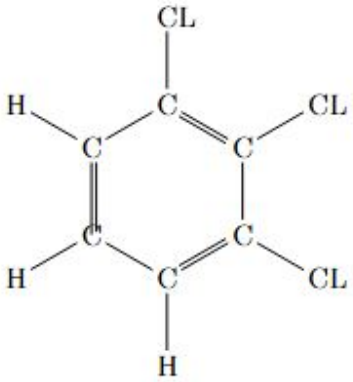
1,2-dichlorobenzene



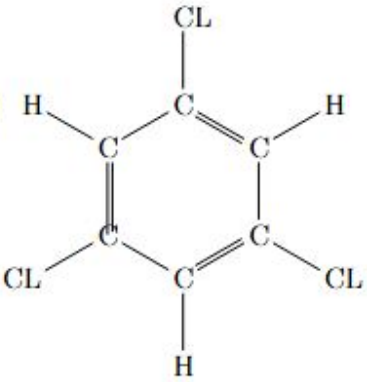
1,3-dichlorobenzene



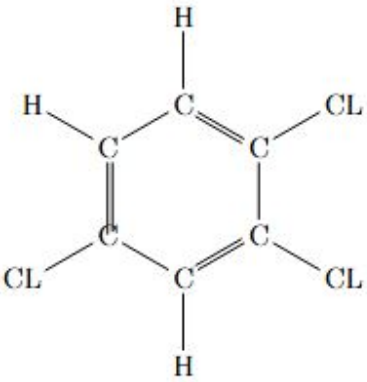
1,4-dichlorobenzene



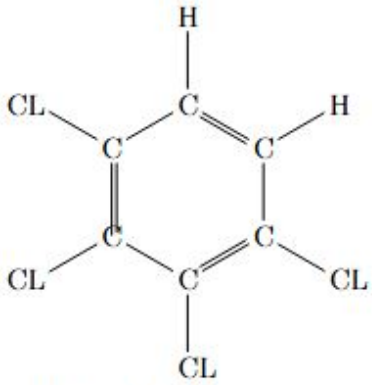
1,2,3-trichlorobenzene



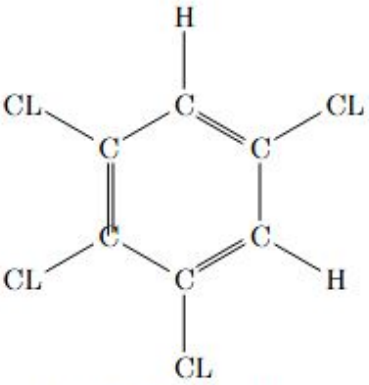
1,3,5-trichlorobenzene



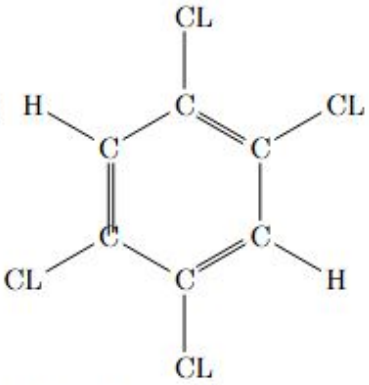
2,3,5-trichlorobenzene



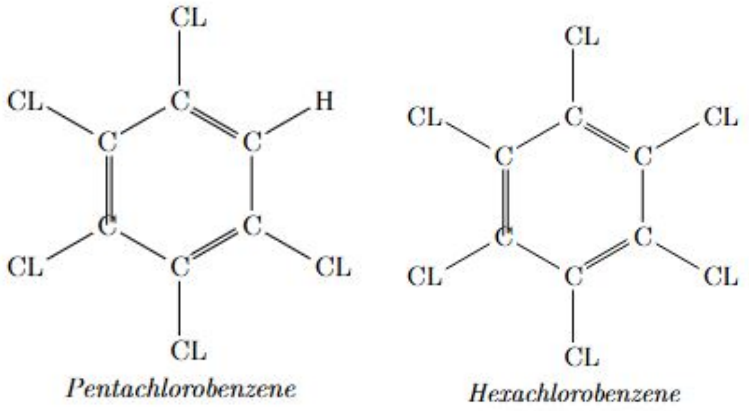
1,2,3,4-tetrachlorobenzene



1,2,3,5-tetrachlorobenzene



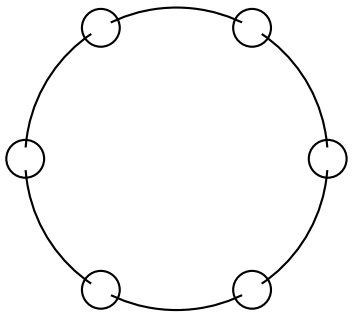
1,2,4,5-tetrachlorobenzene



Example 3. *Regular polygons with colored vertices are sometimes referred to as necklaces, and the vertices are termed beads. PET can be used to enumerate the number of beaded necklaces with n colors (von Bell, 2015). The other one is that enumerating all possible configurations of two chlorine and four hydrogen atoms on a benzene ring is mathematically equivalent to solving a two-color necklace problem, where the colors represent substituents and the necklace's symmetry accounts for molecular rotations and reflections.*

Now, we can solve this problem: (Hernandez, 2013) A jeweler would like to make necklaces containing six beads, each of which could be black or yellow. How many unique necklaces can they make?

The goal of this issue is to figure out how many different necklaces can be created with six beads, each of which can be black or yellow. Burnside's lemma, a method for counting different objects under group symmetries, is used to solve this. We treat the necklace's symmetries as components of the dihedral group D_6 by considering each bead as a vertex of a hexagon. This group captures the necklace's symmetries with six rotations and six reflections. Burnside's lemma allows us to count the number of different colorings that remain after taking into consideration the symmetries in D_6, which can change one of the beads' colorings into another.



The total number of bead colorings is $2^6 = 64$, assuming each bead can independently be black or yellow. However, because the necklace has rotational and reflective

symmetries, many of these colorings are equivalent under the symmetries of D_6. By numbering the beads and using Burnside's Lemma, we determine that the number of distinct necklaces is equal to the number of orbits of the dihedral group D_6 acting on the set of colorings.

An orbit consists of all colorings that can be transformed into one another by applying the symmetries of D_6. Thus, the distinct colorings correspond to the distinct orbits of the group, which accounts for the fact that certain colorings that appear different initially are actually the same under symmetry.

This can be seen as follows:

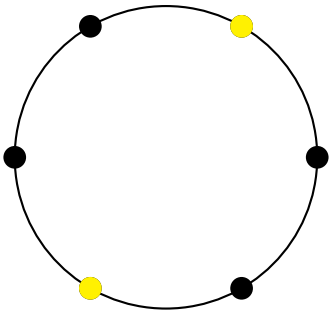


Figure 3.3: Necklace 1

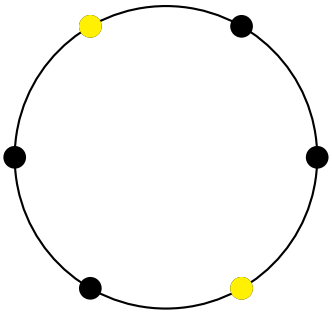


Figure 3.4: Necklace 2

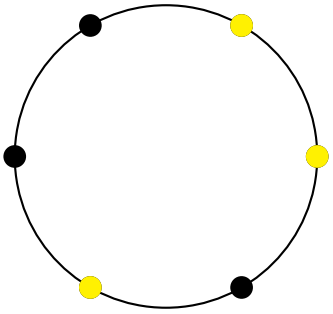


Figure 3.5: Necklace 3

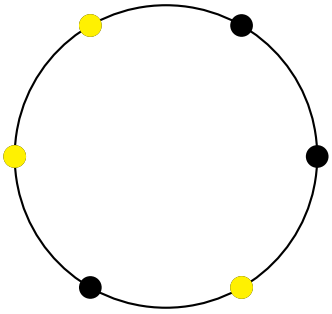


Figure 3.6: Necklace 4

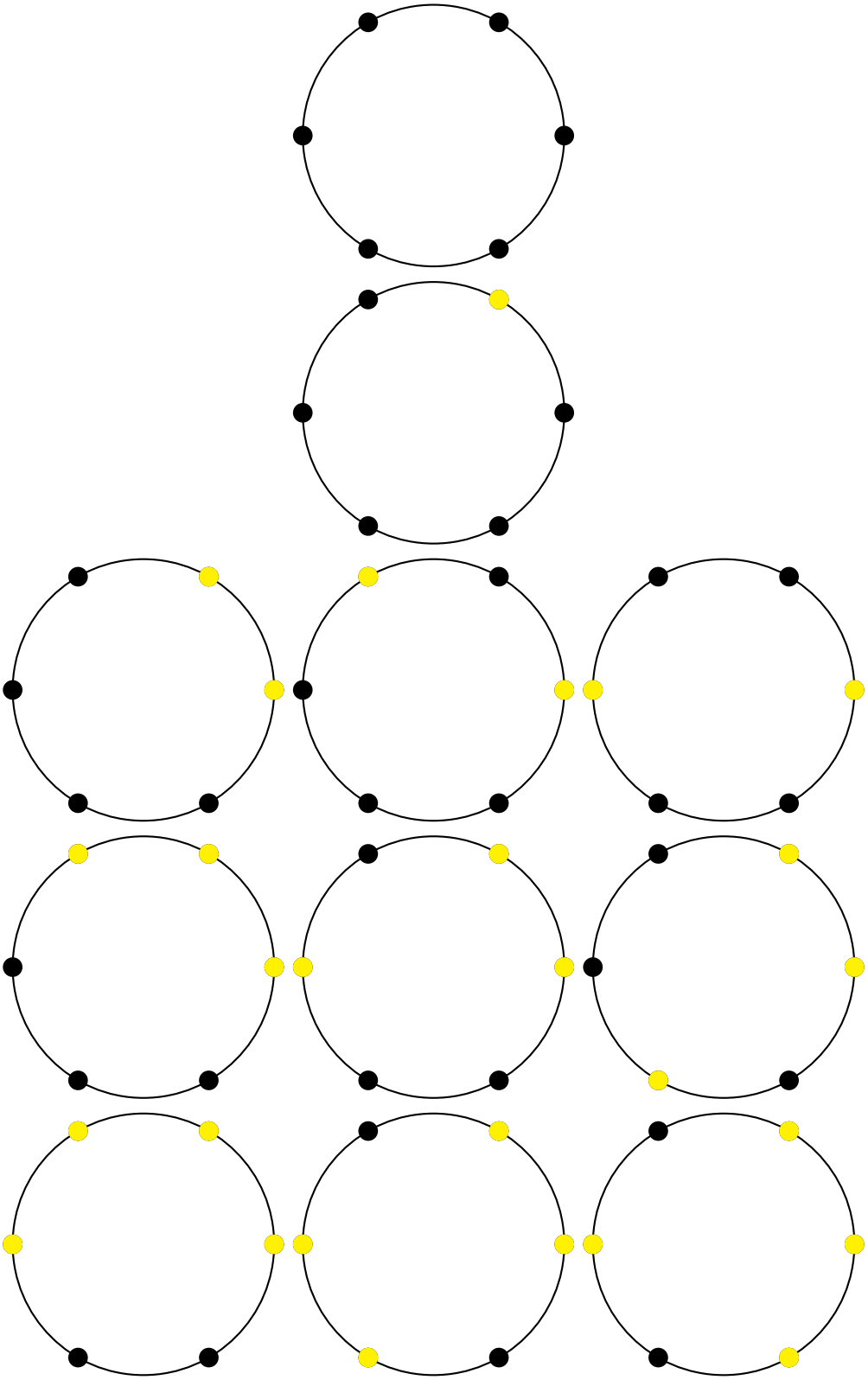
From the above Necklaces, Necklace 1 is equivalent to Necklace 2 and Necklace 3 is equivalent to Necklace 4.

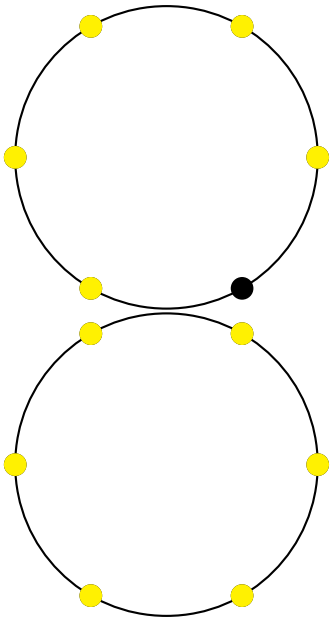
Therefore, from the above Table 3.1 again we can determine the number of unique or distinct $n = 2$ vertex colorings, and hence the number of unique necklaces that can be made is:

$$\frac{1}{|D_6|}\sum_{g\in D_6}|fix(g)| = \frac{1}{12}\left[2^6 + 3(2^4) + 4(2^3) + 2(2^2) + 2(2)\right] = \frac{156}{12} = 13$$

Thus, there are 13 unique options for necklaces.

Therefore, by substituting x_i by $(B^i + Y^i)$ for each $i = \{1, 2, \ldots, 6\}$ in the Equation 3.1 they can make 1 necklace using all black beads, 1 necklace with 5 black beads and 1 yellow bead, 3 necklaces with 4 black beads and 2 yellow beads, 3 necklaces with 3 black beads and 3 yellow beads, 3 necklaces with 2 black beads and 4 yellow beads, 1 necklace with 1 black bead and 5 yellow beads, and 1 necklace using all yellow beads.





CHAPTER FOUR

RESULT AND DISCUSSION

4.1 Application

In this section, we give some application of Burnside's lemma and Polya's Enumeration Theorem to the enumeration of distinct substituted naphthalene and anthracene compounds.

4.1.1 Problems:

Problem 1: The aromatic hydrocarbon naphthalene ($C_{10}H_8$) is made up of two linearly fused benzene rings that contain eight hydrogen atoms and ten carbon atoms (Jia & Batterman, 2010). Through the replacement of one or more hydrogen atoms with chlorine atoms, how many distinct substituted naphthalene compounds are there?

The symmetry group G of naphthalene can be determined by analyzing its molecular structure by numbering it, or as in the Figure 4.2. The flips are done along the lines in Figure 4.1, and the rotations should be obvious.

so, it contains the following elements:

$$R_0 = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\ 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \end{pmatrix} = (1)(2)(3)(4)(5)(6)(7)(8)$$

$$R_{180} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\ 5 & 6 & 7 & 8 & 1 & 2 & 3 & 4 \end{pmatrix} = (1\ 5)(2\ 6)(3\ 7)(4\ 8)$$

$$V = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\ 8 & 7 & 6 & 5 & 4 & 3 & 2 & 1 \end{pmatrix} = (1\ 8)(2\ 7)(3\ 6)(4\ 5)$$

$$H = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\ 4 & 3 & 2 & 1 & 8 & 7 & 6 & 5 \end{pmatrix} = (1\ 4)(2\ 3)(5\ 8)(6\ 7)$$

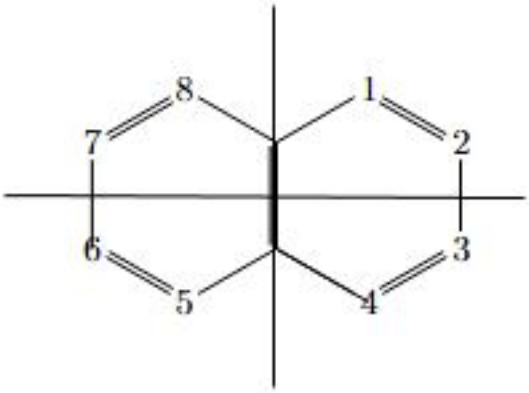


Figure 4.1: The axes for V and H

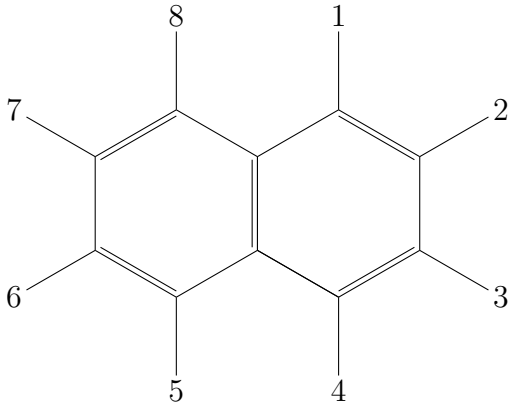


Figure 4.2: Numbered substitution positions on naphthalene

We have $2^8 = 256$ possible attachments as follows: where X be the set of 8 numbered substitution positions to which atoms are attached as shown in Figure 4.2, C the collection of atoms for this situation$C = \{H,\ Cl\}$, and G the symmetry group acting on $X = \{1, 2, 3, 4, 5, 6, 7, 8\}$. Define an attachment as a function $k : X \to C = \{H, Cl\}$ that assigns an atom to each numbered substitution position. Let's K denote the set of all such attachments.

$K =$ { HHHHHHHH, ClHHHHHHH, HClHHHHHH, HHClHHHHH, HHHClHHHH, HHHHClHHH, HHHHHClHH, HHHHHHClH, HHHHHHHCl, ClClHHHHHH, HClClHHHHH, HHClClHHHH, HHHClClHHH, HHHHClClHH, HHHHHClClH, HHHHHHClCl, ClHClHHHHH, ClHHClHHHH, ClHHHClHHH, ClHHHHClHH, ClHHHHHClH, ClHHHHHHCl, HClHClHHHH, HClHHClHHH, HClHHHClHH, HClHHHHClH, HClHHHHHCl, HHClHClHHH, HHClHHClHH, HHClHHHClH, HHClHHHHCl, HHHClHClHH, HHHClHHClH, HHHClHHHCl, HHHHClHClH, HHHHClHHCl, HHHHHClHCl, ClClClHHHHH, HClClClHHHH, HHClClClHHH,

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Some orbits of $k \in K$ under symmetry group $G = \{R_0,\ R_{180},\ V,\ H\}$:

$$\mathrm{orb}_G(HHHHHHHH) = \Big\{HHHHHHHH\Big\}$$

$$\mathrm{orb}_G(ClHHHHHHH) = \begin{Bmatrix} ClHHHHHHH, \\ HHHClHHHH, \\ HHHHClHHH, \\ HHHHHHHCl \end{Bmatrix}$$

$$\mathrm{orb}_G(HClHHHHHH) = \begin{Bmatrix} HClHHHHHH, \\ HHClHHHHH, \\ HHHHHClHH, \\ HHHHHHClH \end{Bmatrix}$$

$$\mathrm{orb}_G(ClClHHHHHH) = \begin{Bmatrix} ClClHHHHHH, \\ HHClClHHHH, \\ HHHHClClHH, \\ HHHHHHClCl \end{Bmatrix}$$

$$\mathrm{orb}_G(ClHClHHHHH) = \begin{Bmatrix} ClHClHHHHH, \\ HClHClHHHH, \\ HHHHClHClH, \\ HHHHHClHCl \end{Bmatrix}$$

$$\mathrm{orb}_G(ClHHClHHHH) = \begin{Bmatrix} ClHHClHHHH, \\ HHHHClHHCl \end{Bmatrix}$$

$$\mathrm{orb}_G(ClHHHClHHH) = \begin{Bmatrix} ClHHHClHHH, \\ HHHClHHHCl \end{Bmatrix}$$

$$\mathrm{orb}_G(ClHHHHClHH) = \begin{Bmatrix} ClHHHHClHH, \\ HClHHClHHH, \\ HHHClHHClH, \\ HHClHHHHCl \end{Bmatrix}$$

$$\mathrm{orb}_G(ClHHHHHClH) = \begin{Bmatrix} ClHHHHHClH, \\ HClHHHHHCl, \\ HHClHClHHH, \\ HHHClHClHH \end{Bmatrix}$$

$$\mathrm{orb}_G(ClHHHHHHCl) = \begin{Bmatrix} ClHHHHHHCl, \\ HHHClClHHH \end{Bmatrix}$$

$$\mathrm{orb}_G(HClClHHHHH) = \begin{Bmatrix} HClClHHHHH, \\ HHHHHClClH \end{Bmatrix}$$

$$\mathrm{orb}_G(HClHHHClHH) = \begin{Bmatrix} HClHHHClHH, \\ HHClHHHClH \end{Bmatrix}$$

$$\mathrm{orb}_G(HClHHHHClH) = \begin{Bmatrix} HClHHHHClH, \\ HHClHHClHH \end{Bmatrix}$$

$$\mathrm{orb}_G(ClClClHHHHHH) = \begin{Bmatrix} ClClClHHHHHH, \\ HClClClHHHH, \\ HHHHClClClH, \\ HHHHHClClCl \end{Bmatrix}$$

$$\mathrm{orb}_G(ClClHClHHHH) = \begin{Bmatrix} ClClHClHHHH, \\ HHHHClClHCl, \\ HHHHClHClCl, \\ ClHClClHHHH \end{Bmatrix}$$

$$\mathrm{orb}_G(ClClHHClHHH) = \begin{Bmatrix} ClClHHClHHH, \\ ClHHHClClHH, \\ HHClClHHHCl, \\ HHHClHHClCl \end{Bmatrix}$$

and so on.

But we have to know that if $k_1 \in \mathrm{orb}_G(k_2)$ then $k_2 \in \mathrm{orb}_G(k_1)$. This result is based on the existence of inverses in a group.

Fixed attachments by $g \in G$ in K:

$fix(R_0) = K$

$fix(R_{180})$ = {HHHHHHHH, ClHHHClHHH, HClHHHClHH,HHClHHHClH,HHHClHHHCl, ClClHHClClHH, ClHClHClHClH, ClHHClClHHCl, HClClHHClClH, HClHClHClHCl, HHClClHHClCl,ClClClHClClClH,ClClHClClClHCl,HClClClHClClCl,ClHClClClHClCl, ClClClClClClClCl}

$fix(V)$ = {HHHHHHHH,ClHHHHHHCl,HClHHHHClH,HHClHHClHH,HHHClClHHH, ClClHHHHClCl,HClClHHClClH,HHClClClClHH,ClHClHHClHCl,ClHHHClHHCl, HClHClClHClH,ClClClHHClClCl,ClClHClClHClCl,HClClClClClClH,ClHClClClClHCl, ClClClClClClClCl}

$fix(H)$ = {HHHHHHHH,ClHHClHHHH,HClClHHHHH,HHHHClHHCl,HHHHHClClH, ClClClClHHHH,HClClHHClClH,HHHHClClClCl,HClClHClHHCl,ClHHClClHHCl, ClHHClHClClH,ClClClClHClClH,HClClClHClClCl,ClHHClClClClCl,ClClClClClHHCl, ClClClClClClClCl}

By using Burnside's lemma, we can easily determine the number of distinct attachments corresponding to unique substituted naphthalene compounds. for $(n = 2)$:

Table 4.1: Number of cycles of g (cyc(g))), values of $|\text{fix}(g)|$, types of g and cycle index of $g \in G$ symmetry group of naphthalene

$g \in G$	cyc(g)	$\lvert fix(g)\rvert$	type of g	cycle index
(1)(2)(3)(4)(5)(6)(7)(8)	8	n^8	(8,0,0,0,0,0,0,0)	x_1^8
(1 5)(2 6)(3 7)(4 8)	4	n^4	(0,4,0,0,0,0,0,0)	x_2^4
(1 8)(2 7)(3 6)(4 5)	4	n^4	(0,4,0,0,0,0,0,0)	x_2^4
(1 4)(2 3)(5 8)(6 7)	4	n^4	((0,4,0,0,0,0,0,0)	x_2^4

$$\frac{1}{|G|}\sum_{g\in G}|fix(g)| = \frac{1}{4}\left[n^8 + 3(n^4)\right] = \frac{1}{4}\left[2^8 + 3(2^4)\right]$$
$$= \frac{1}{4}\left[256 + 3(16)\right] = \frac{304}{4} = 76 \quad (4.1)$$

Thus, there are 76 distinct substituted naphthalene compounds.

Since Burnside's lemma cannot fully resolve this enumeration problem, we now employ Polya's Enumeration Theorem for further analsis.
The cycle index of G is:

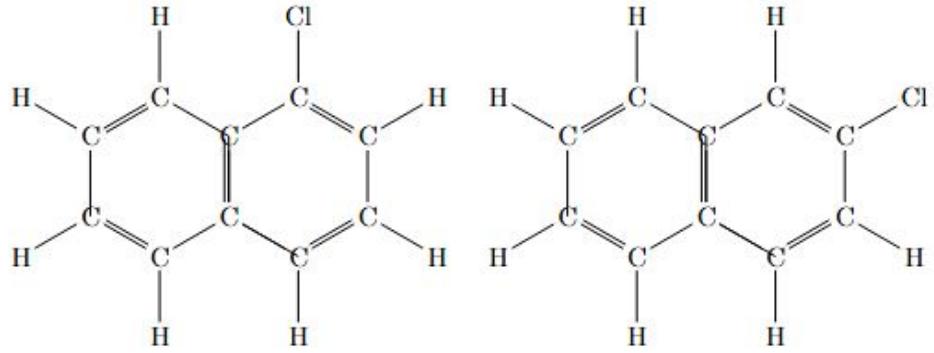
$$P_G(x_1, x_2, ...x_8) = \frac{1}{4}\left(x_1^8 + 3x_2^4\right). \quad (4.2)$$

Now, we can get the details information of this distinct substituted compounds by substituting x_i by $H^i + Cl^i$ in equation 4.2 for each $i = \{1, 2, \ldots, 8\}$:

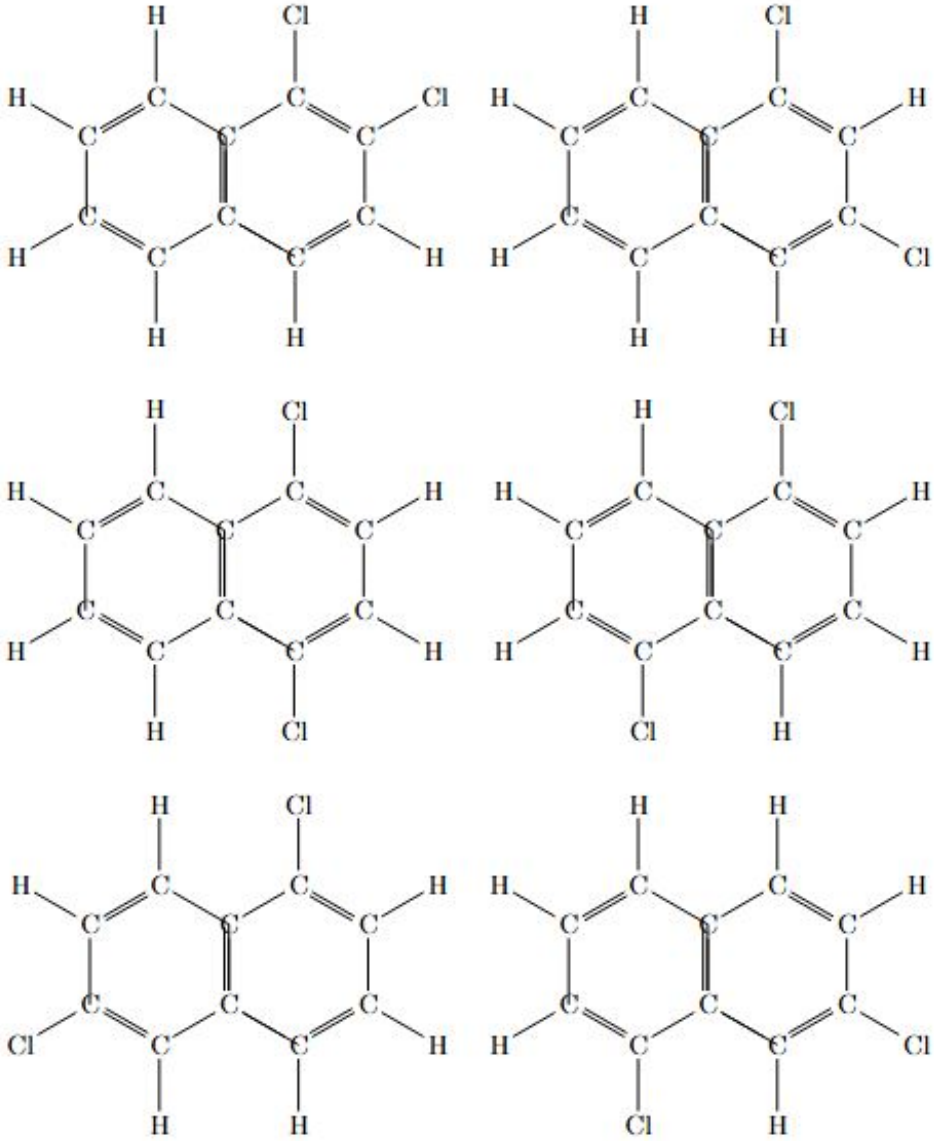
$$\begin{aligned} &P_G((H + \text{Cl}), (H^2 + \text{Cl}^2), (H^3 + \text{Cl}^3), \ldots, (H^8 + \text{Cl}^8)) \\ &= \frac{1}{4}\Big((H + \text{Cl})^8 + 3(H^2 + \text{Cl}^2)^4\Big) \\ &= H^8 + 2H^7\text{Cl} + 10H^6\text{Cl}^2 + 14H^5\text{Cl}^3 + 22H^4\text{Cl}^4 \\ &\quad + \ 14H^3\text{Cl}^5 + 10H^2\text{Cl}^6 + 2H\text{Cl}^7 + \text{Cl}^8 \end{aligned} \quad (4.3)$$

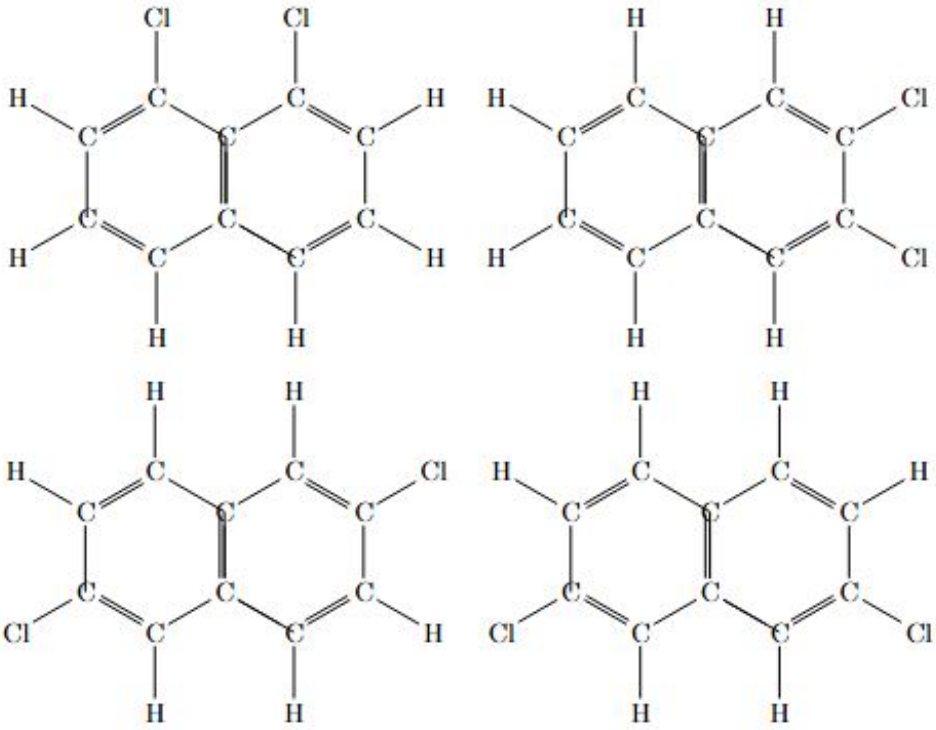
The coefficients of each term of equation 4.3 represents that how many distinct substituted naphthalene compounds with $1, 2, 3, ...,$ and 8 chlorine (Cl) are there.

Therefore, the coefficient of H^7Cl indicates that there are 2 distinct substituted naphthalene compounds (chloronaphthalene) with one chlorine, as listed below:

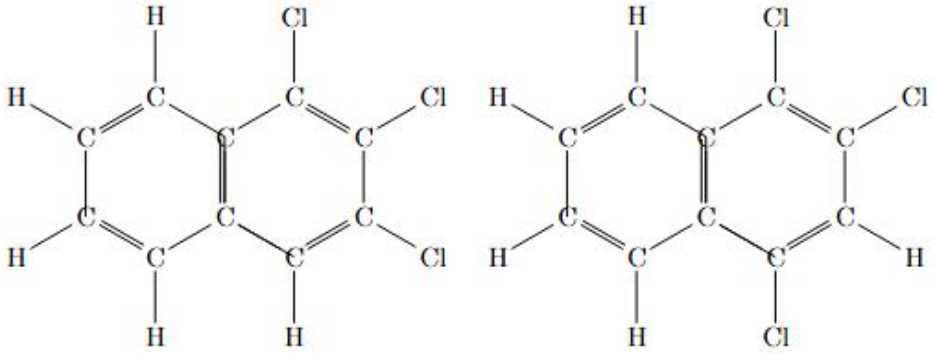


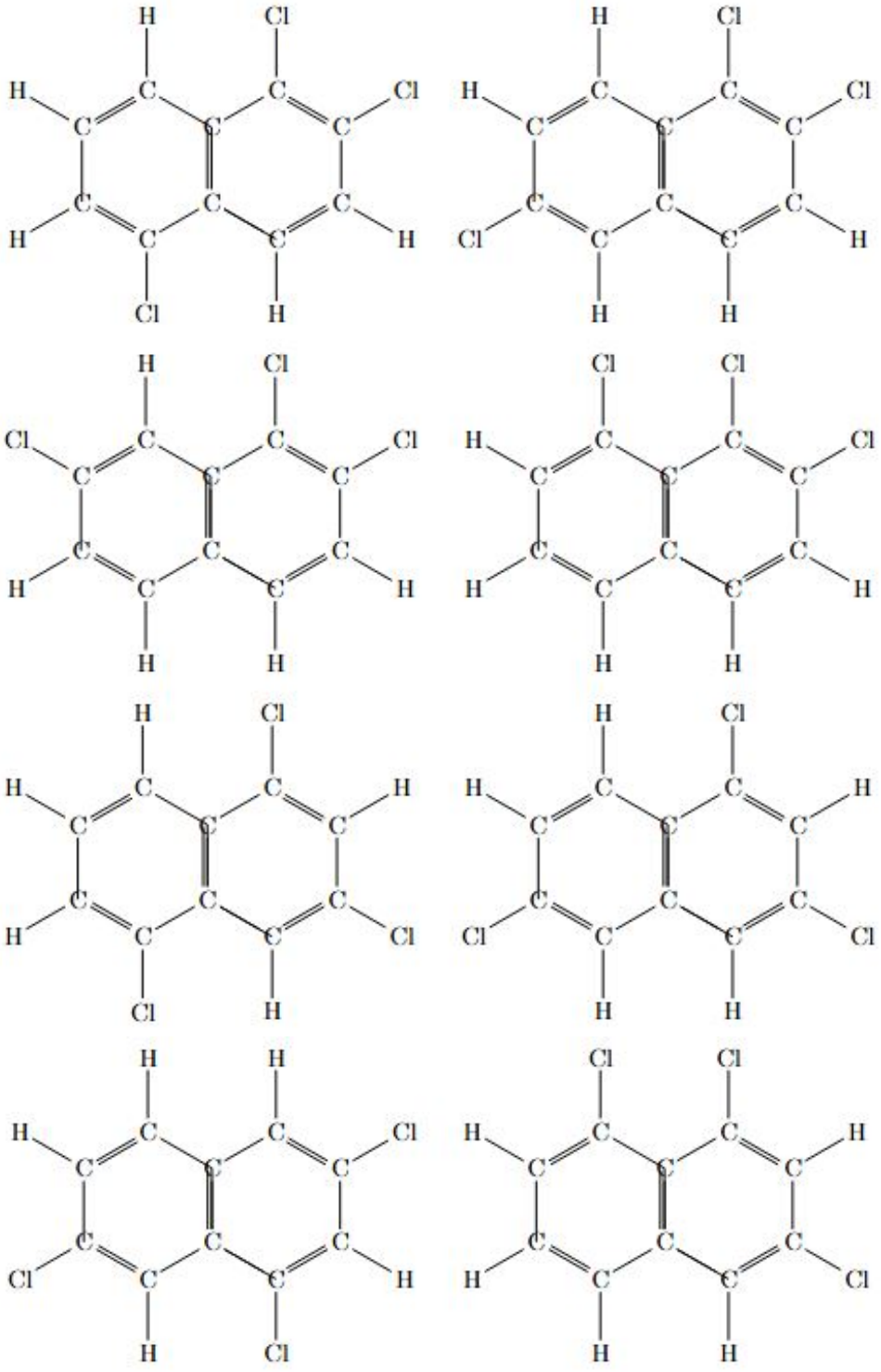
The coefficient of H^6Cl^2 indicates that there are 10 distinct substituted naphthalene compounds (dichloronaphthalene) with two chlorines, as listed below:

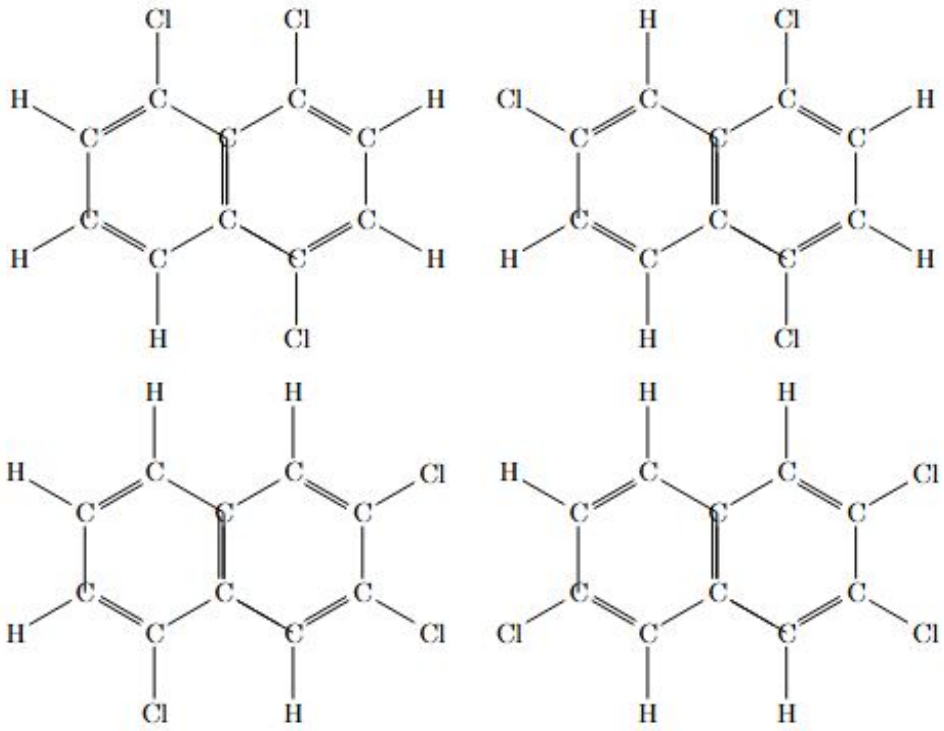




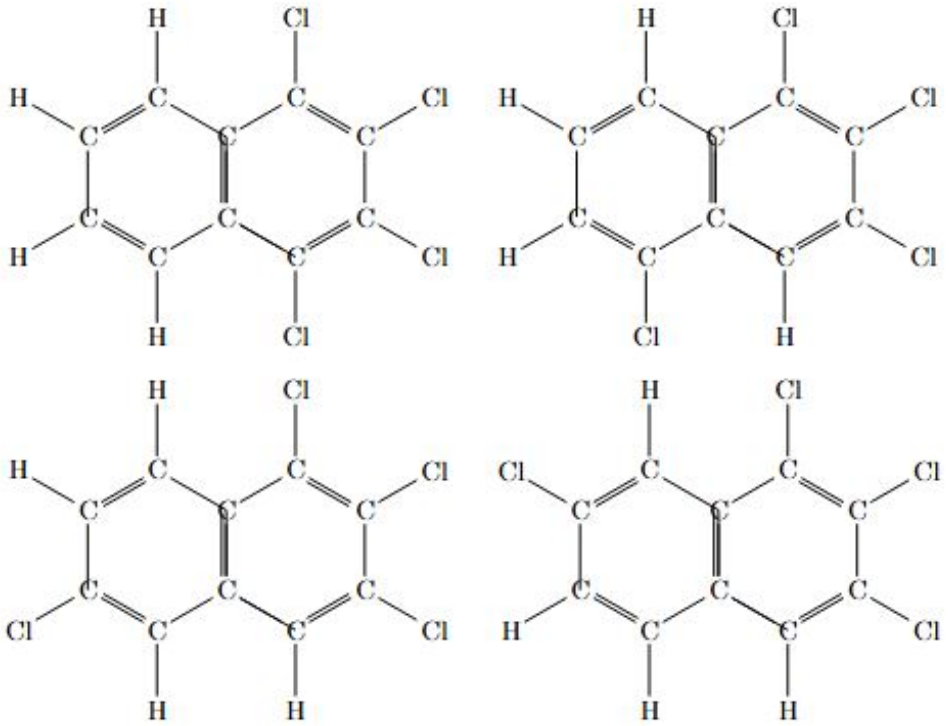
The coefficient of H^5Cl^3 indicates that there are 14 distinct substituted naphthalene compounds (trichloronaphthalene) with three chlorines, as listed below:

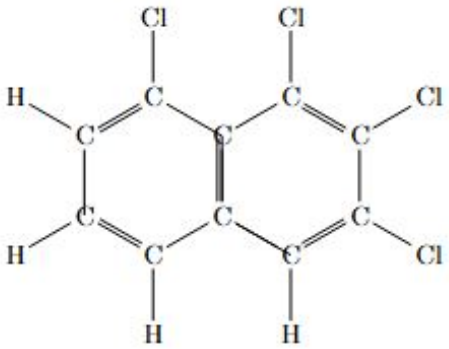


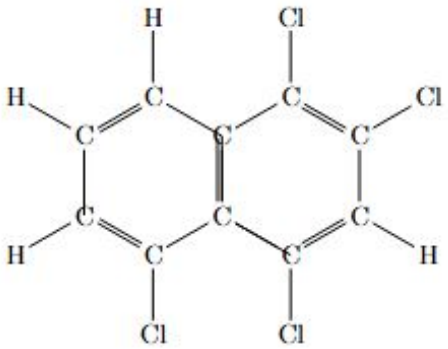


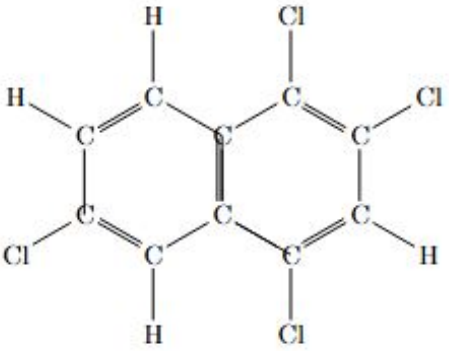


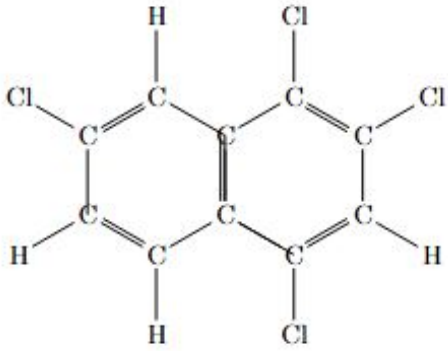
The coefficient of H^4Cl^4 indicates that there are 22 distinct substituted naphthalene compounds (tetrachloronaphthalene) with four chlorines, as listed below:

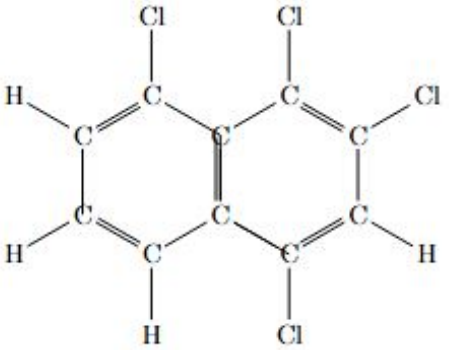


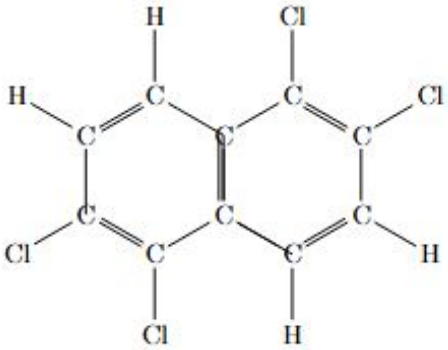


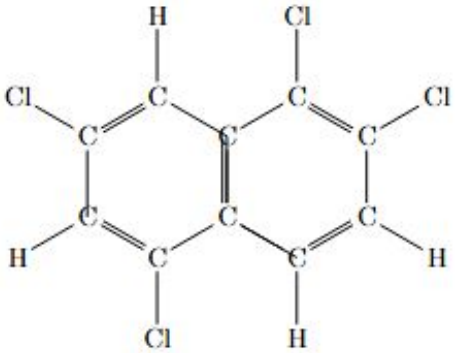


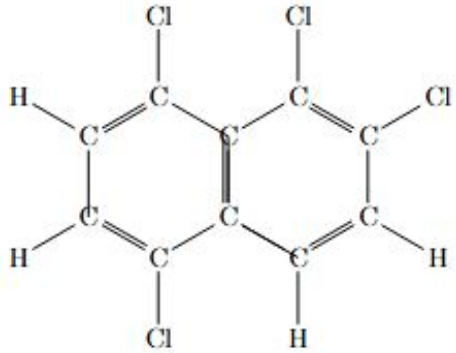


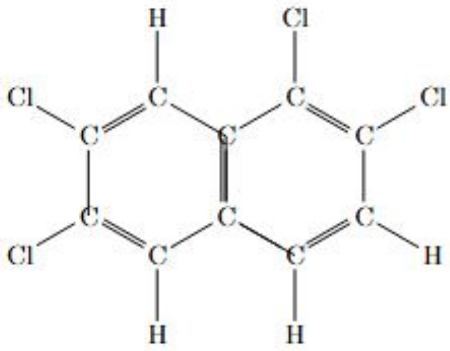


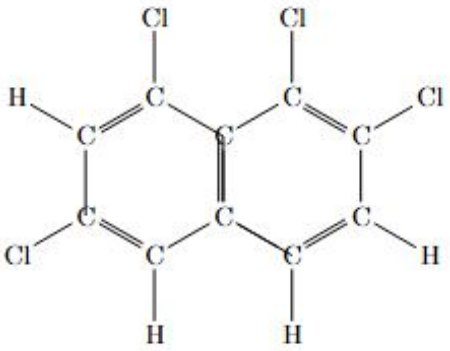


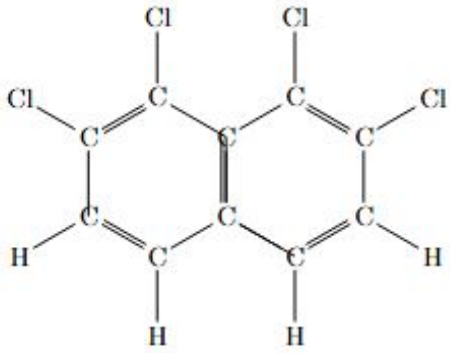


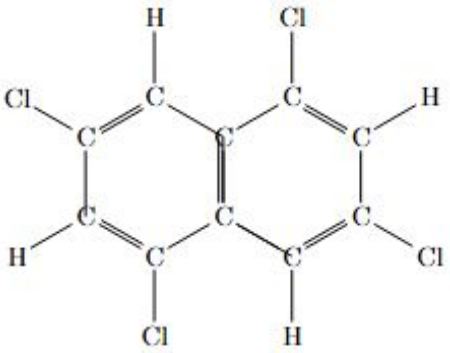


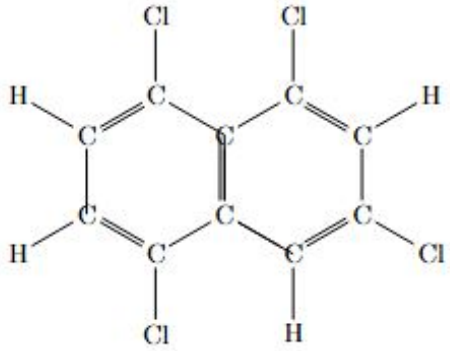


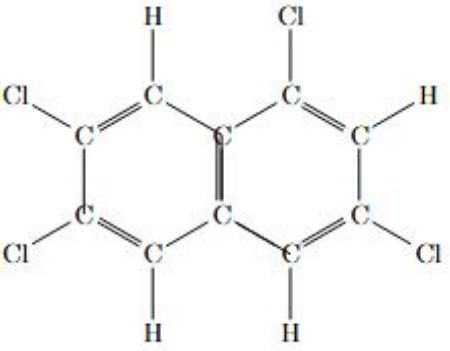


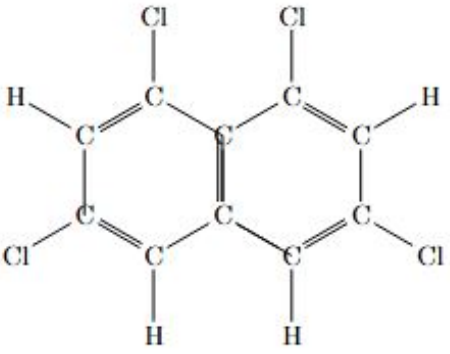


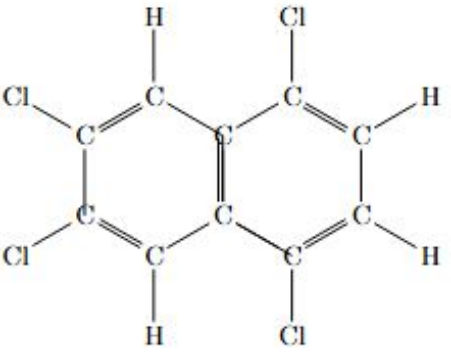


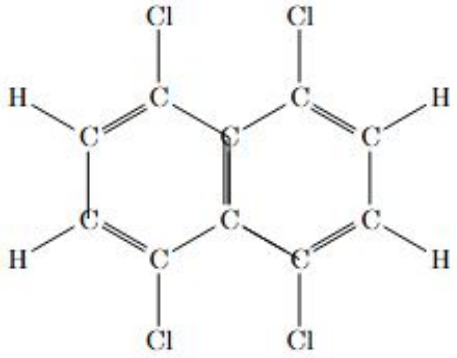
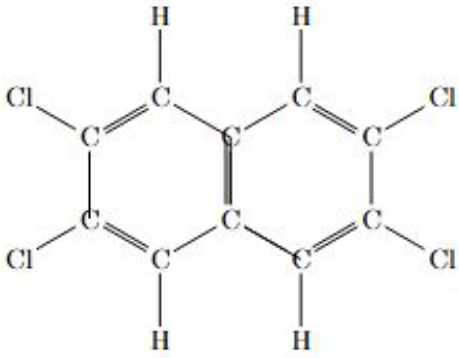




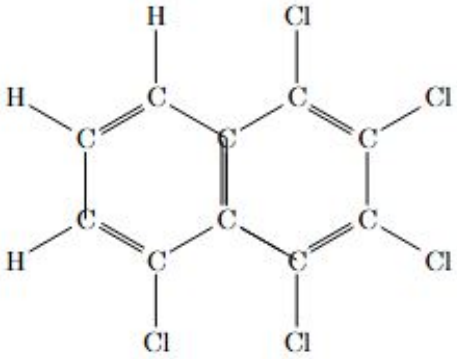
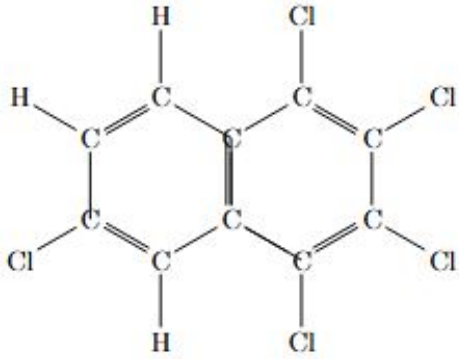
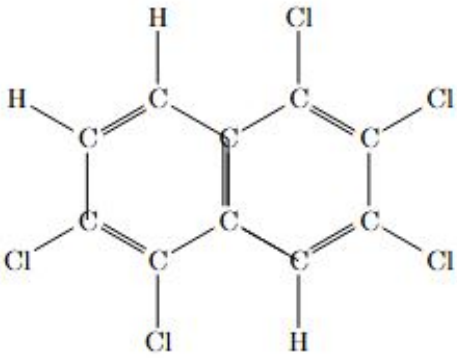
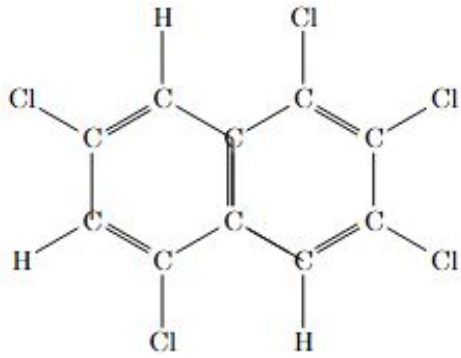
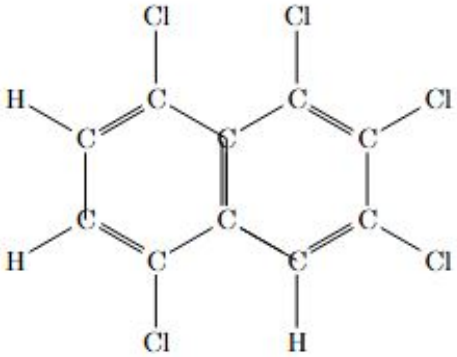
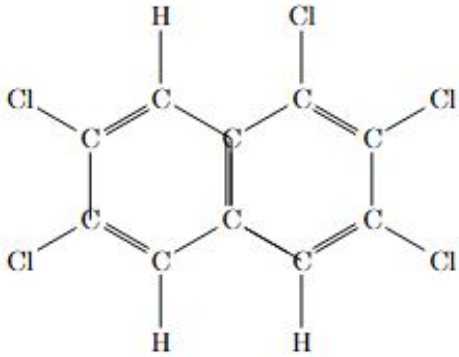


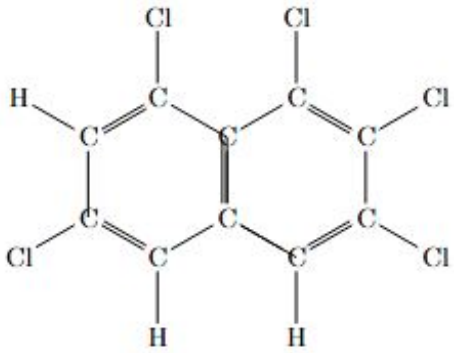


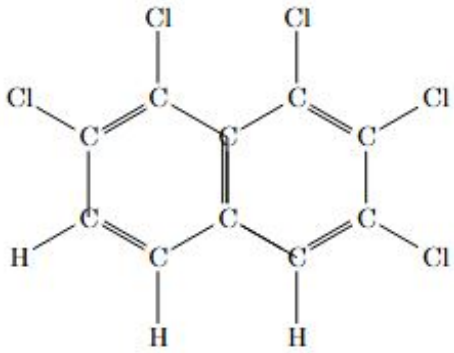


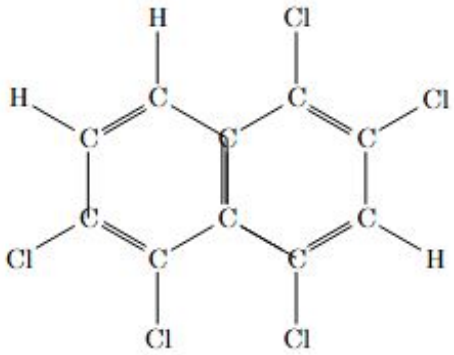



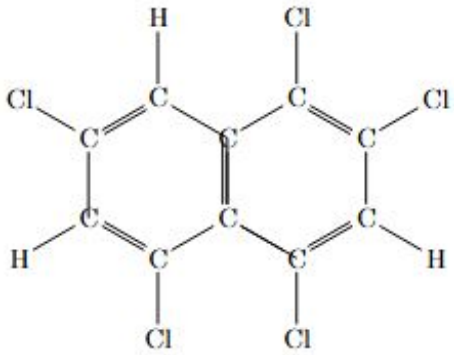
The coefficient of H^3Cl^5 indicates that there are 14 distinct substituted naphthalene compounds (pentachloronaphthalene) with five chlorines, as listed below:

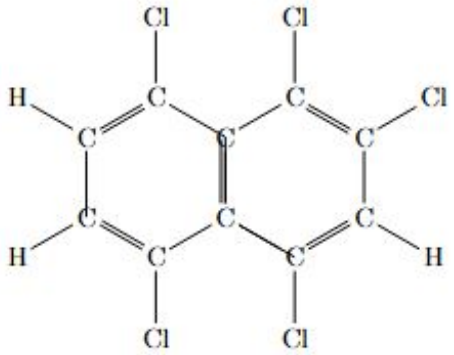







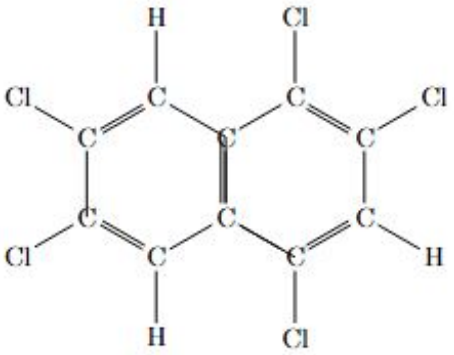


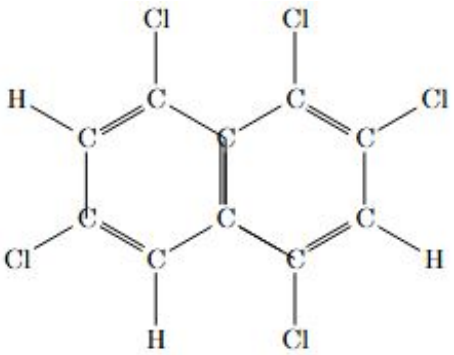


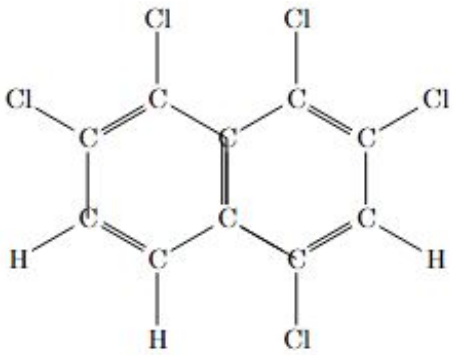




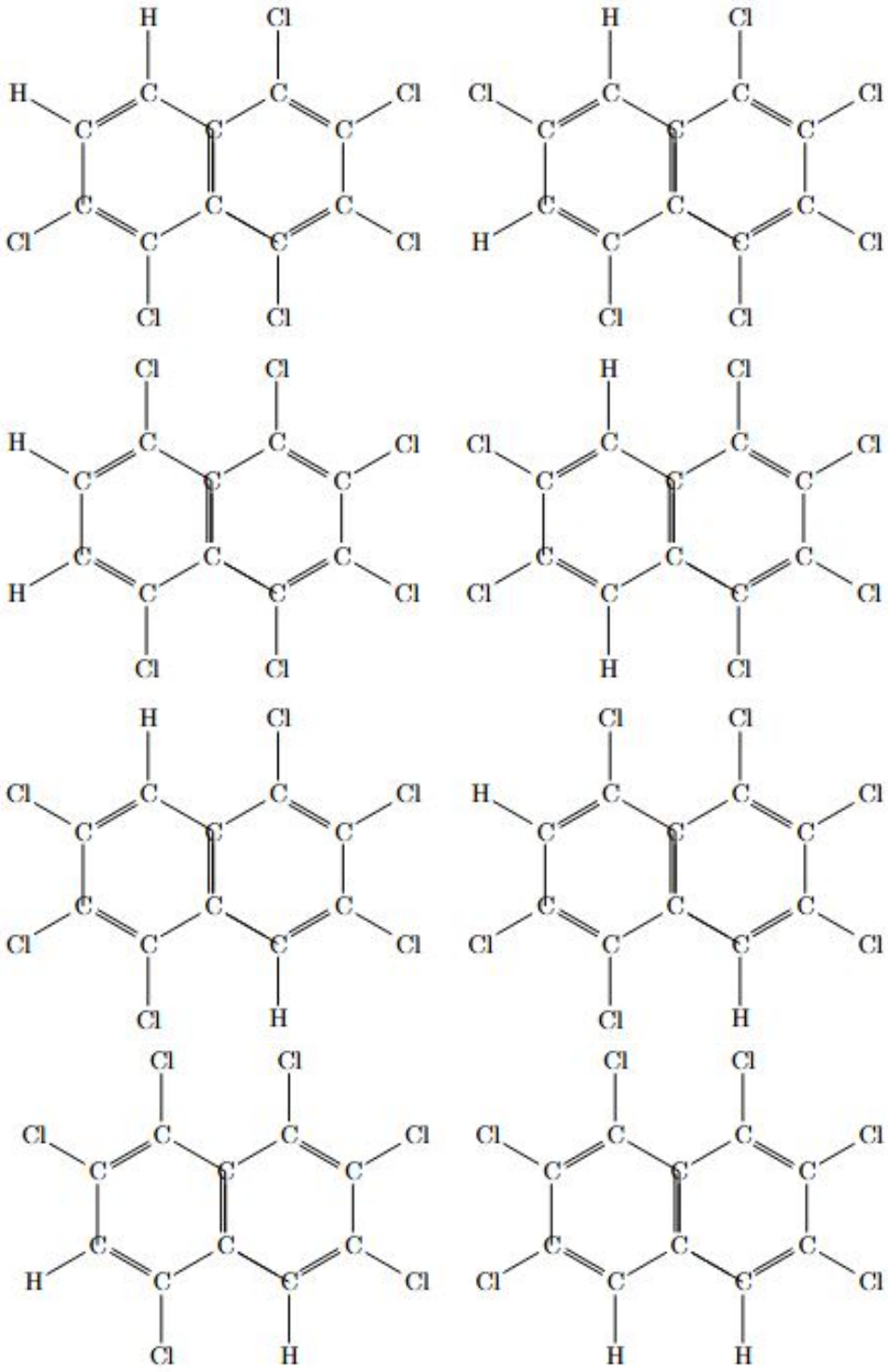


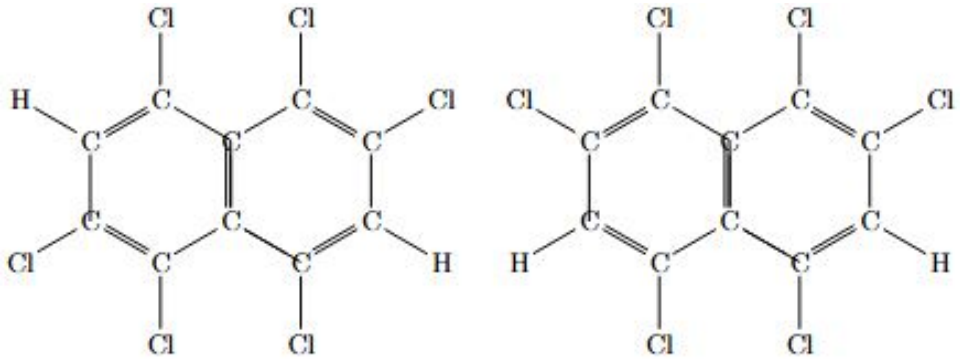




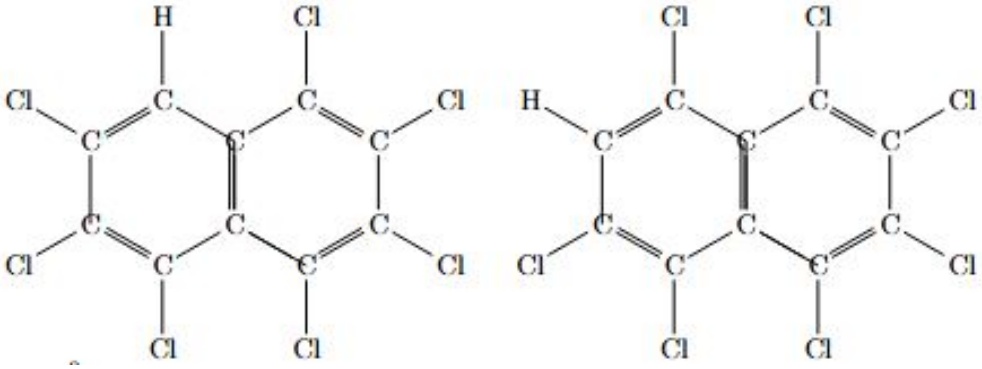


The coefficient of H^2Cl^6 indicates that there are 10 distinct substituted naphthalene compounds (hexachloronaphthalene) with six chlorines, as listed below:

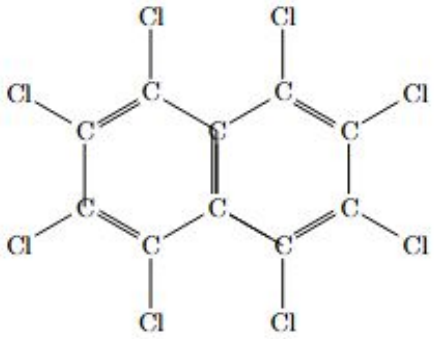




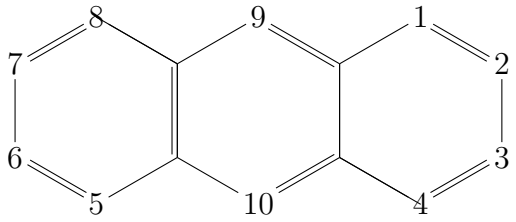
The coefficient of $H\mathrm{Cl}^7$ indicates that there are 2 distinct substituted naphthalene compounds (heptachloronaphthalene) with seven chlorines, as listed below:



The coefficient of Cl^8 indicates that there are 1 distinct substituted naphthalene compounds (heptachloronaphthalene) with eight chlorines, as listed below:



Problem 2: The aromatic hydrocarbon anthracene ($C_{14}H_{10}$) is made up of three linearly fused benzene rings that contain ten hydrogen atoms and fourteen carbon atoms. By replacing one or more hydrogen atoms with bromine atoms, how many distinct substituted anthracene compounds are there?



The symmetry group G of anthracene contains the following elements:

$$R_0 = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 \\ 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 \end{pmatrix} = (1)(2)(3)(4)(5)(6)(7)(8)(9)(10)$$

$$R_{180} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 \\ 5 & 6 & 7 & 8 & 1 & 2 & 3 & 4 & 10 & 9 \end{pmatrix} = (1\ 5)(2\ 6)(3\ 7)(4\ 8)(9\ 10)$$

$$V = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 \\ 8 & 7 & 6 & 5 & 4 & 3 & 2 & 1 & 9 & 10 \end{pmatrix} = (1\ 8)(2\ 7)(3\ 6)(4\ 5)(9)(10)$$

$$H = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 \\ 4 & 3 & 2 & 1 & 8 & 7 & 6 & 5 & 10 & 9 \end{pmatrix} = (1\ 4)(2\ 3)(5\ 8)(6\ 7)(9\ 10)$$

We have $2^{10} = 1024$ possible attachments. where X be the set of 10 numbered substitution positions to which atoms are attached or replaced as shown in Figure 4.3, C the collection of atoms for this situation, $C = \{H,\ Br\}$ and G the symmetry group acting on $X = \{1, 2, 3, 4, 5, 6, 7, 8, 9, 10\}$. Define an attachment as a function $k : X \to C$ that assigns an atom to each numbered substitution position. Let K denote the set of all such attachments.

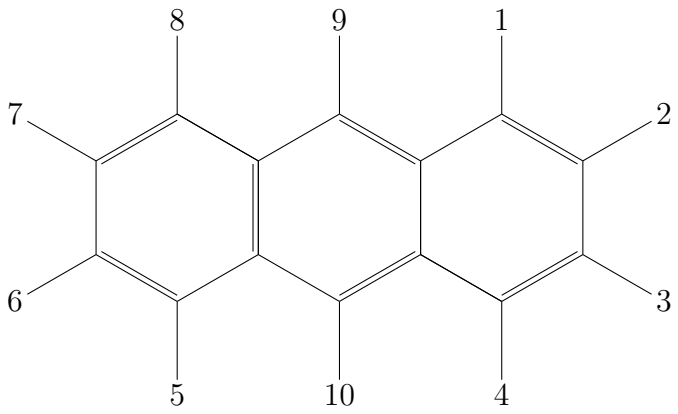


Figure 4.3: Numbered substitution positions on anthracene

Table 4.2: Number of cycles of g (cyc(g)), values of |fix(g)|, types of g and cycle index of $g \in G$ symmetry group of anthracene

$g \in G$	cyc(g)	$\lvert fix(g)\rvert$	type of g	cycle index
(1)(2)(3)(4)(5)(6)(7)(8)(9)(10)	10	n^{10}	(10,0,0,0,0,0,0,0,0,0)	x_1^{10}
(1 5)(2 6)(3 7)(4 8)(9 10)	5	n^5	(0,5,0,0,0,0,0,0,0,0)	x_2^5
(1 8)(2 7)(3 6)(4 5)(9)(10)	6	n^6	(2,4,0,0,0,0,0,0,0,0)	$x_1^2x_2^4$
(1 4)(2 3)(5 8)(6 7)(9 10)	5	n^5	((0,5,0,0,0,0,0,0,0,0)	x_2^5

Now, we can determine the total number of unique substituted anthracene compounds using Burnside's lemma ($n = 2$):

$$\frac{1}{|G|}\sum_{g\in G}|fix(g)| = \frac{1}{4}\left[n^{10} + n^6 + 2(n^5)\right] = \frac{1}{4}\left[2^{10} + 2^6 + 2(2^5)\right] = \frac{1152}{4} = 288$$

Thus, there are 288 distinct compounds.

But then Burnside's lemma is no longer enough on its own. Therefore, we now turn to Polya's Enumeration Theorem for further analysis.
Now, the cycle index of G is:

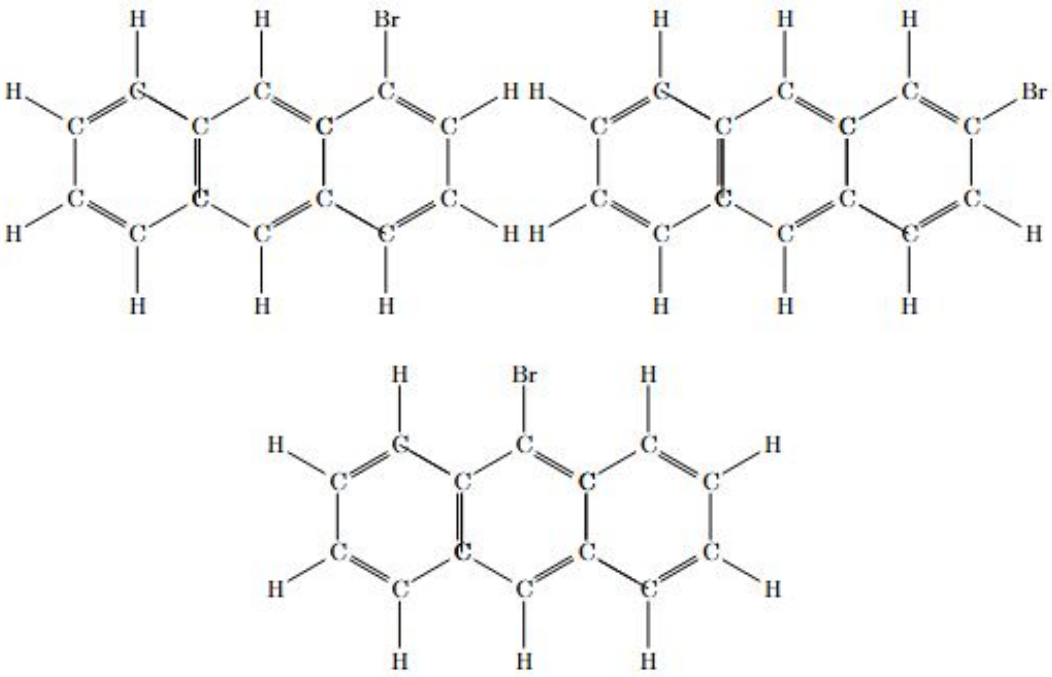
$$P_G(x_1, x_2, ...x_{10}) = \frac{1}{4}\left(x_1^{10} + 2x_2^5 + x_1^2x_2^4\right). \tag{4.4}$$

we can get the details information of this distinct substituted compounds by substituting x_i by $H^i + Br^i$ in equation 4.4 for each $i = \{1, 2, 3, \ldots, 10\}$:

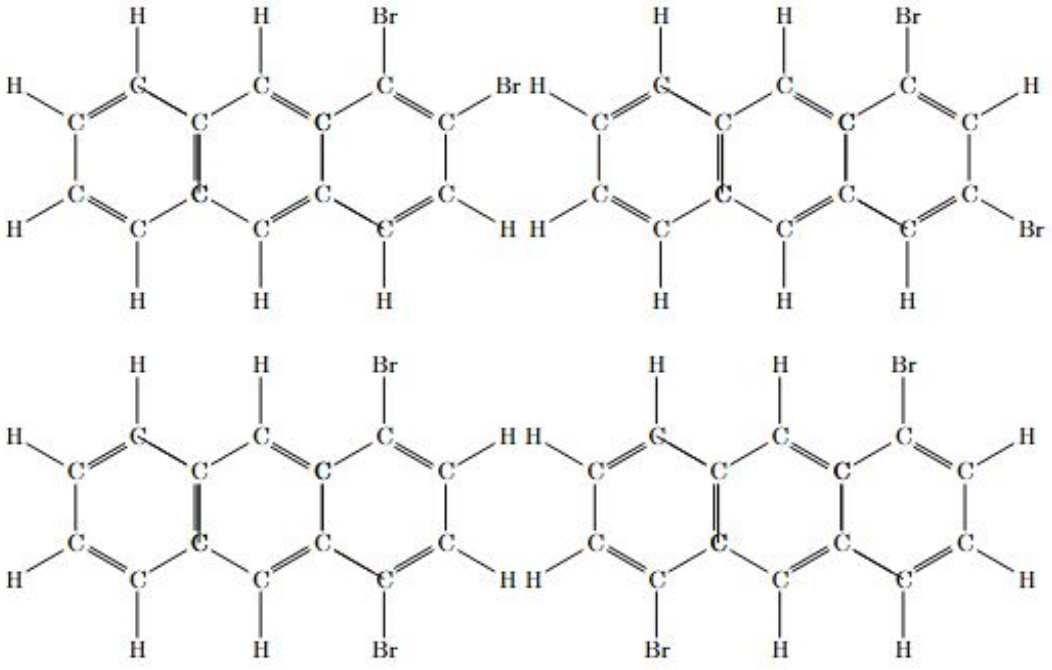
$$\begin{aligned}
&P_G((H + \mathrm{Br}), (H^2 + \mathrm{Br}^2), (H^3 + \mathrm{Br}^3), \ldots, (H^{10} + \mathrm{Br}^{10})) \\
&\quad = \frac{1}{4}\Big((H + \mathrm{Br})^{10} + 2(H^2 + \mathrm{Br}^2)^5 + (H + \mathrm{Br})^2(H^2 + \mathrm{Br}^2)^4\Big) \\
&\quad = H^{10} + 3H^9\mathrm{Br} + 15H^8\mathrm{Br}^2 + 32H^7\mathrm{Br}^3 + 60H^6\mathrm{Br}^4 + 66H^5\mathrm{Br}^5 \\
&\qquad + \ 60H^4\mathrm{Br}^6 + 32H^3\mathrm{Br}^7 + 15H^2\mathrm{Br}^8 + 3H\mathrm{Br}^9 + \mathrm{Br}^{10}
\end{aligned} \tag{4.5}$$

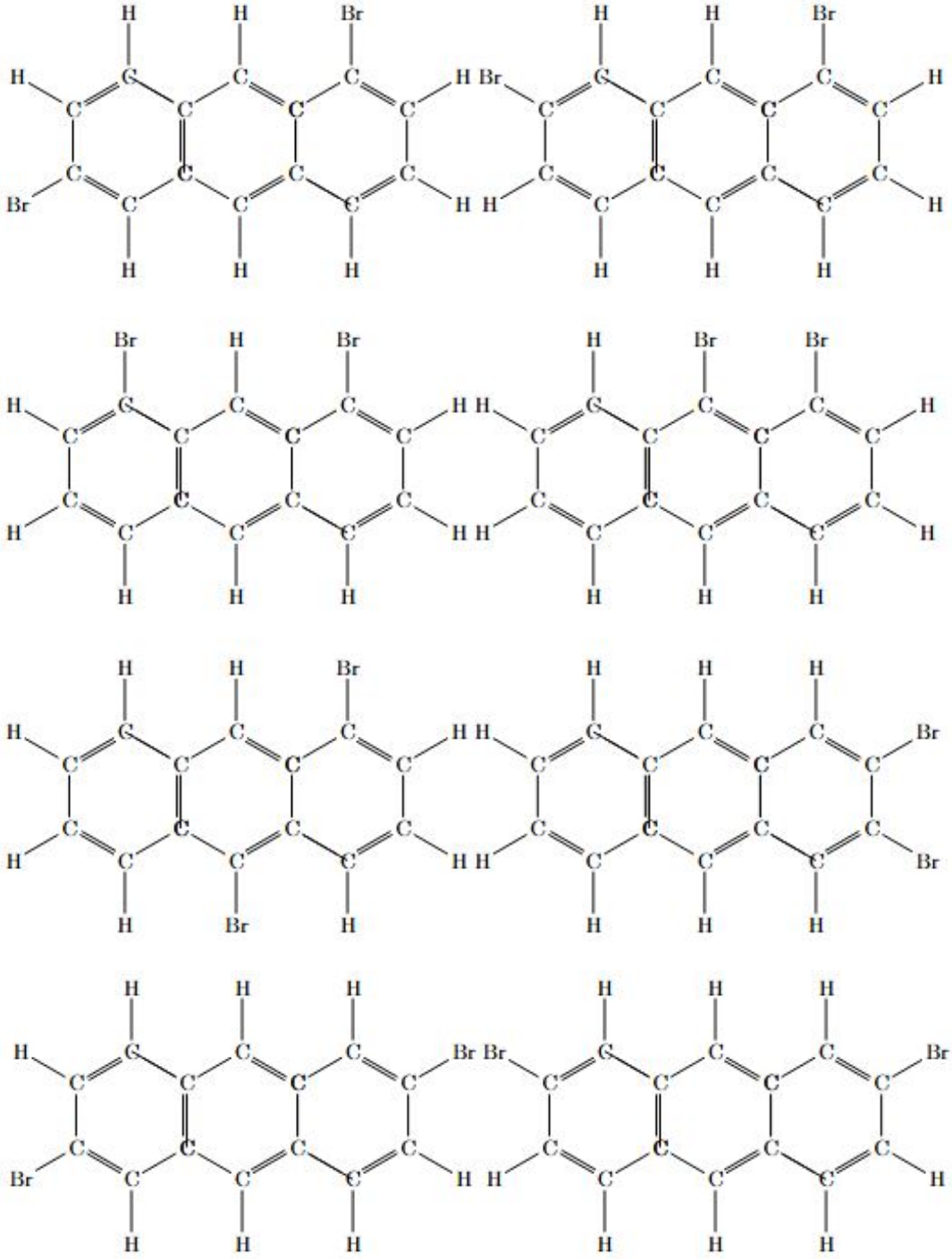
The coefficients of each term of equation 4.5 shows that how many distinct substituted anthracene with $1, 2, 3, ...,$ and 10 bromine are there.

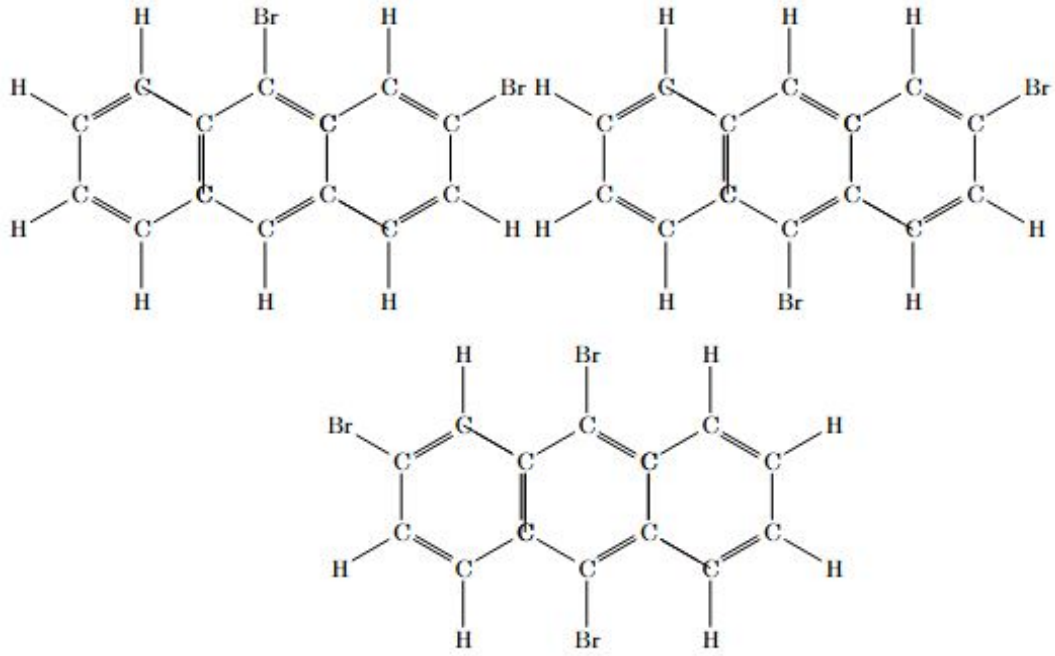
Therefore, the coefficient of $H^9\mathrm{Br}$ indicates that there are 3 distinct substituted anthracene compounds (bromoanthracene) with one bromine, as listed below:



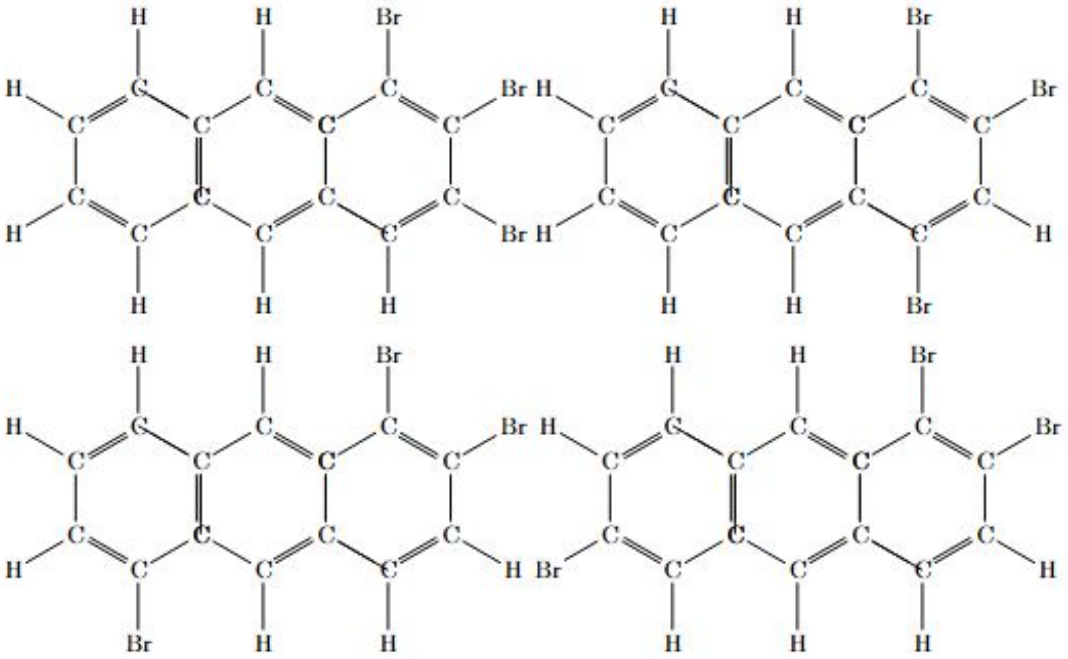
The coefficient of $H^8\mathrm{Br}^2$ indicates that there are 15 distinct substituted anthracene compounds (dibromoanthracene) with two bromine, as listed below:

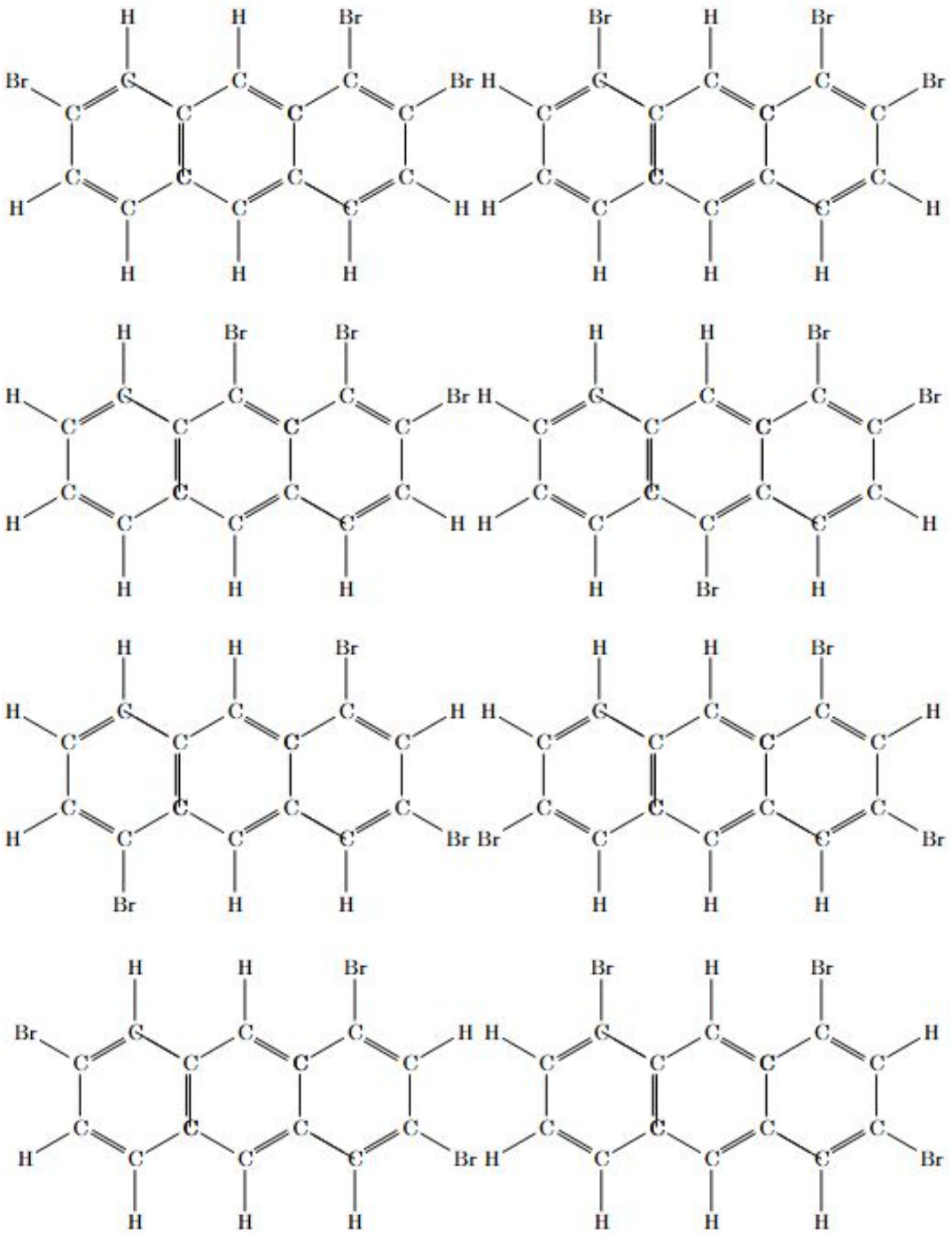


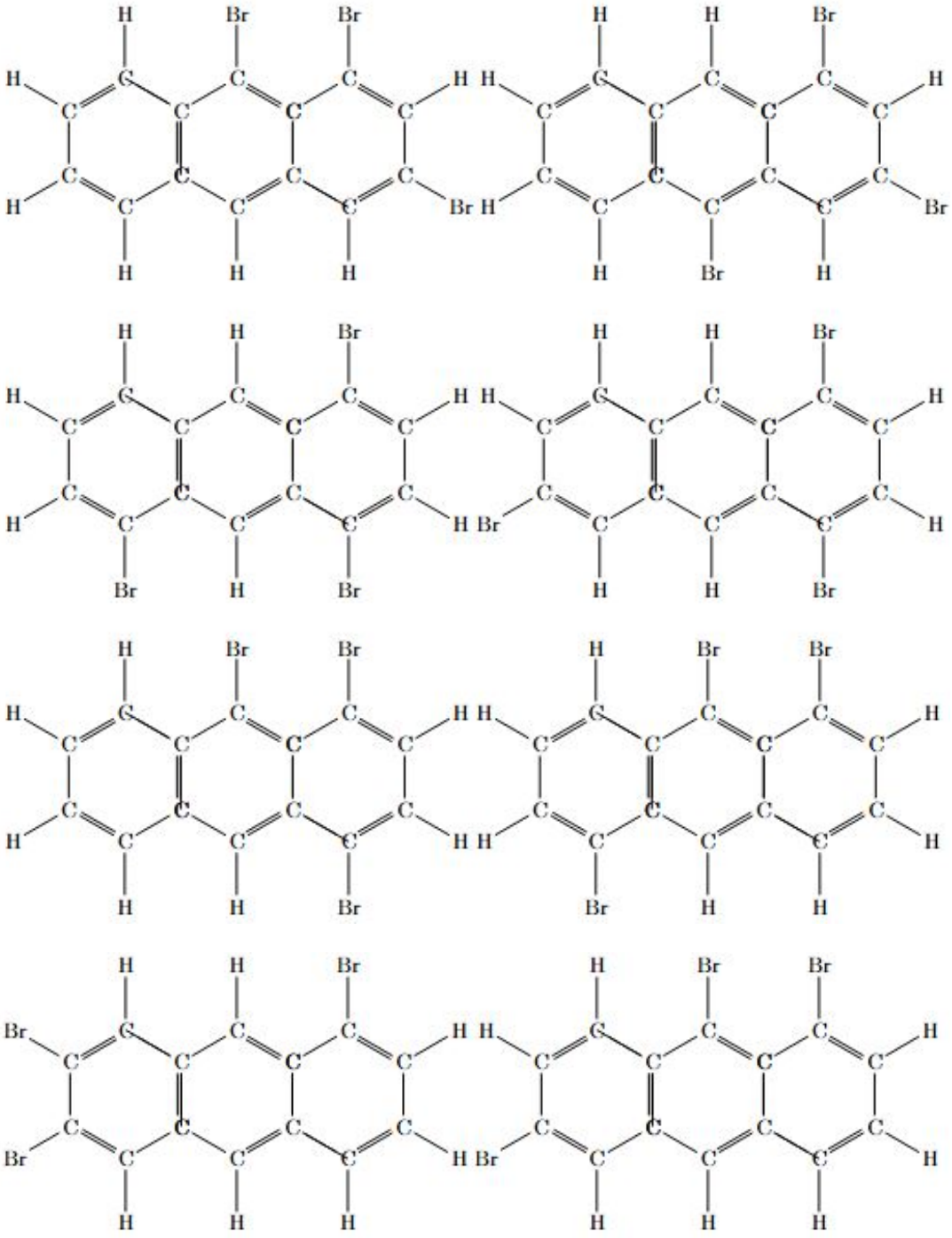


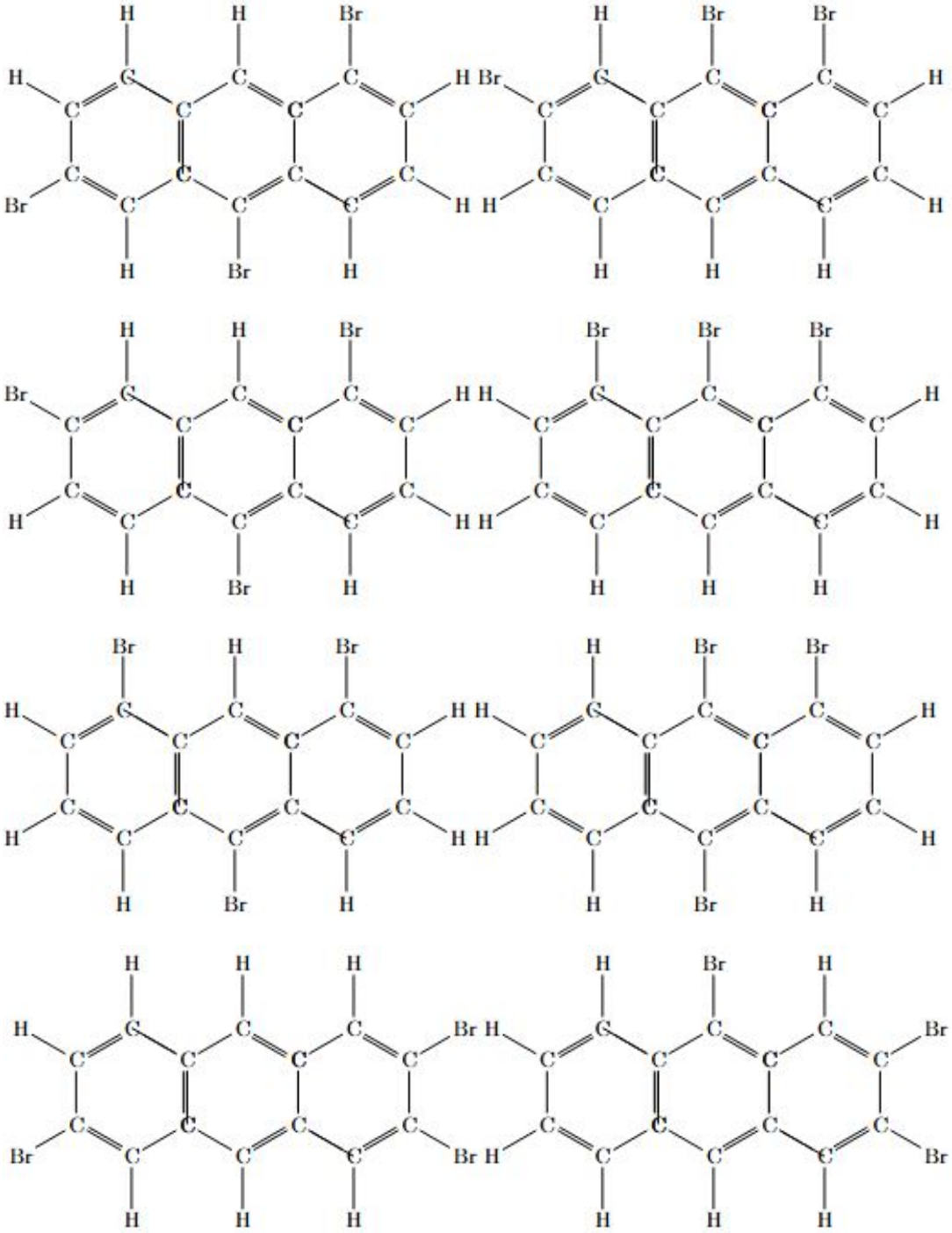


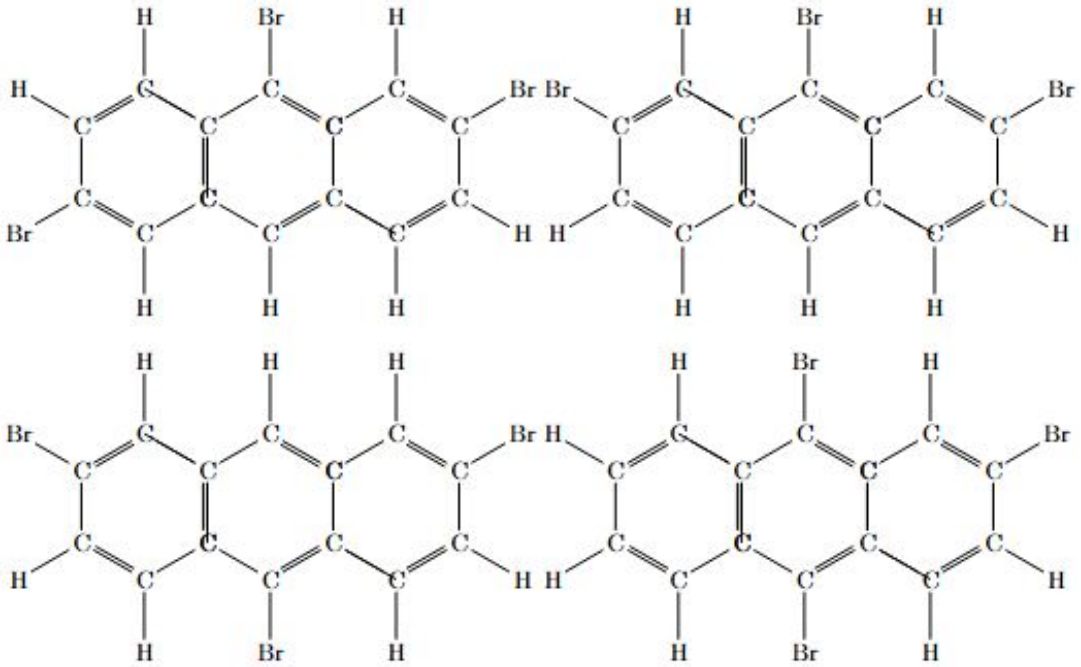
The coefficient of H^7Br^3 indicates that there are 32 distinct substituted anthracene compounds (tribromoanthracene) with three bromine, as listed below:



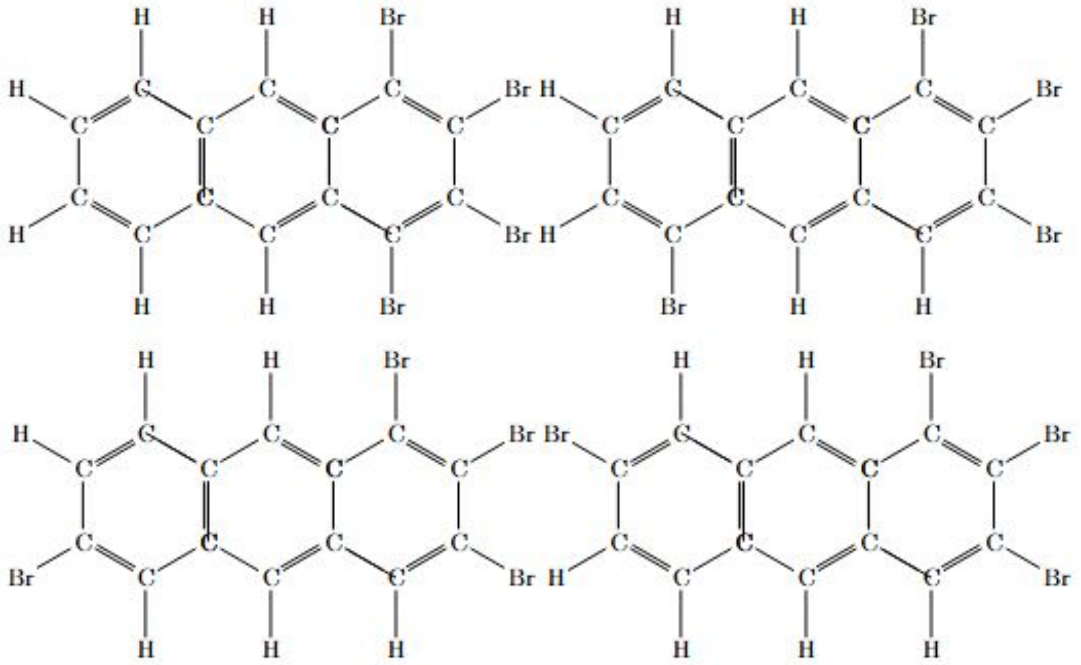


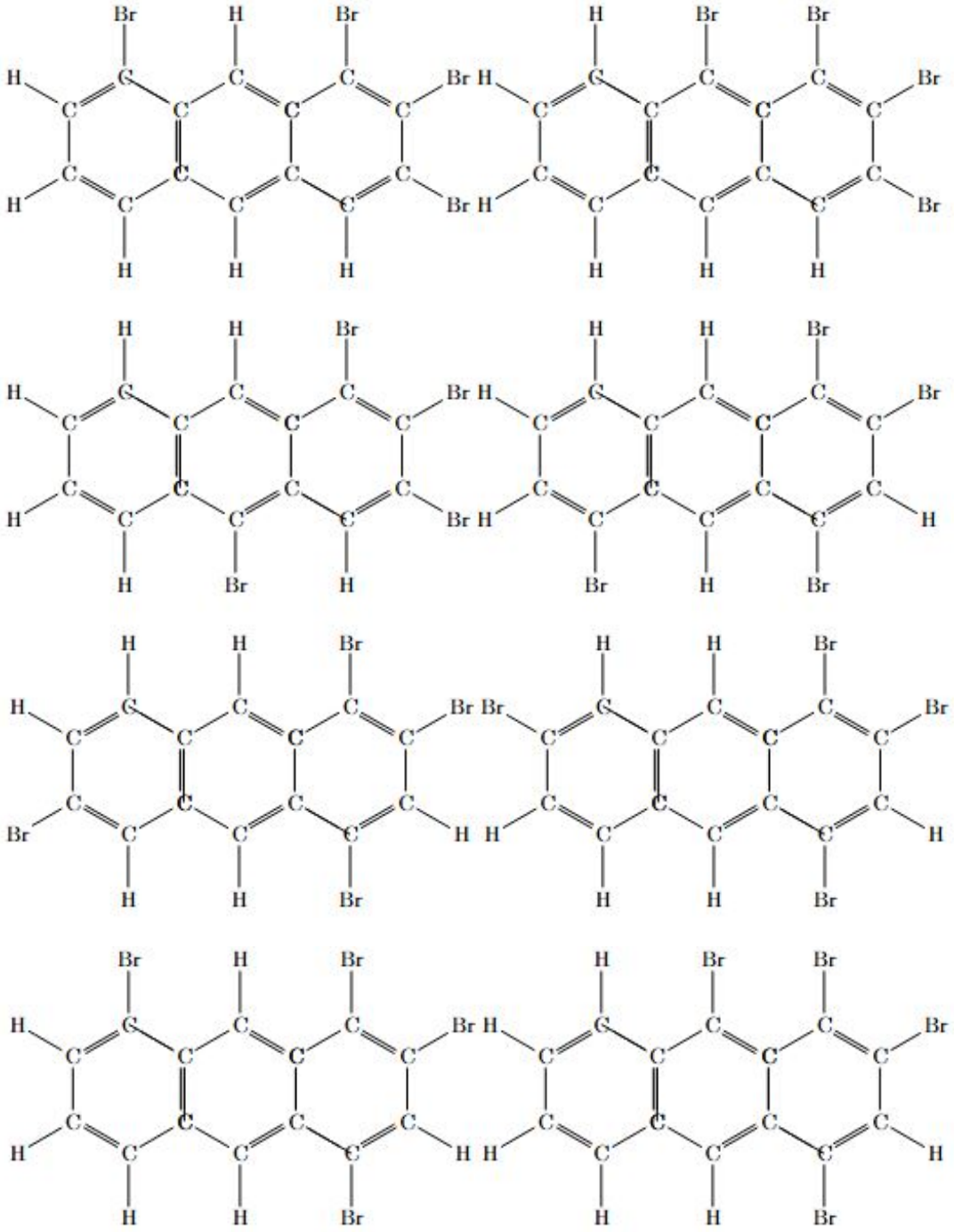


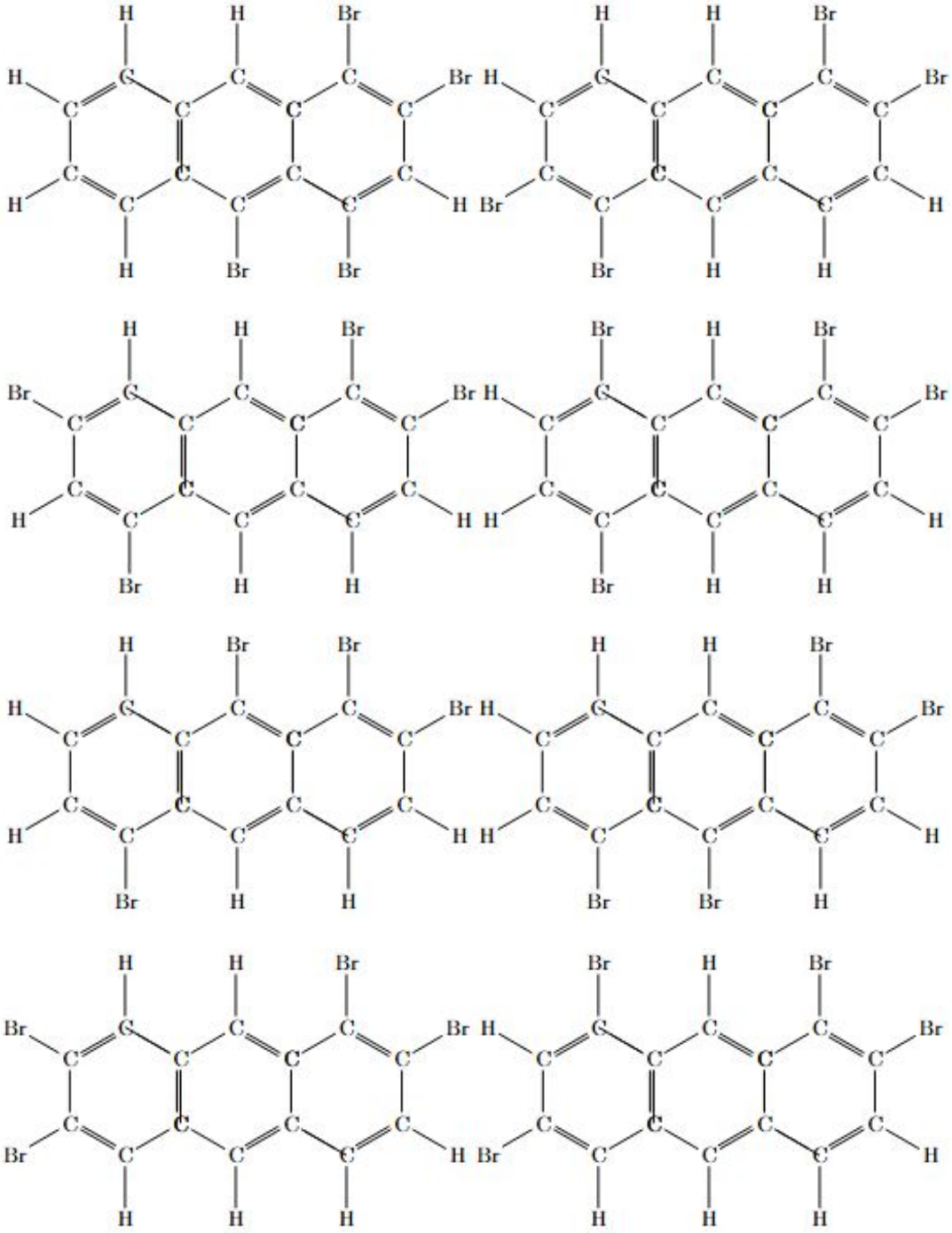


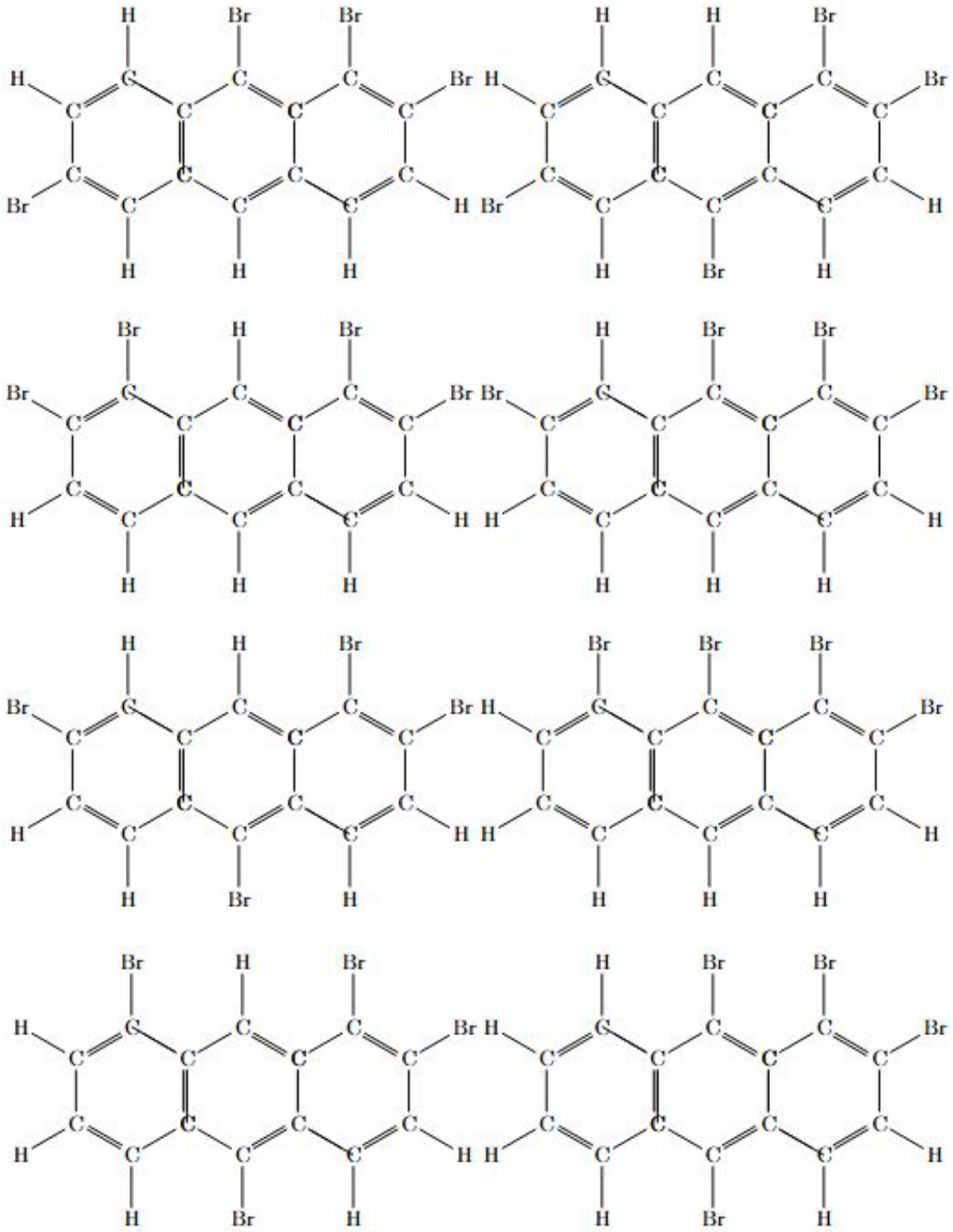


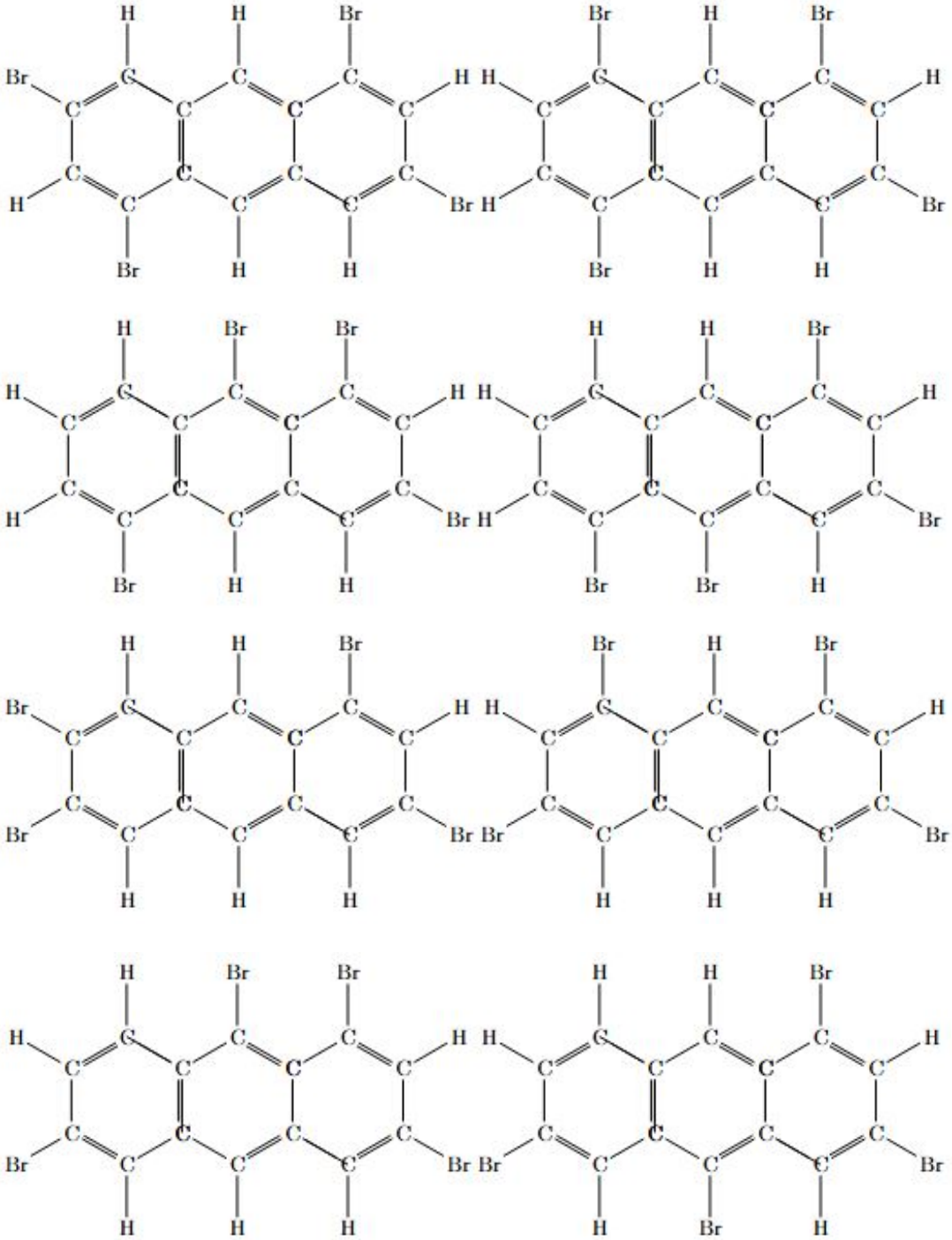
The coefficient of H^6Br^4 indicates that there are 60 distinct substituted anthracene compounds (tetrabromoanthracene) with four bromines, as listed below:

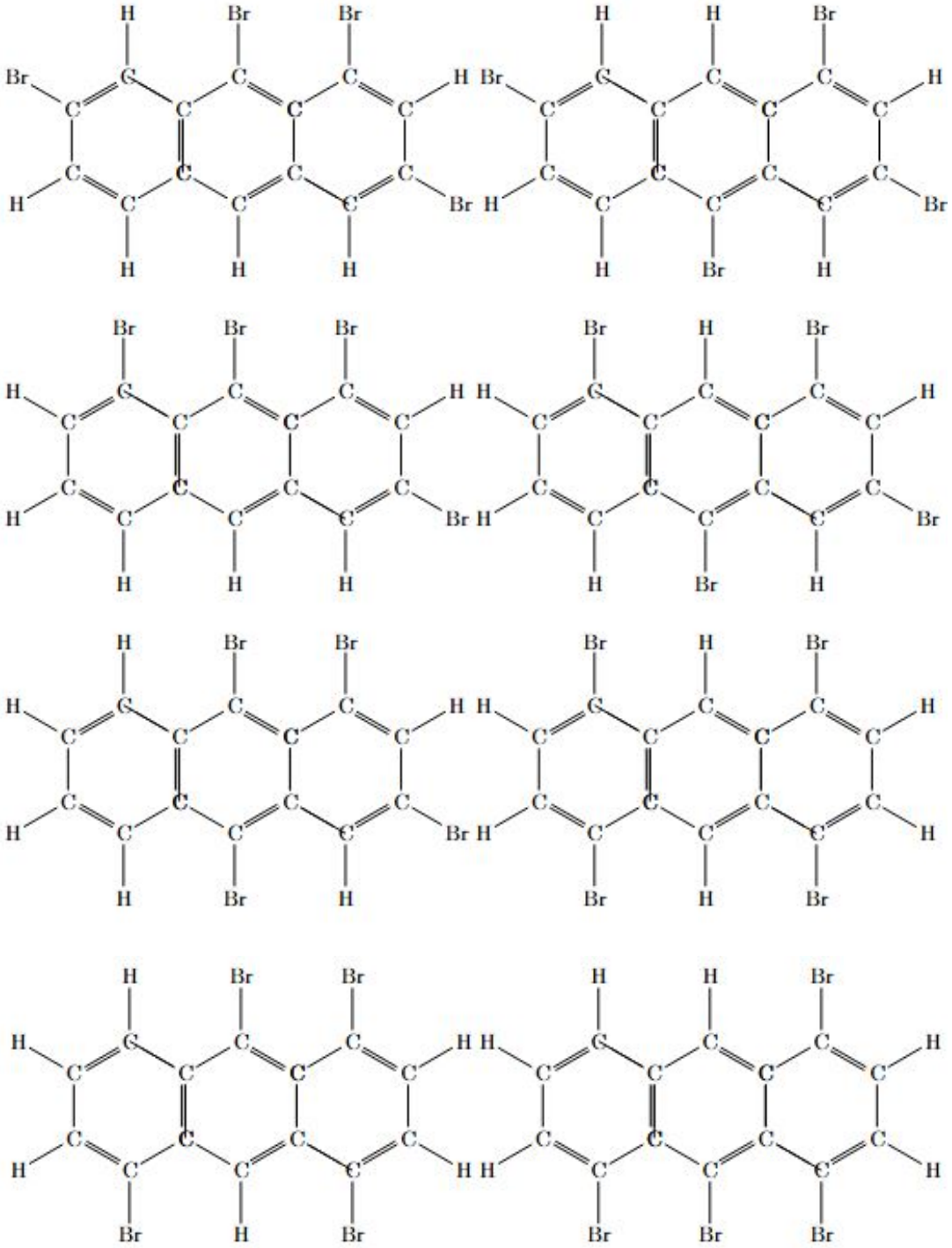


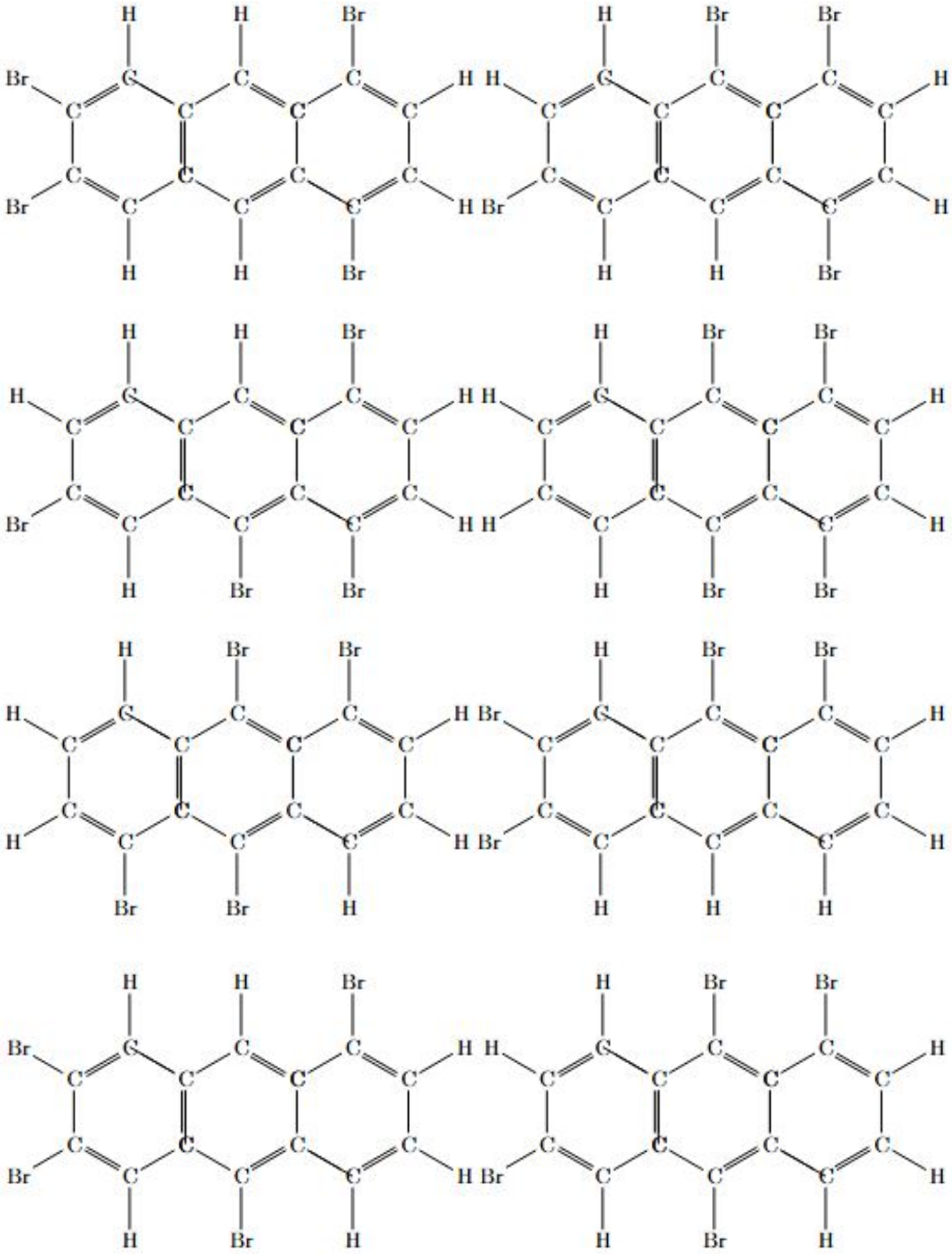


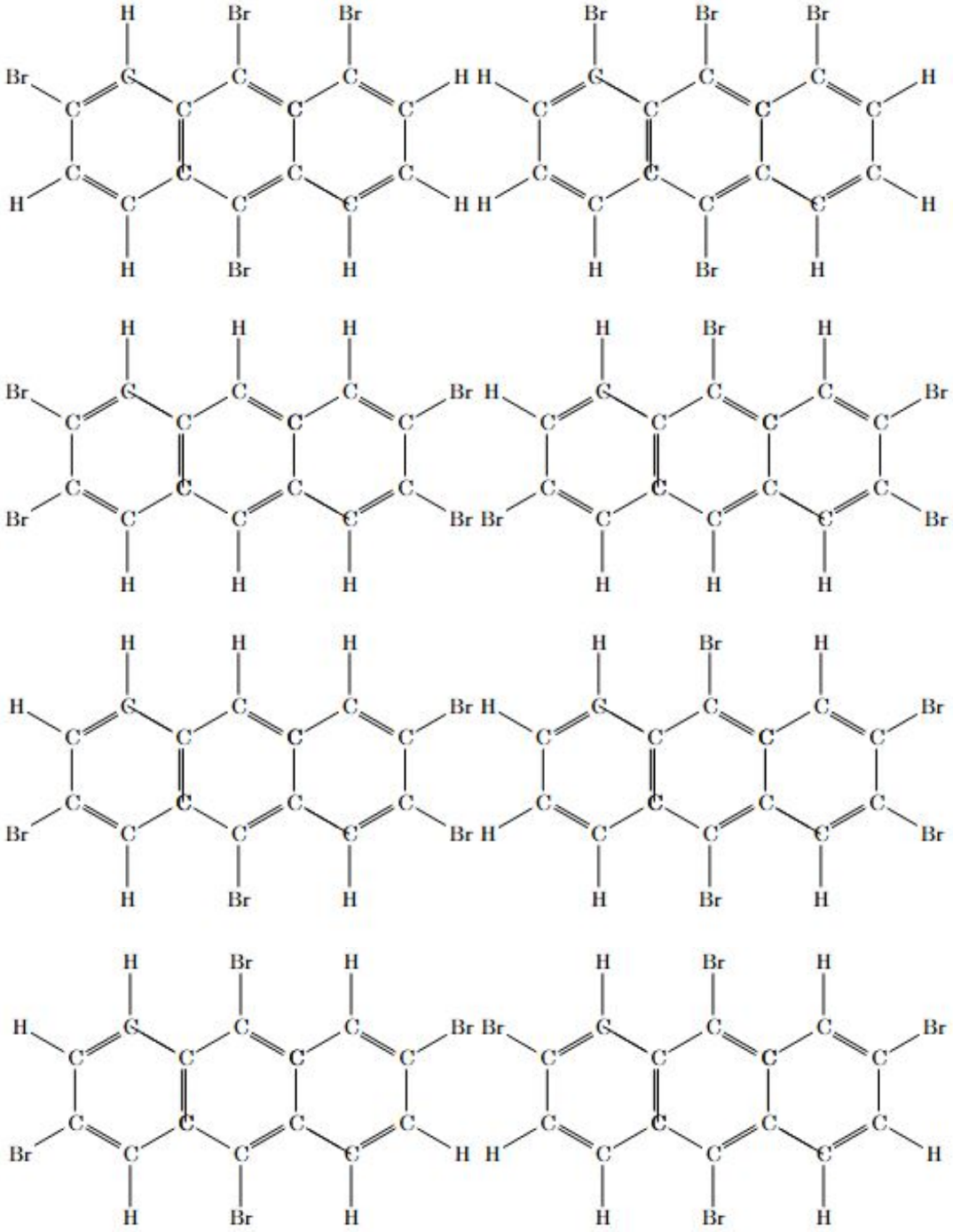




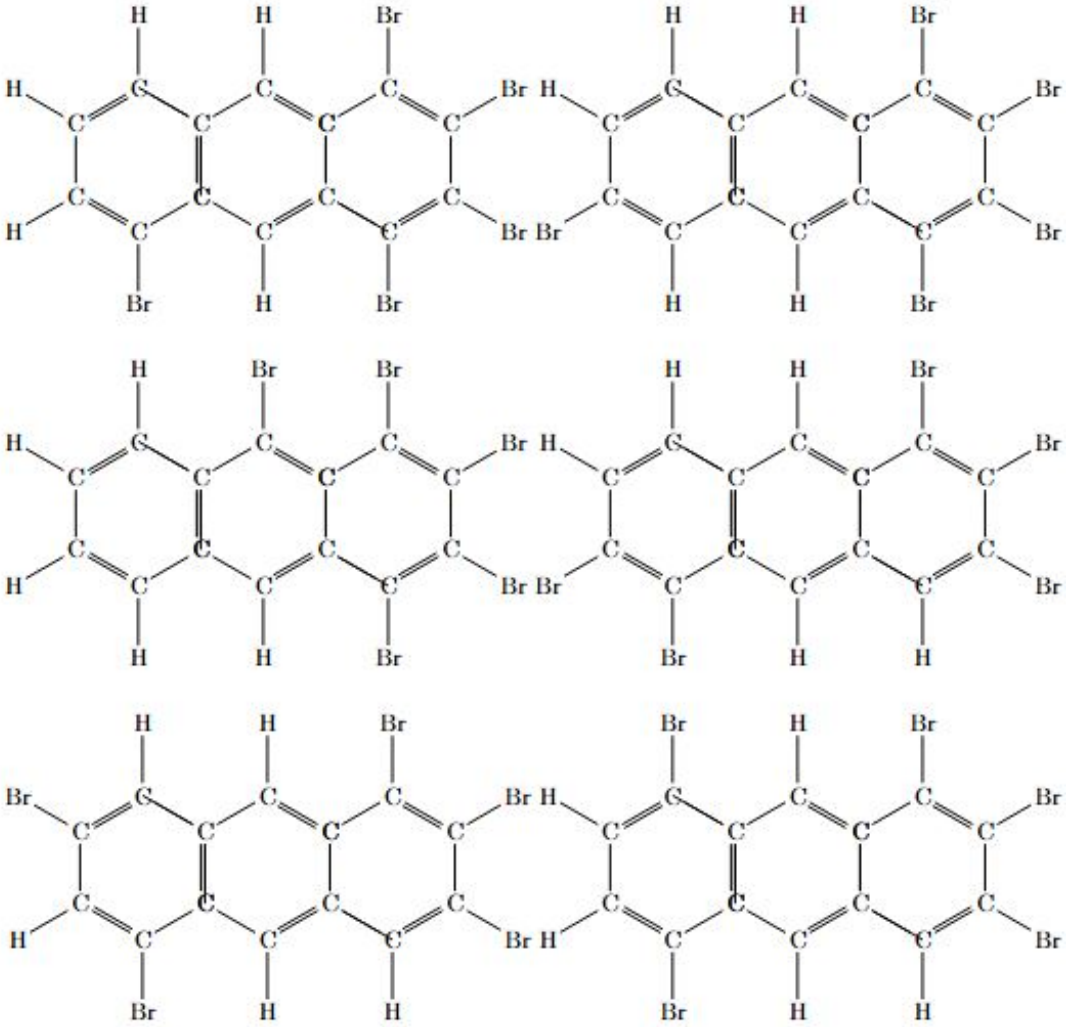


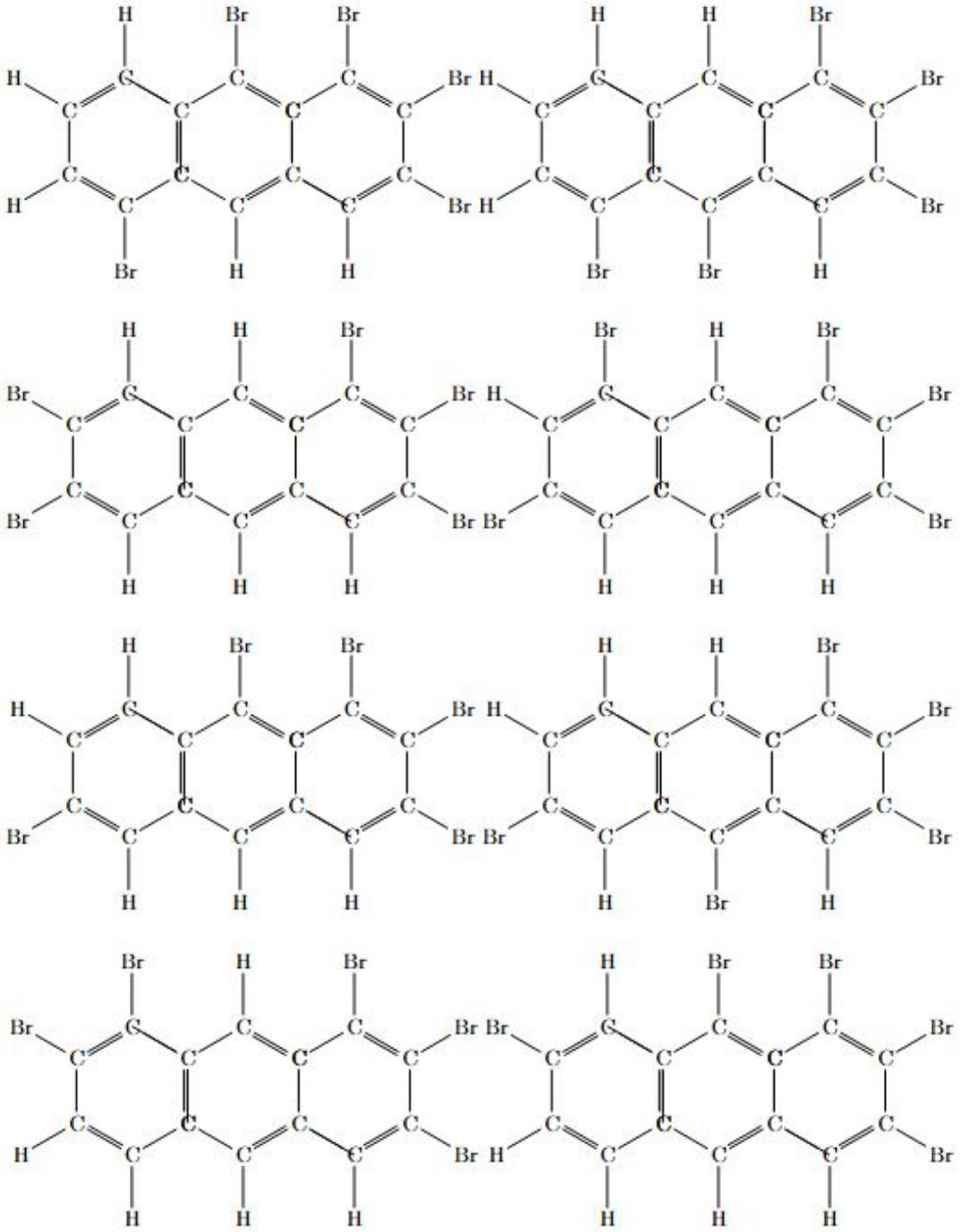


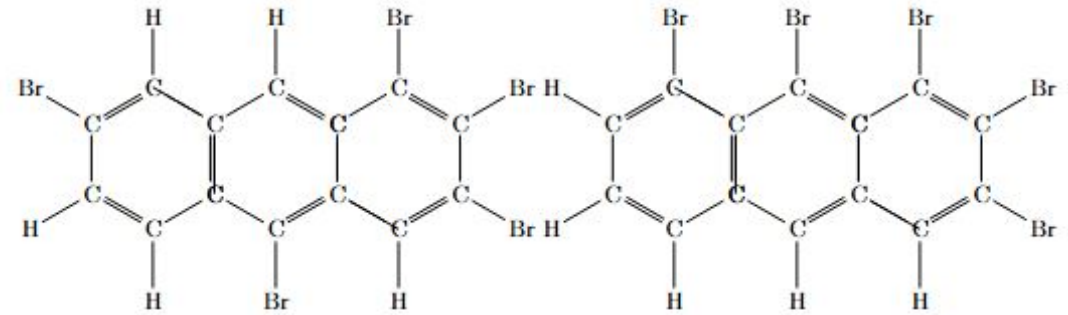


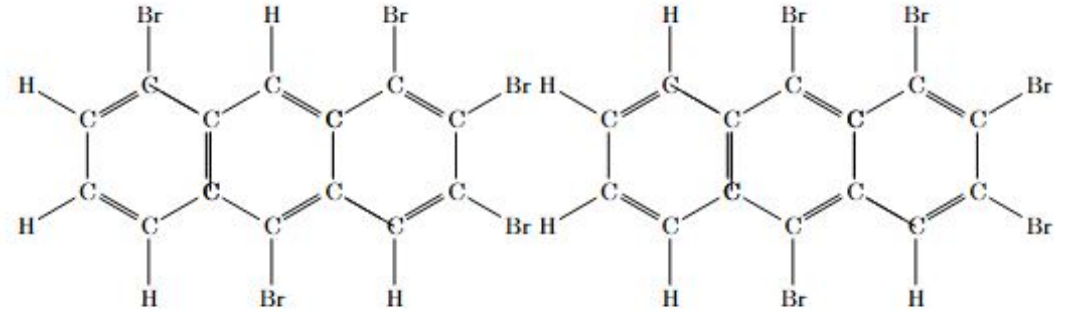


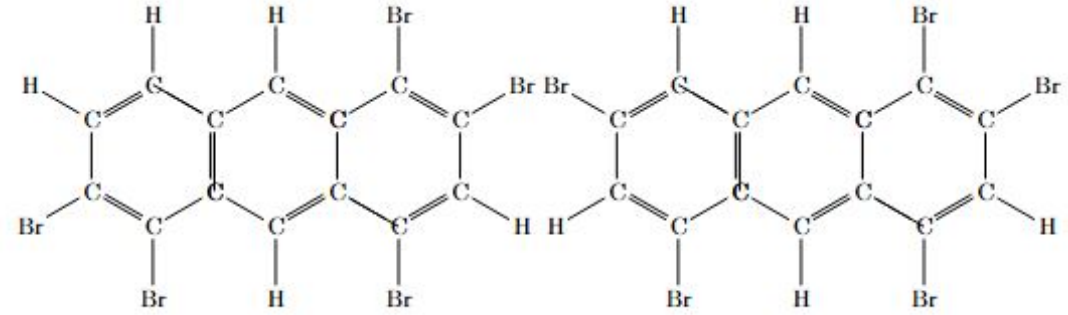
The coefficient of H^5Br^5 indicates that there are 66 distinct substituted anthracene compounds (pentabromoanthracene) with five bromines, as listed below:

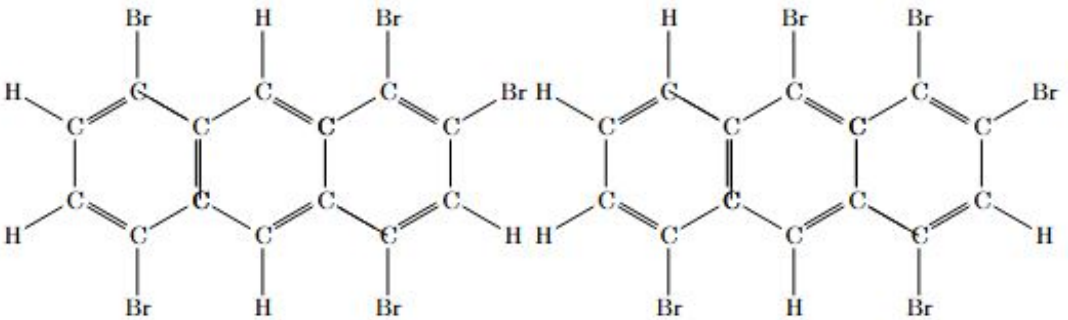


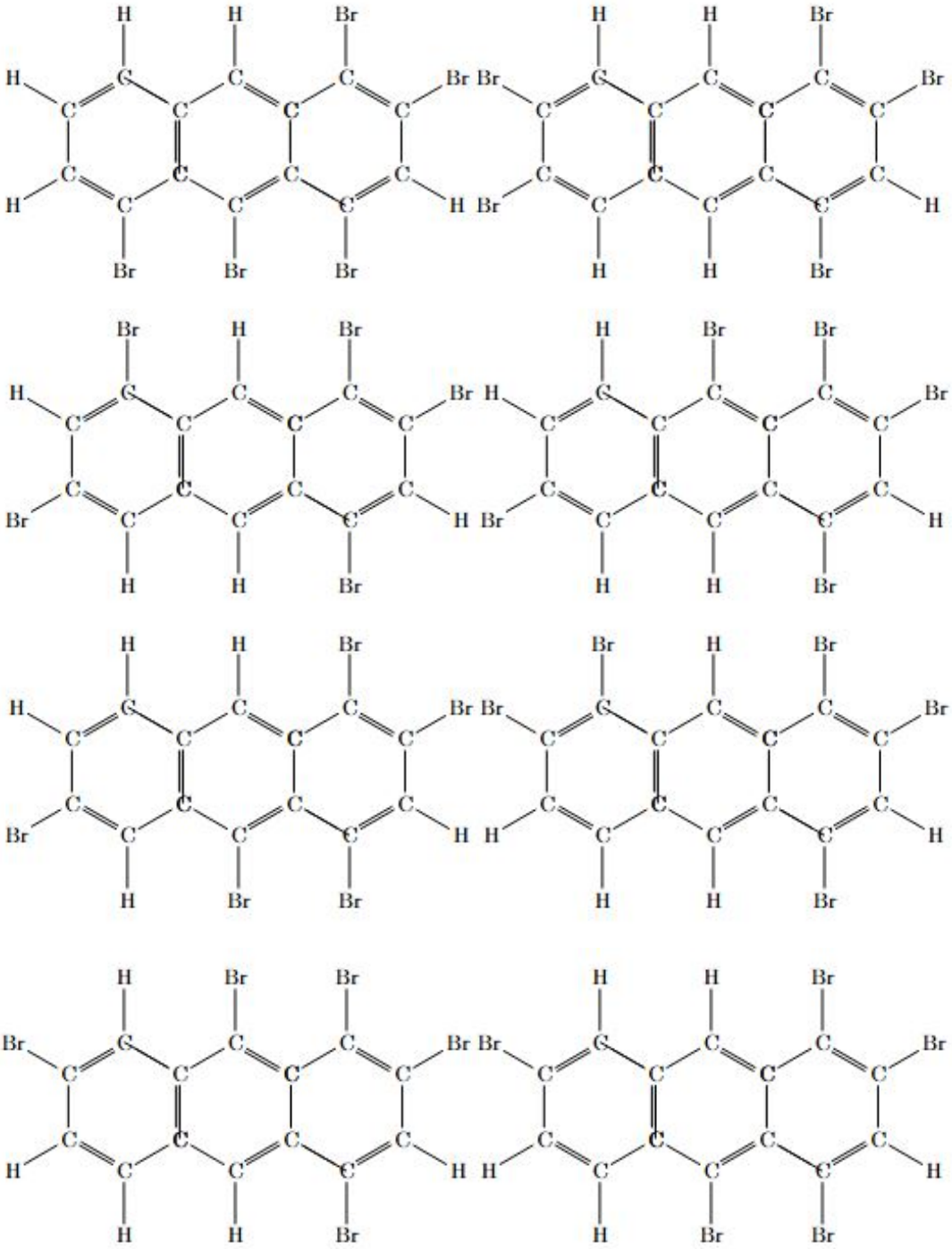


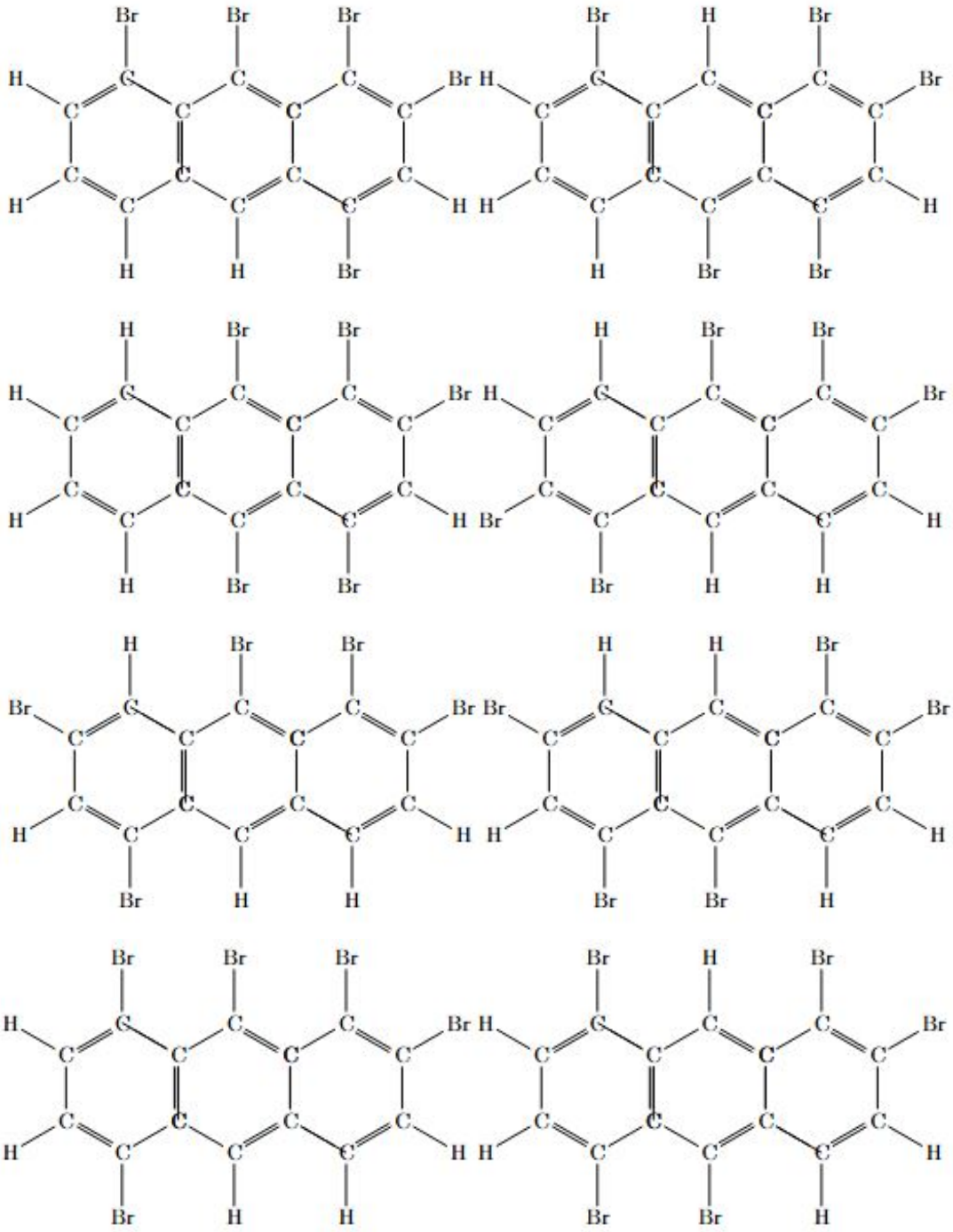


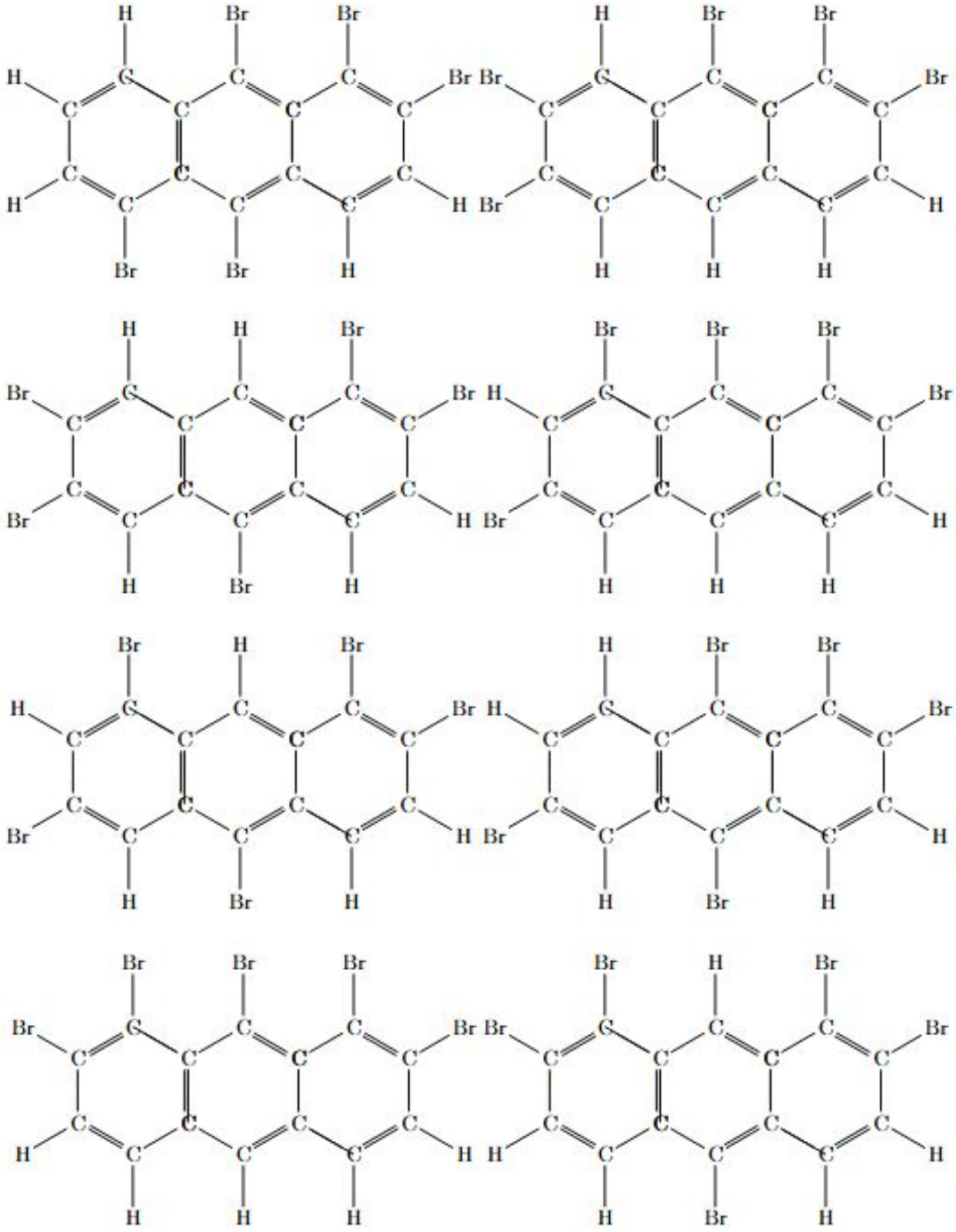


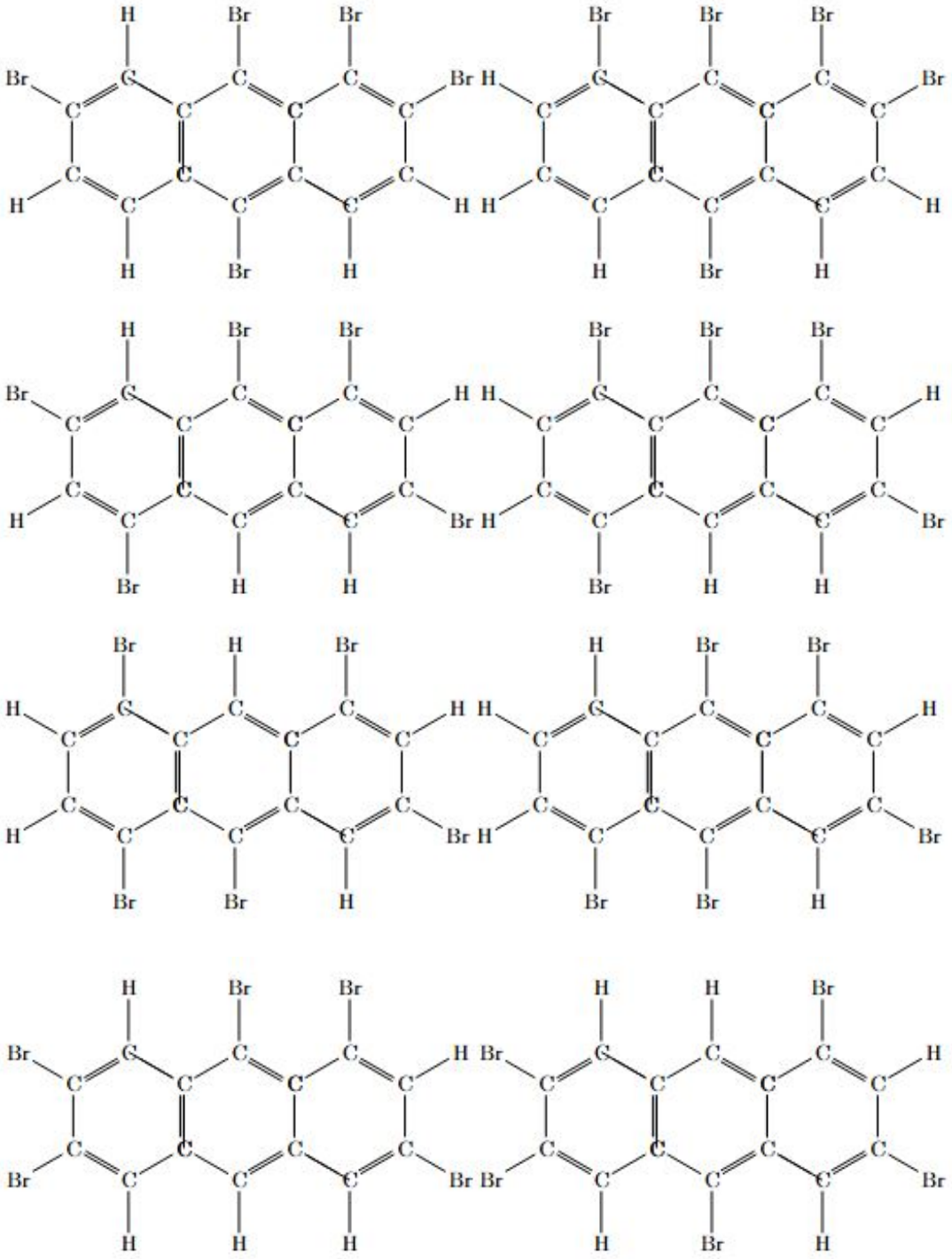


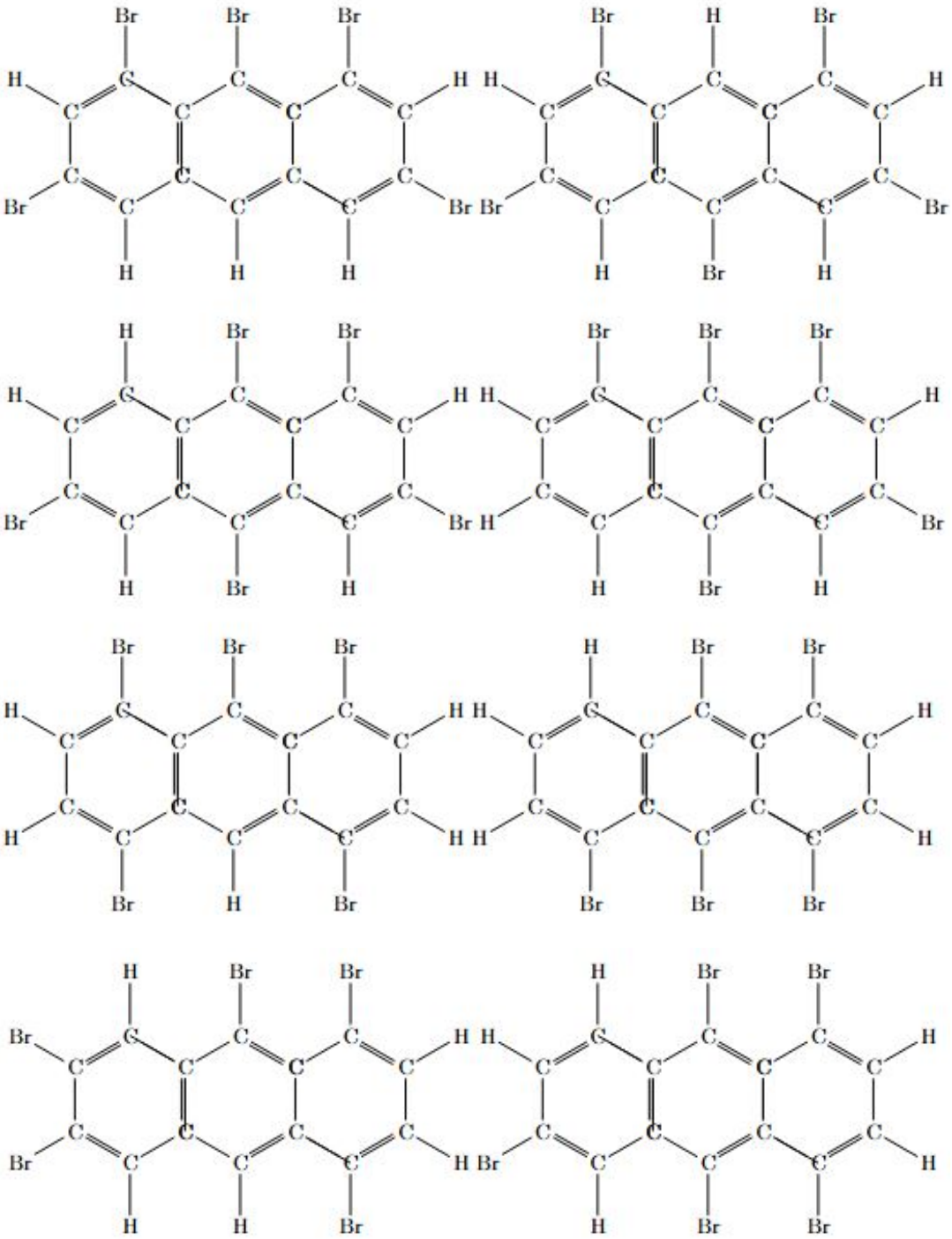


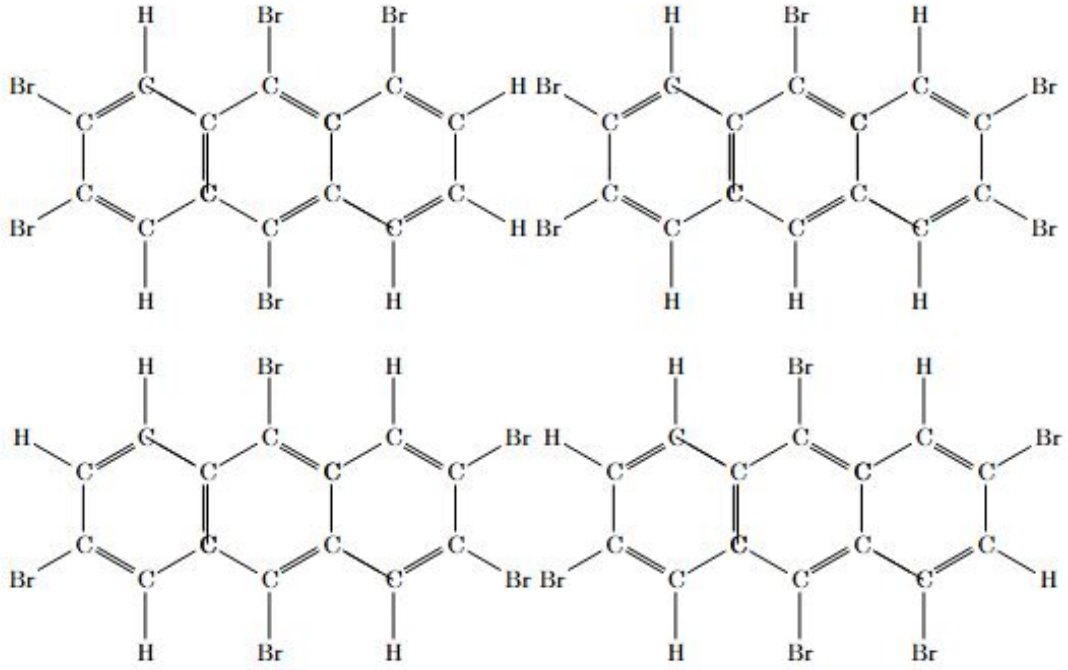




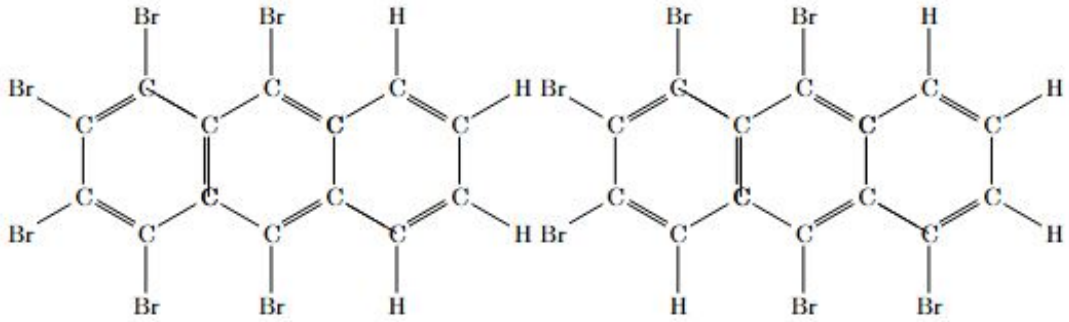


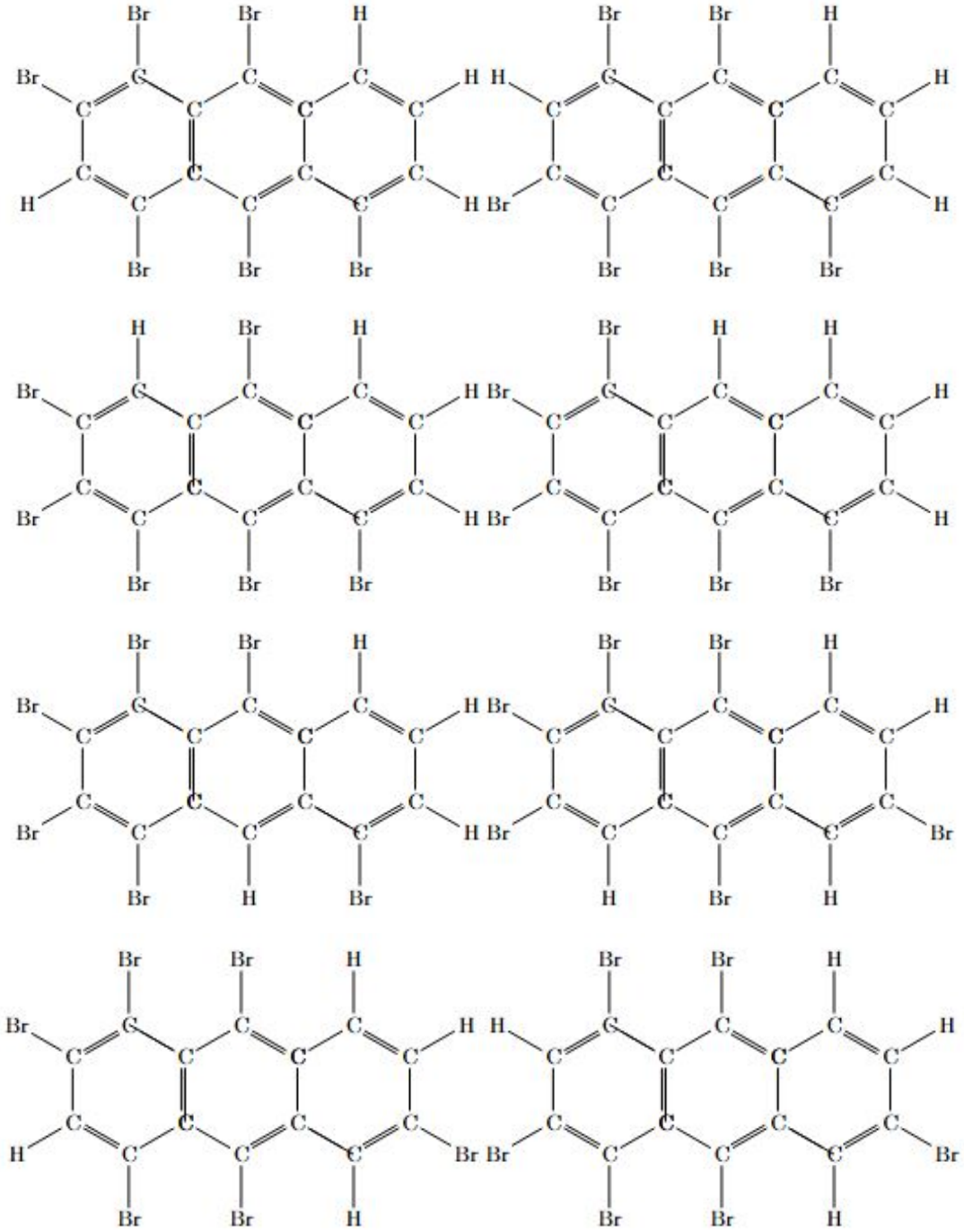


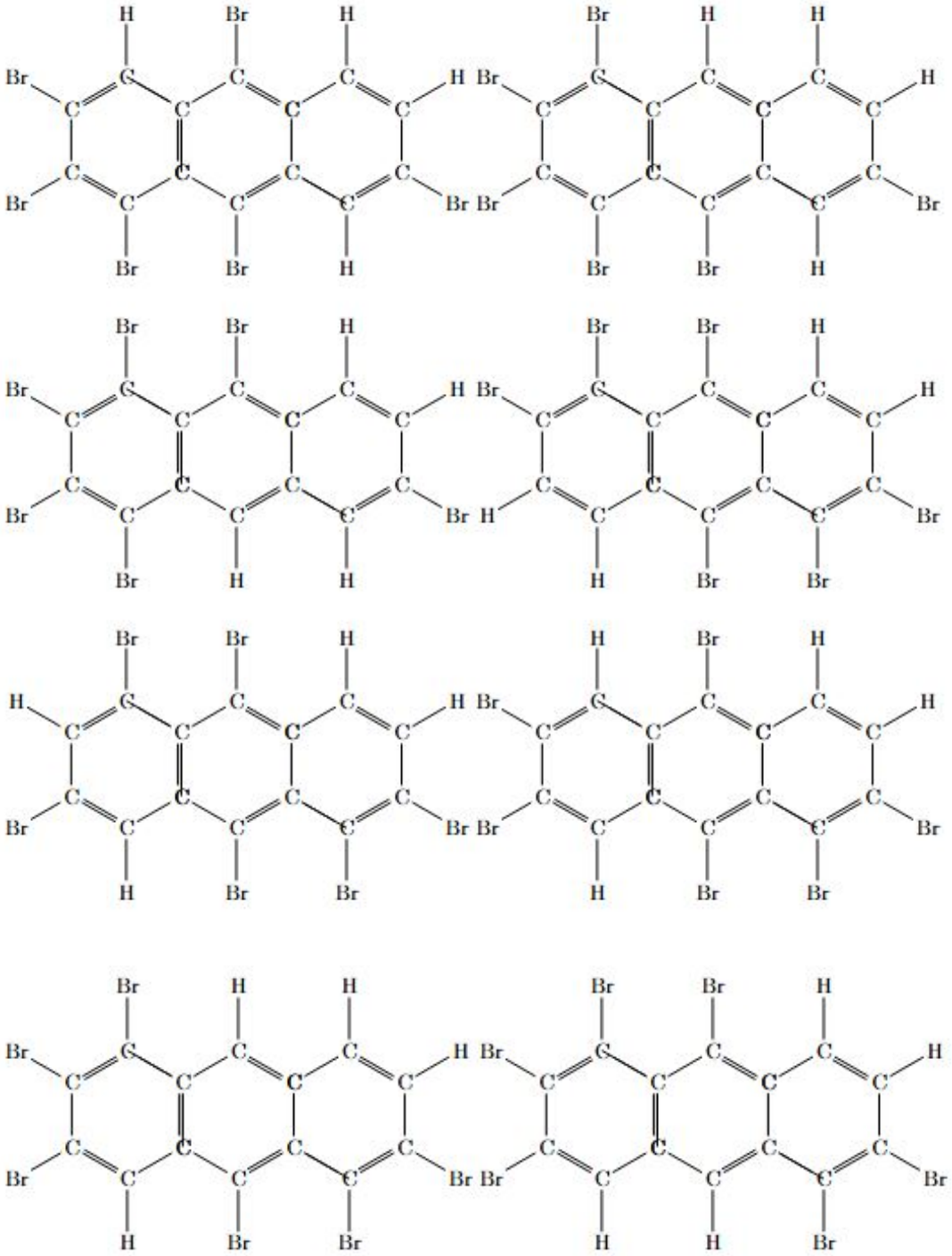


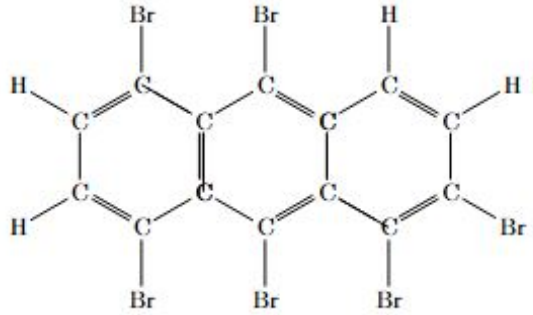


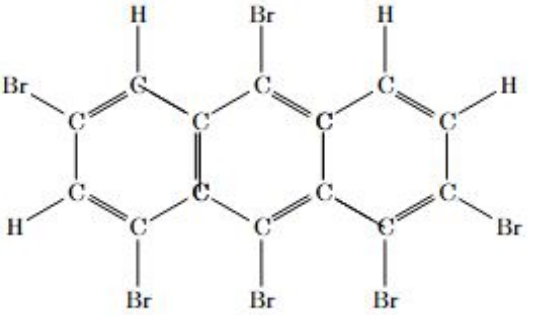
The coefficient of H^4Br^6 indicates that there are 60 distinct substituted anthracene compounds (hexabromoanthracene) with six bromines, as listed below:

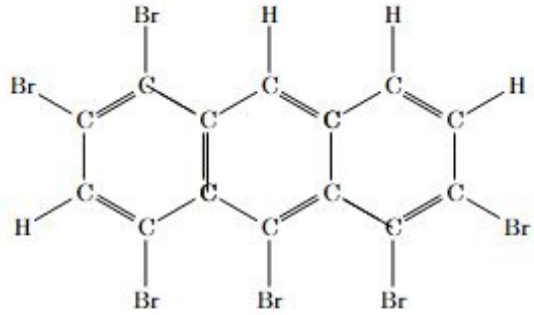


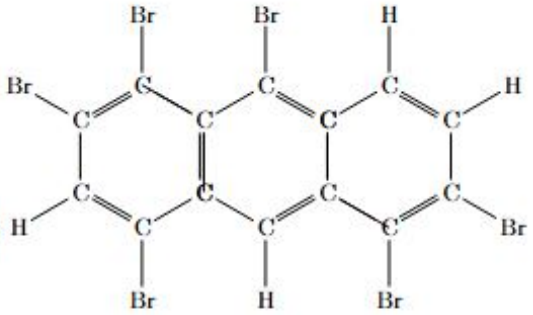


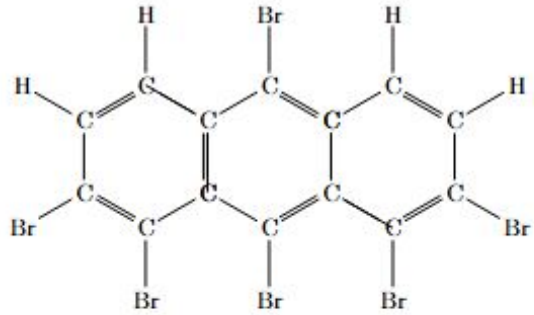


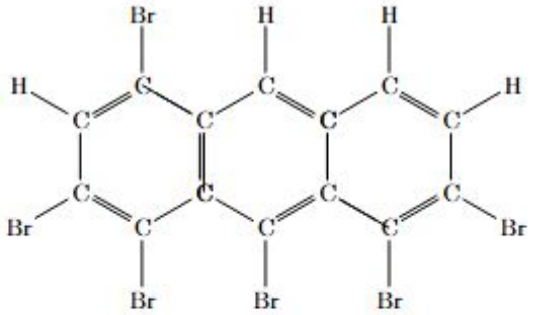


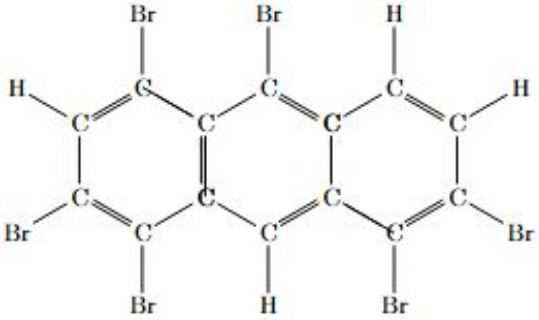


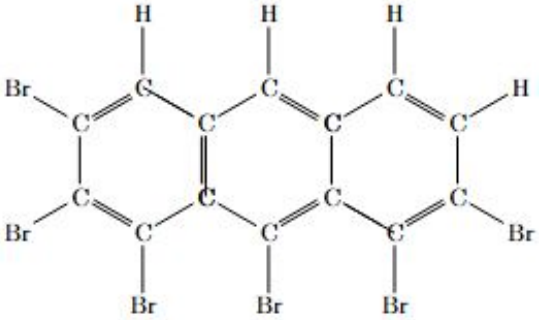


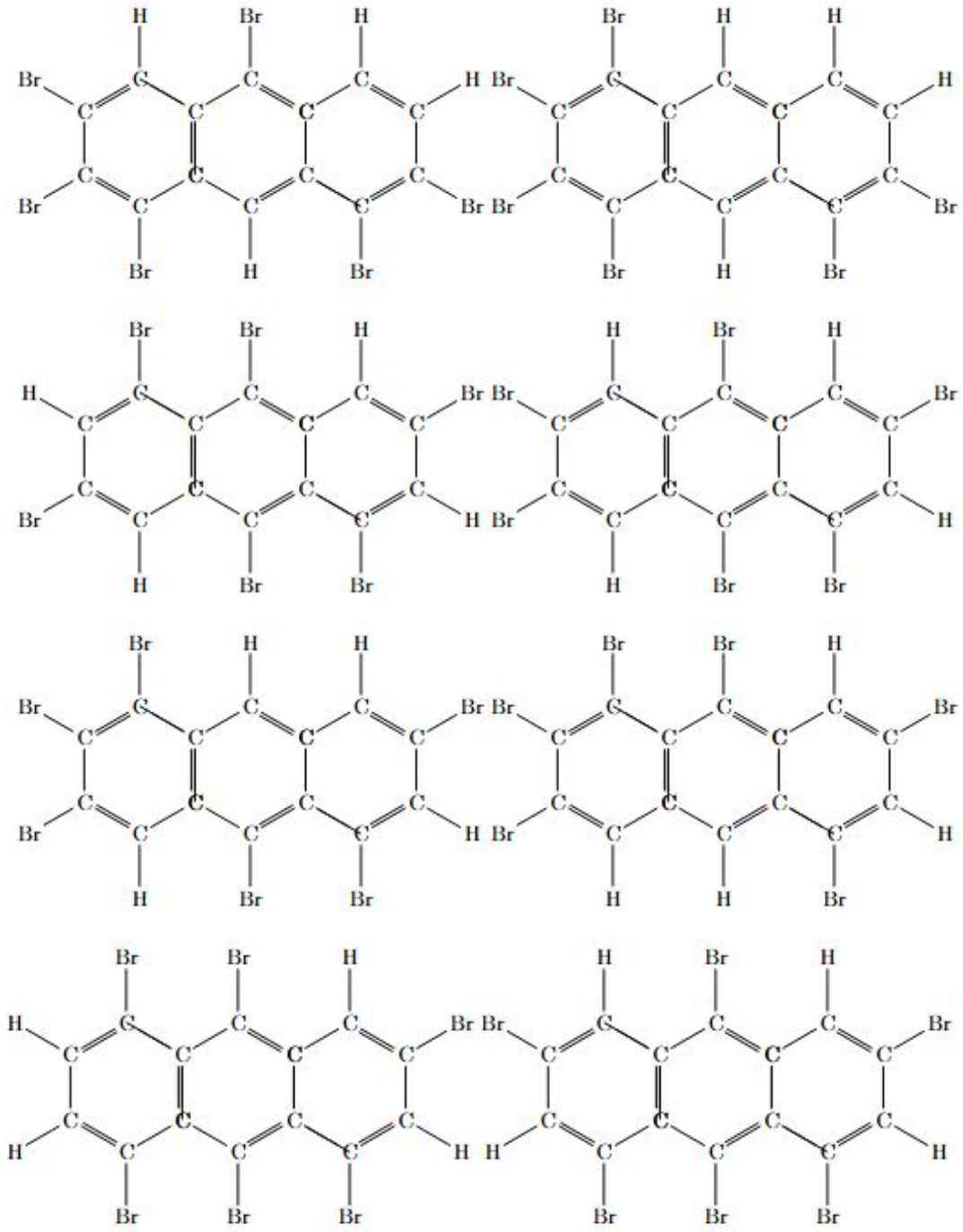


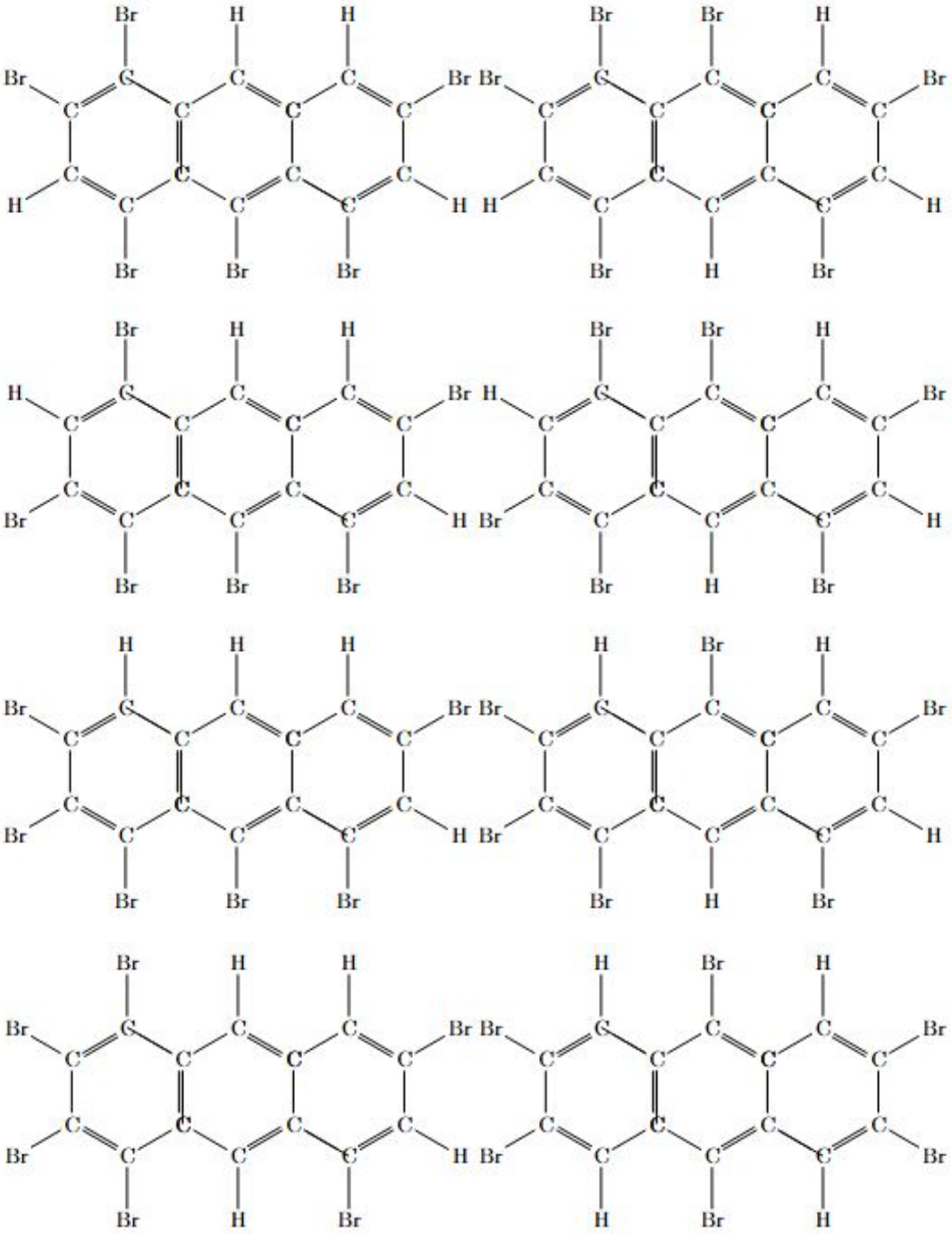


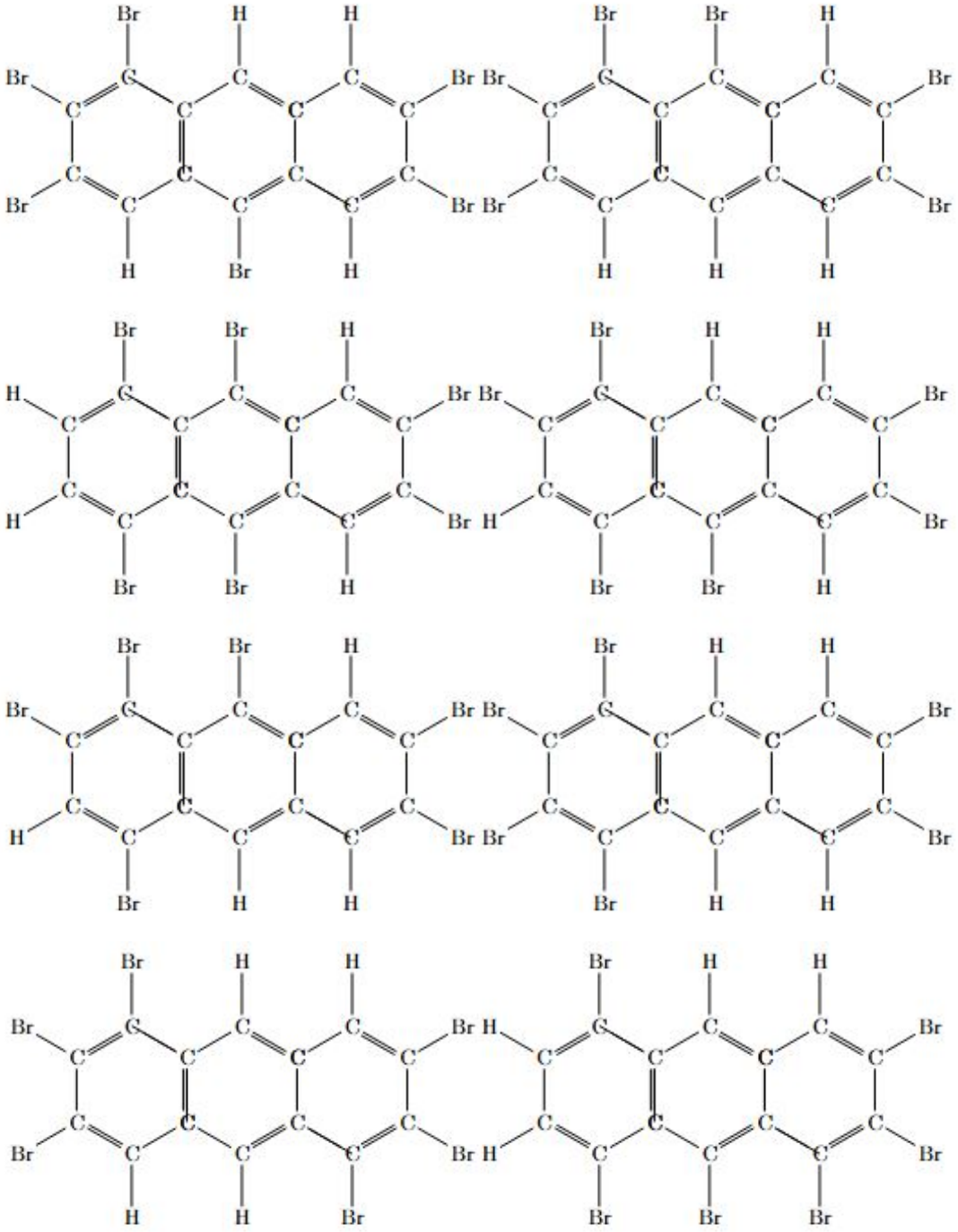


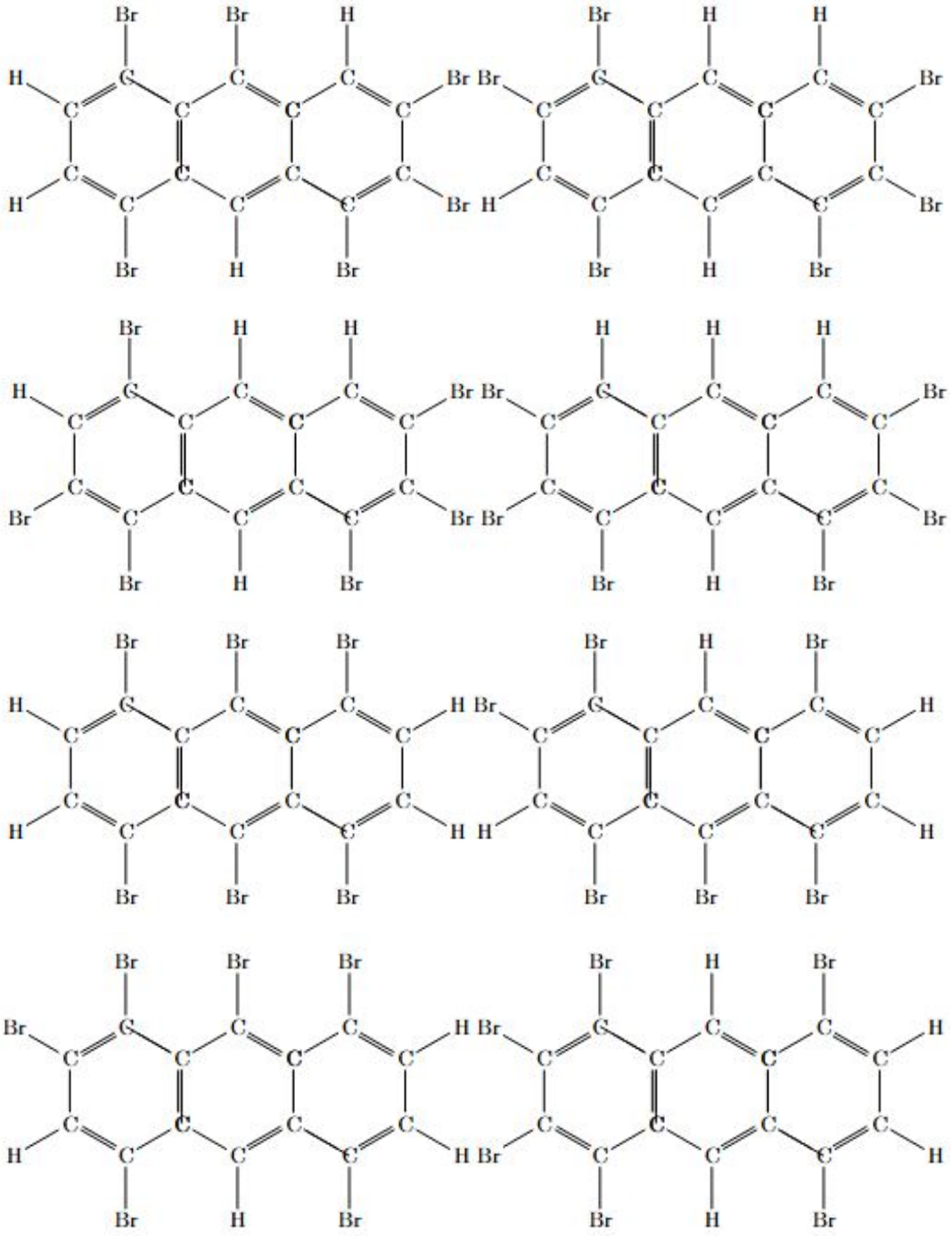


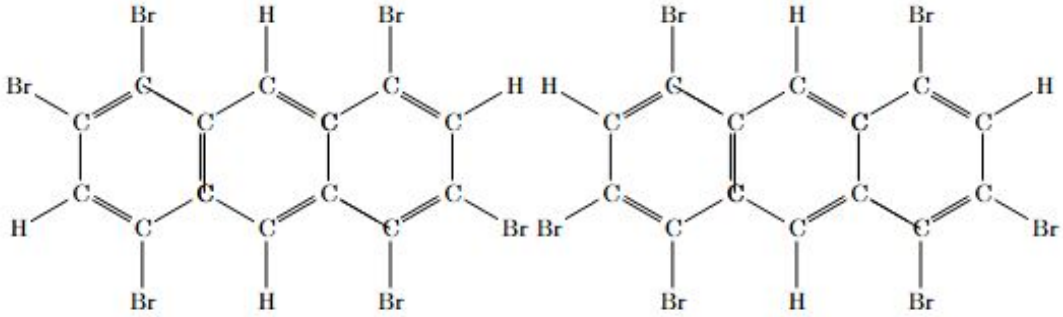




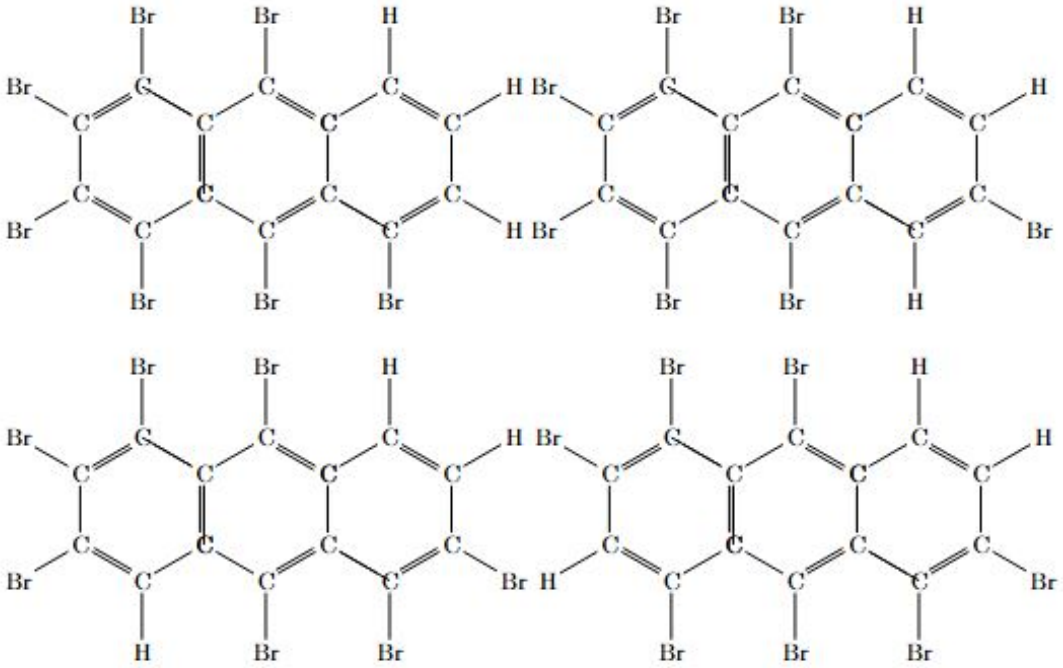


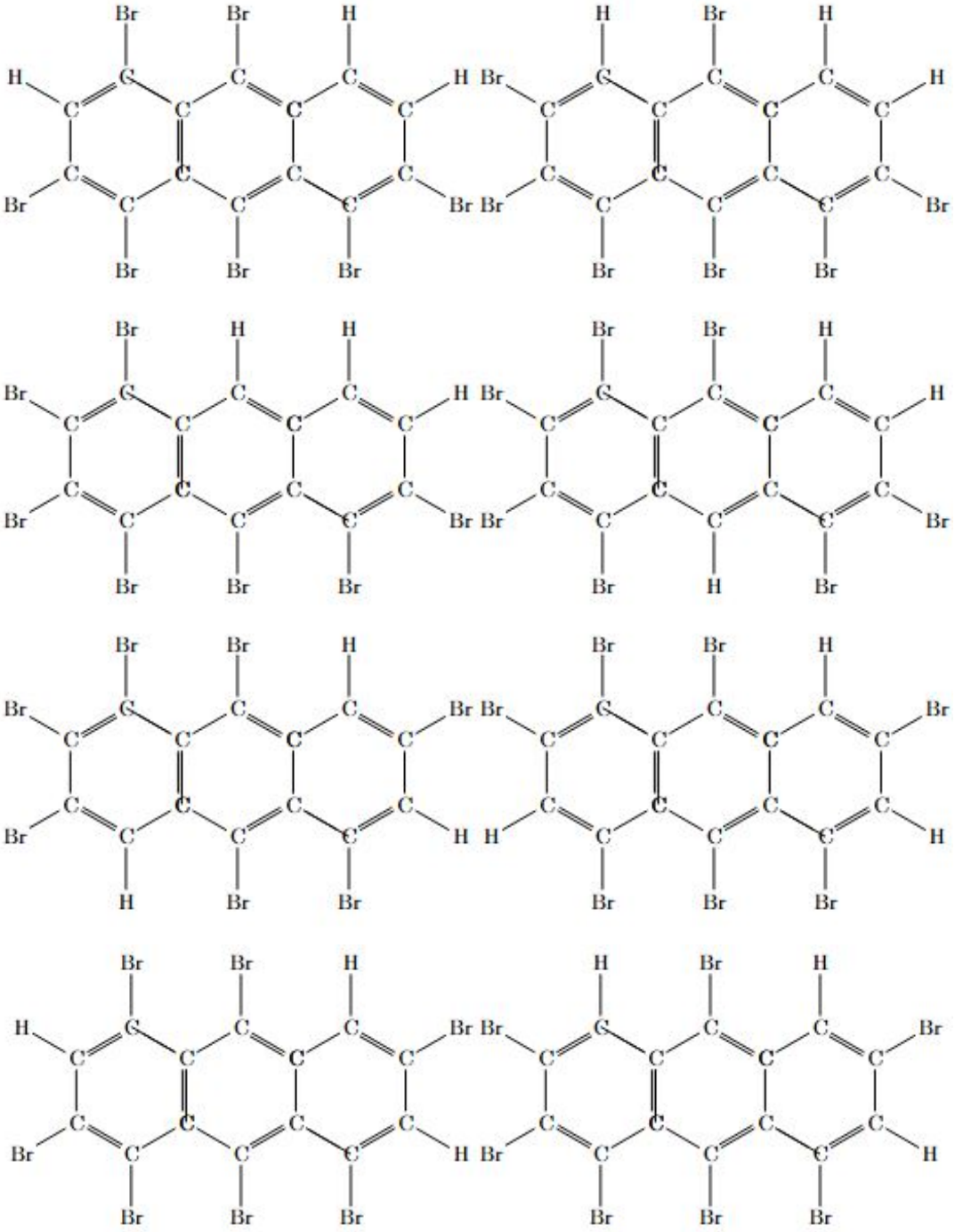


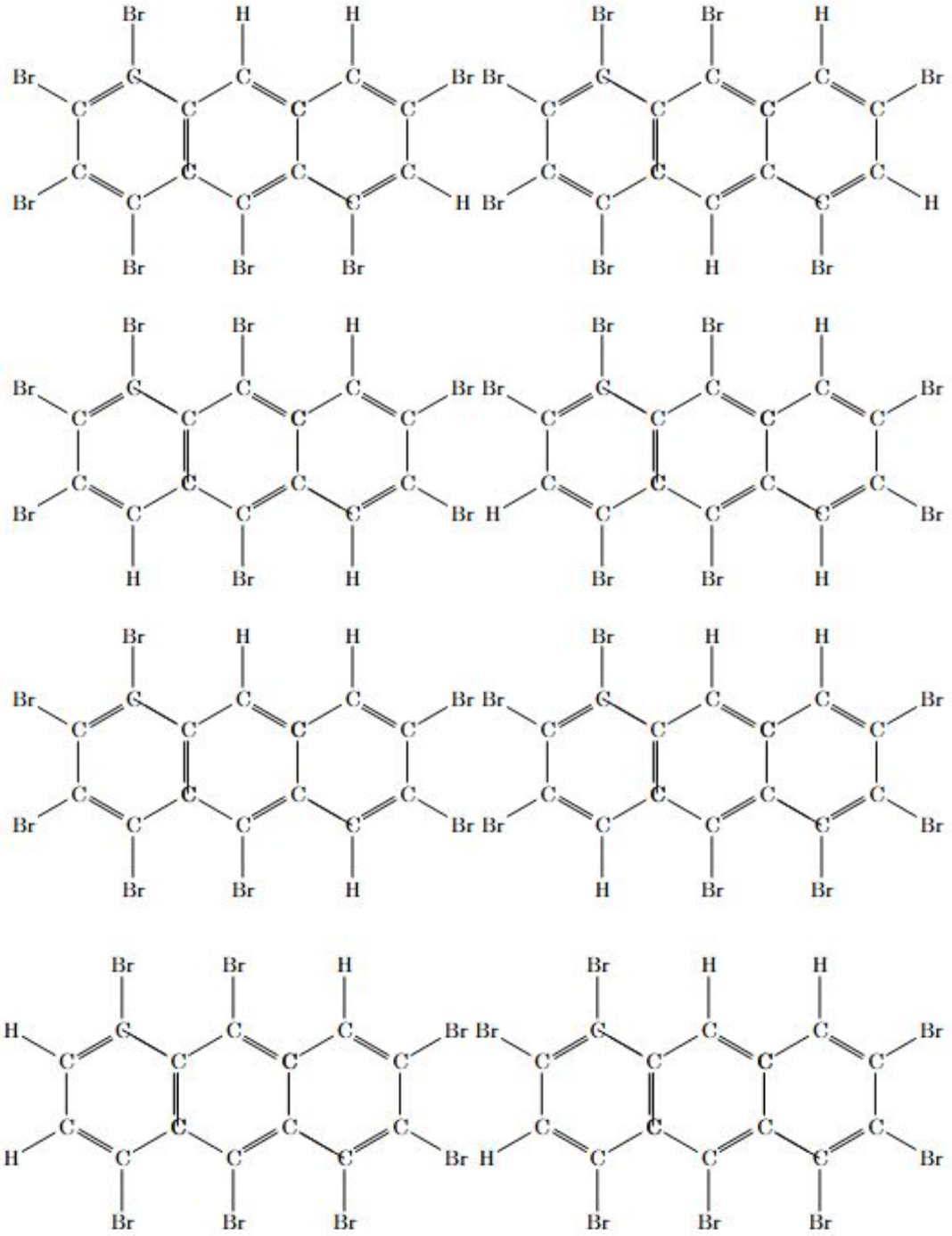


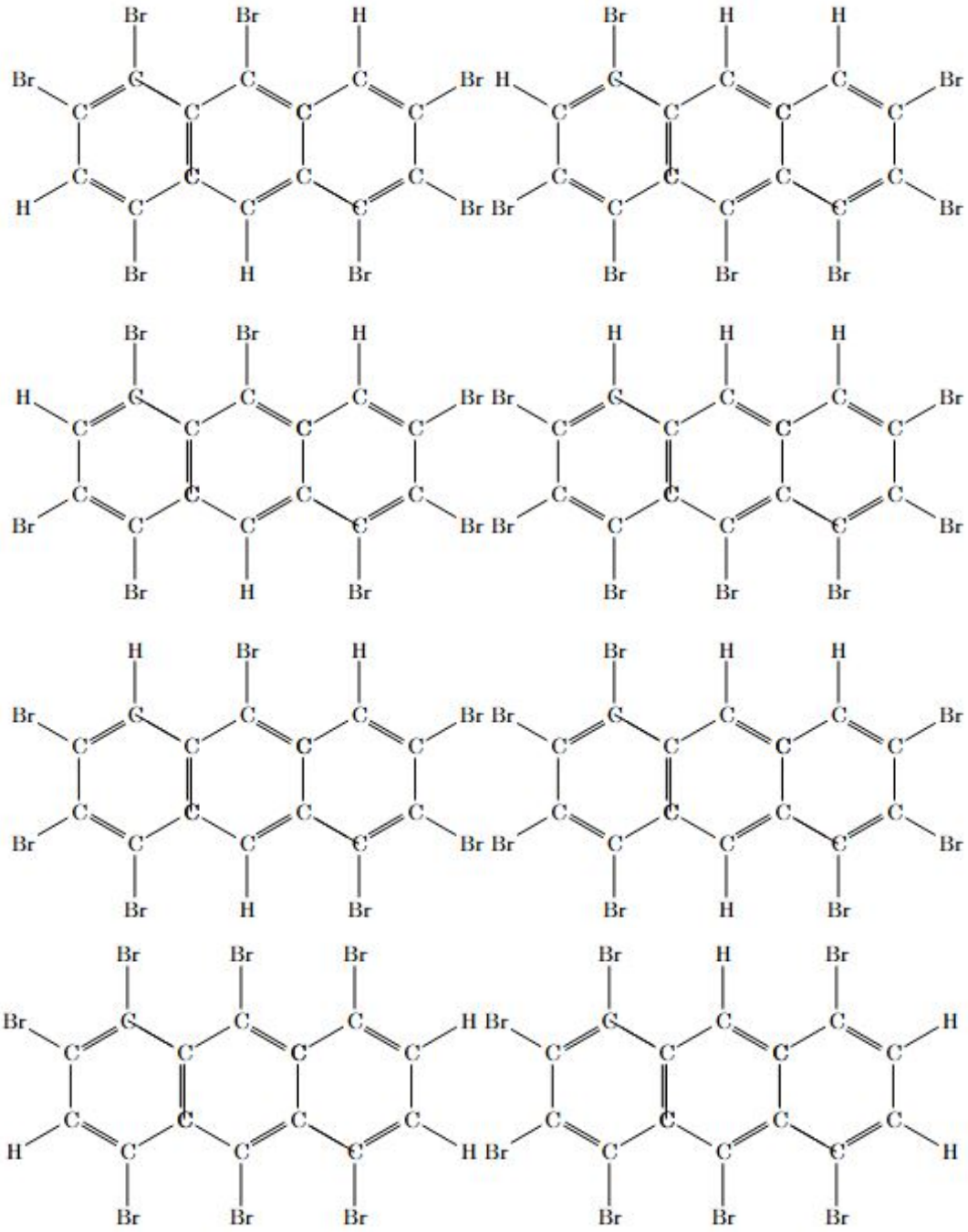


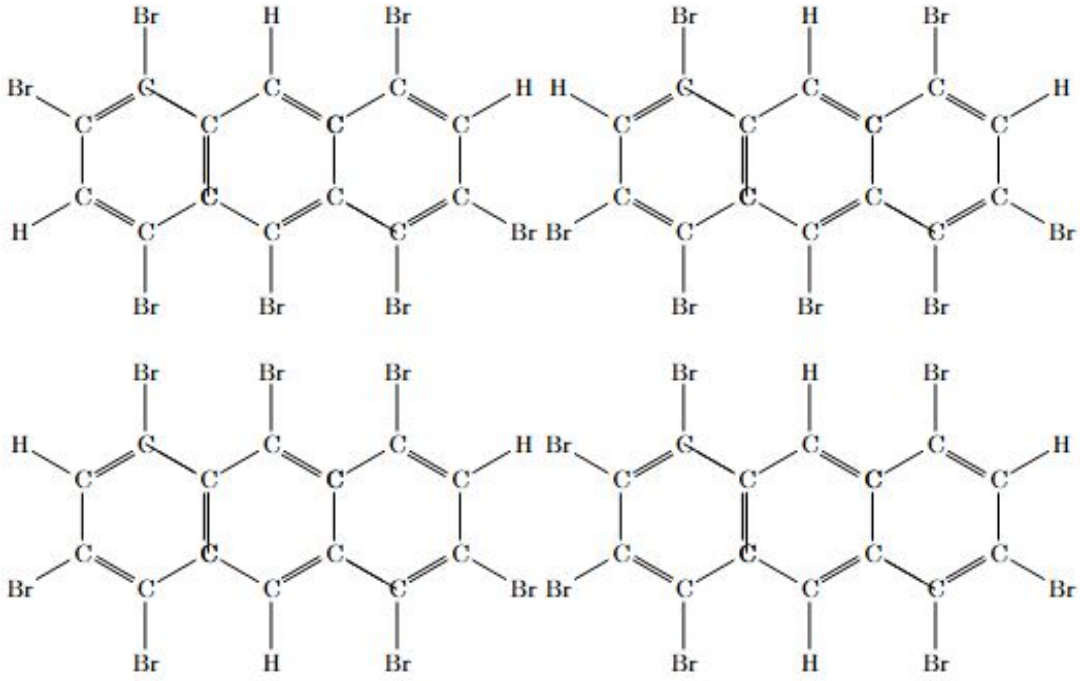
The coefficient of H^3Br^7 indicates that there are 32 distinct substituted anthracene compounds (heptabromoanthracene) with seven bromines, as listed below:



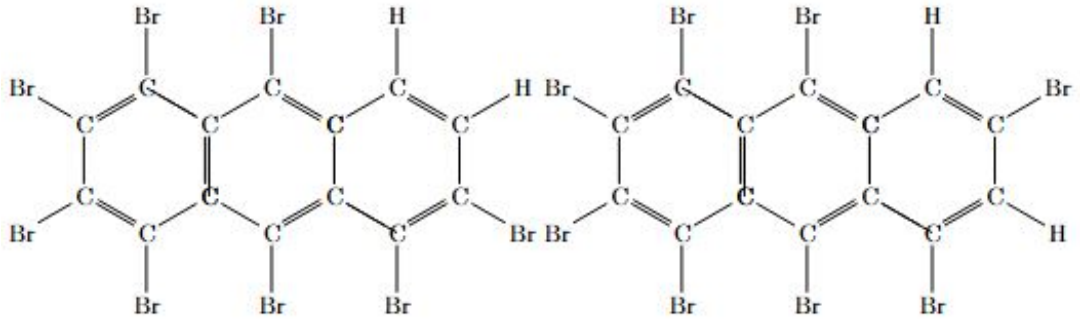


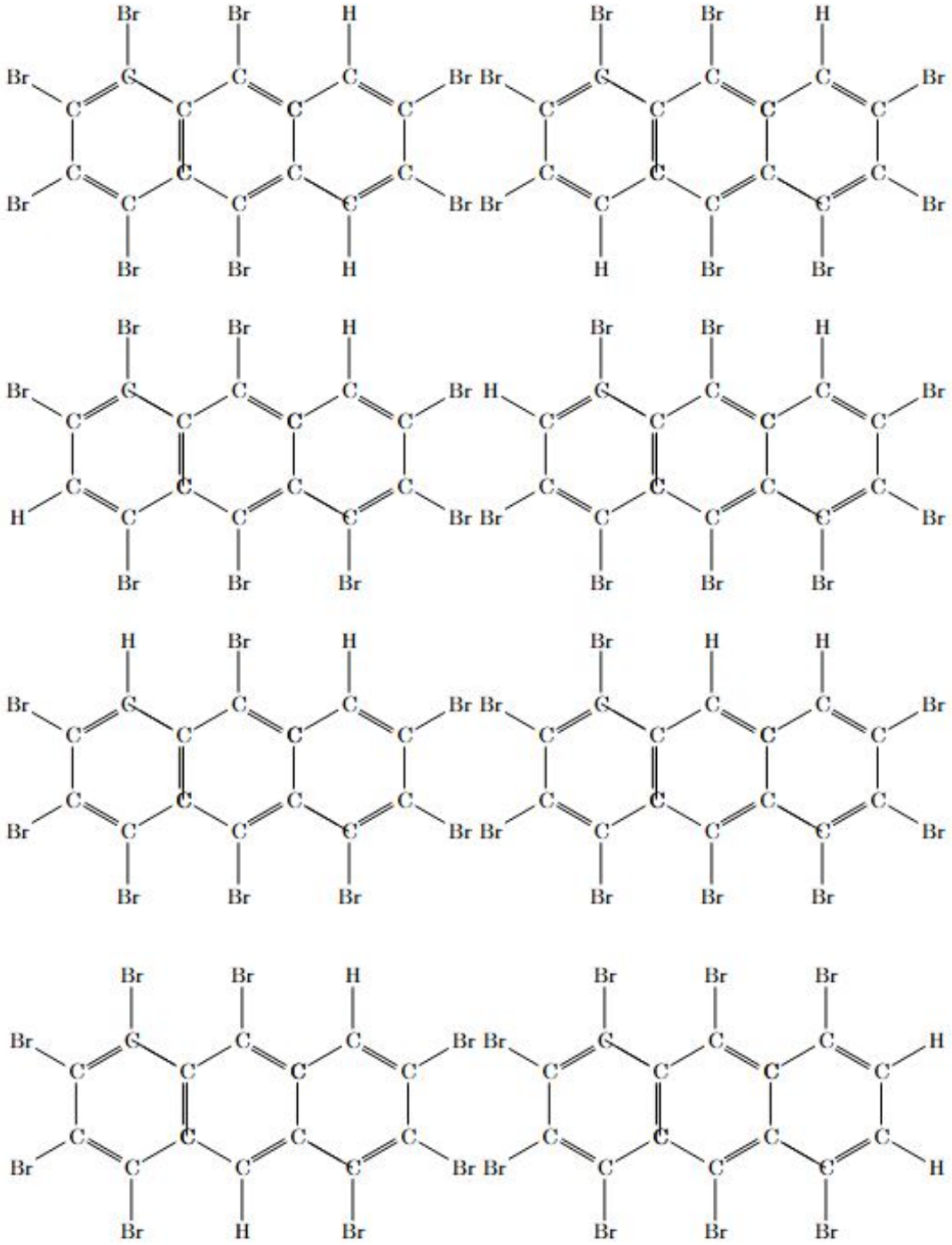


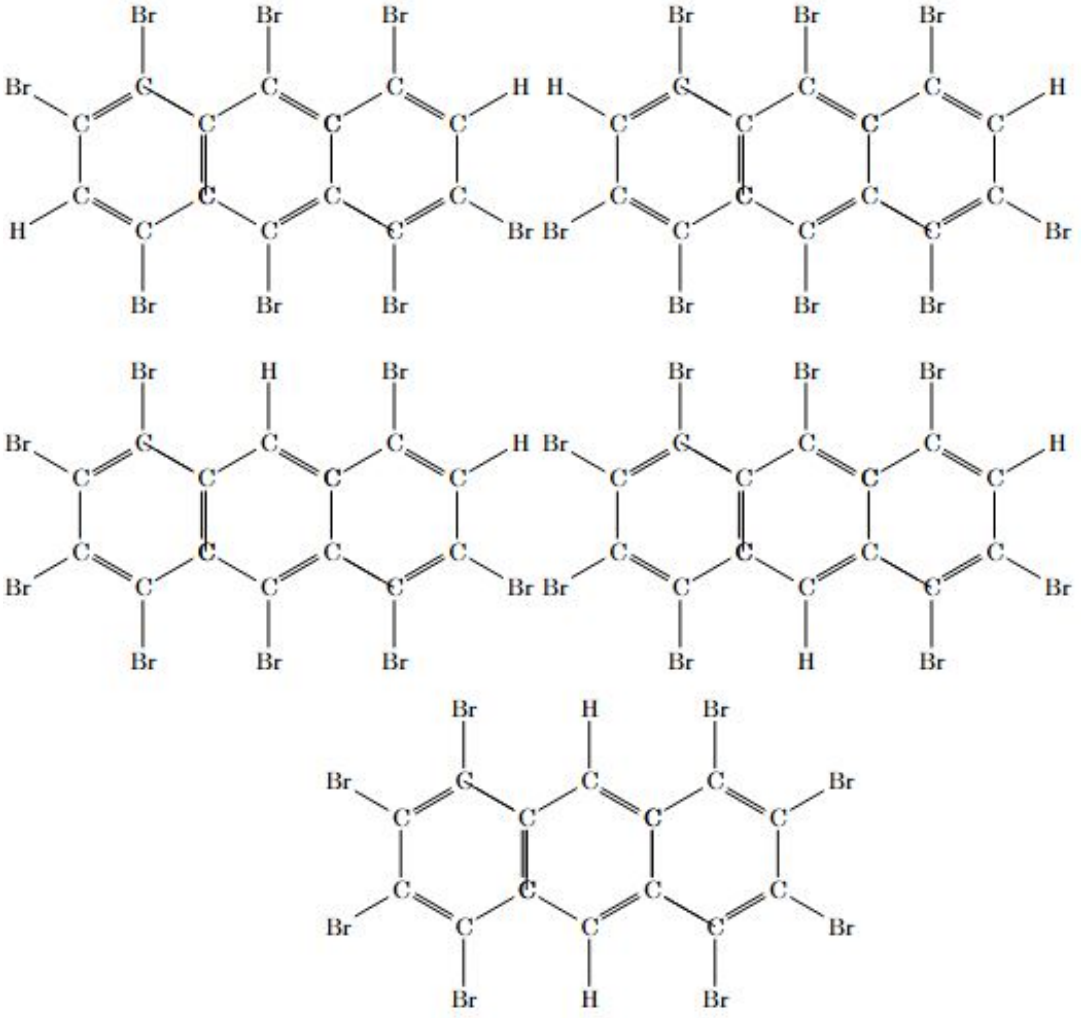




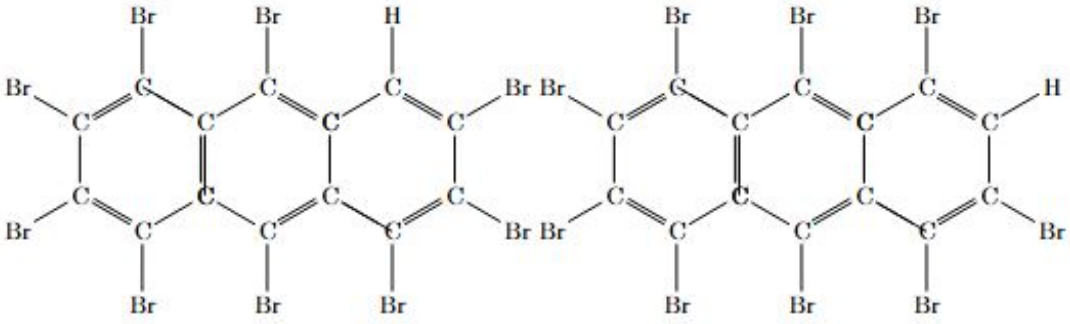
The coefficient of H^2Br^8 indicates that there are 15 distinct substituted anthracene compounds (octabromoanthracene) with eight bromines, as listed below:

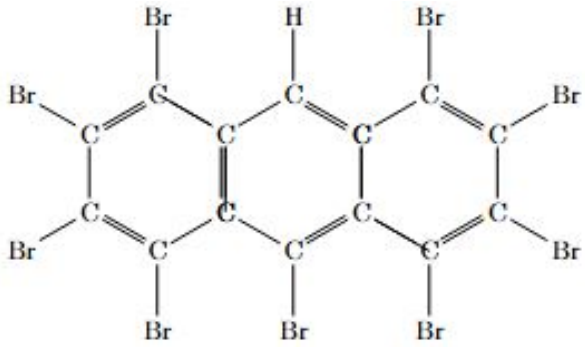




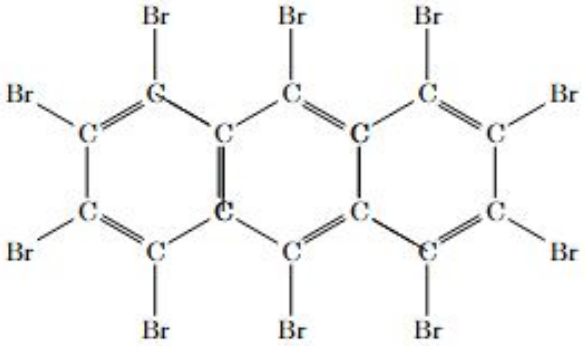


The coefficient of $H\mathrm{Br}^9$ indicates that there are 3 distinct substituted anthracene compounds (nonabromoanthracene) with nine bromines, as listed below:





The coefficient of Br^{10} indicates that there is only 1 substituted anthracene compound (decabromoanthracene) with ten bromines, as below:



4.2 Discussion

In this thesis, we used Burnside's lemma and PET to systematically address chemical enumeration problems involving substituted polycyclic aromatic hydrocarbons such as naphthalene and anthracene compounds, in which 1 atom of chlorine and 7 hydrogen atoms, 2 atoms of chlorine and 6 hydrogen atoms, 3 atoms of chlorine and 5 hydrogen atoms,..., and 8 chlorine atoms and no hydrogen atoms are attached; and 1 atom of bromine and 9 hydrogen atoms, 2 atoms of bromine and 8 hydrogen atoms, 3 atoms of bromine and 7 hydrogen atoms,..., and 10 atoms of bromine and no hydrogen atoms are attached, respectively.

We began by identifying the relevant symmetry groups and their associated operations. For each group element, we calculated the fixed points (attachments) substitution configurations that remain invariant under the corresponding symmetry operation (rotation and reflection). Applying Burnside's lemma, we then determined the number of distinct substitution patterns (orbits) by averaging the fixed attachments across all elements of the symmetry group.

Subsequently, Polya's Enumeration Theorem (PET) was used to derive and analyze the cycle index polynomials of the symmetry groups. This approach enables the enumeration of all distinct substitution configurations in a compact and algebraically structured manner. Thus, by examining the coefficients of each term in the cycle index polynomial, we were able to enumerate with confidence the distinct substituted naphthalene and anthracene compounds.

CONCLUSION AND RECOMMENDATION

Conclusion

This thesis successfully applies Burnside's lemma and Polya's Enumeration Theorem to determine the number of distinct substituted naphthalene and anthracene compounds formed through substitution of hydrogen atom or atoms with chlorine and bromine atoms, respectively. By modeling molecular symmetries as group actions on the set of possible substitution patterns, we systematically accounted for indistinguishable structures due to symmetry, thereby avoiding redundancy in enumeration.

For substituted naphthalene compounds, by replacing hydrogen atom or atoms with $1, 2, 3, 4, 5, 6, 7$, and 8 chlorine atoms, there are $2, 10, 14, 22, 14, 10, 2$, and 1 distinct substituted naphthalene compounds, respectively. This means, for instance, that chloronaphthalene ($C_{10}H_7Cl$) has 2 isomers, dichloronaphthalene ($C_{10}H_6Cl_2$) has 10 isomers, trichloronaphthalene ($C_{10}H_5Cl_3$) has 14 isomers, tetrachloronaphthalene ($C_{10}H_4Cl_4$) has 22 isomers, pentachloronaphthalene ($C_{10}H_3Cl_5$) has 14 isomers, hexachloronaphthalene ($C_{10}H_2Cl_6$) has 10 isomers, heptachloronaphthalene ($C_{10}H_1Cl_7$) has 2 isomers, and octachloronaphthalene ($C_{10}Cl_8$) has 1 isomers.

And for substituted anthracene compounds, by replacing hydrogen atom or atoms with $1, 2, 3, 4, 5, 6, 7, 8, 9$, and 10 bromine atoms, there are $3, 15, 32, 60, 66, 60, 32, 15, 3$, and 1 distinct substituted anthracene compounds, respectively. Again, from this one can understand that bromoanthracene ($C_{14}H_9Br$) has 3 isomers, dibromoanthracene ($C_{14}H_8Br_2$) has 15 isomers, tribromoanthracene ($C_{14}H_7Br_3$) has 32 isomers, tetrabromoanthracene ($C_{14}H_6Br_4$) has 60 isomers, pentabromoanthracene ($C_{14}H_5Br_5$) has 66 isomers, hexabromoanthracene ($C_{14}H_4Br_6$) has 60 isomers, heptabromoanthracene ($C_{14}H_3Br_7$) has 32 isomers, octabromoanthracene ($C_{14}H_2Br_8$) has 15 isomers, nonabromoanthracene ($C_{14}H_1Br_9$) has 3 isomers, and decabromoanthracene ($C_{14}Br_{10}$) has 1 isomers.

These results highlight the powers of combinatorial enumeration techniques and group actions in predicting molecular diversity, particularly when accounting for indistinguishability due to symmetry.

Recommendation

This thesis focuses on specifically the application of Burnside's lemma and Polya's Enumeration Theorem to solve enumeration problems related to substituted naphthalene and anthracene compounds, demonstrating their effectiveness in the systematic counting of distinct isomers. Given the success of these methods in handling such structures, it is recommended that future researchers extend this approach to the enumeration of distinct substituted tetracene, pentacene, hexacene, and heptacene.

Research Fund Acknowledgment

This research project is funded by Adama Science and Technology University under the grant number ASTU/SM-R/1159/25, Adama, Ethiopia.

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