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ISOMERISM AS MANIFESTATION OF INTRINSIC SYMMETRY OF MOLECULES: LUNN–SENIOR'S THEORY[*]

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> *. . . I trust that you will go on with the consideration of chemical phenomena from a mathematical point of view, for I am convinced that the future progress of chemistry, as an exact science, depends very much indeed upon the alliance of mathematics. . .*
>
> London, October 13, 1878
>
> (from a letter of Dr. Frankland to Mr. Sylvester, see [2]

Abstract. This paper is an extended review of our doctoral thesis " Isomerism as Intrinsic Symmetry of Molecules" in which we present, continue, generalize, and trace out Lunn–Senior's theory of isomerism in organic chemistry.

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Key words: Mathematical model of isomerism, enumeration of isomers, substitution reactions.

[*] This article presents the principal results of the doctoral thesis "Isomerism as internal symmetry of molecules" by Valentin Vankov Iliev (Institute of Mathematics and Informatics), successfully defended before the Specialised Academic Council for Informatics and Mathematical Modelling on 15 December, 2008.

1. Introduction.

1.1. Historical background and the idea of symmetry. To quote Berzelius, one of the great pioneers of chemistry: "... By isomeric substances I understand those which possess the same chemical composition and the same atomic [molecular] weight, but different properties" (see [1]). The explanation of these different properties varies and is a reflection of a more general dispute between idealistic and materialistic philosophy, between Plato and Democritus.

Contrary to Democritus' atoms considered to be building blocks of all material objects and the only truly existing things, Plato's atoms were perceived also as geometrical forms: those of the five regular solids. The surface of these solids can be decomposed into triangles which commute and this interchange models the interactions. According to W. Heisenberg, in this way "Plato was able to escape the problem of the indefinite divisibility of matter. For as two-dimensional surfaces the triangles were not bodies, not matter any longer; hence matter could not be further divided *ad infinitum.* At the lower end, therefore, in the realm, that is, of minimal spatial dimensions, the concept of matter is resolved into that of mathematical form. This form determines the behavior, first of the smallest part of matter, then of matter itself. To a certain extend it replaces the natural law of later physics; for without making explicit references to the course of time, it characterizes the tendencies in the behavior of matter." (see [4]).

It is not a coincidence that the original author of quantum mechanics — Arthur Constant Lunn, see [37] and [25], and one of the two official authors — Werner Heisenberg, share the same opinion on the nature of the things that underlay matter — that of Plato, or as Heisenberg says: "... I think that on this point the modern physics has definitely decided for Plato. For the smallest units of matter are, in fact, not physical objects in the ordinary sense of the word; they are forms, structures or — in Plato's sense — Ideas, which can be unambiguously spoken of only in the language of mathematics ..." Moreover, "... Plato's symmetries were not yet the correct ones, but he was right in believing that ultimately, at the heart of nature, among the smallest units of matter, we find mathematical symmetries. It was an unbelievable achievement of the ancient philosophers to have asked the right questions. But, lacking all knowledge of the empirical details, we could not have expected them to find answers that were correct in detail as well".

Thus, the idea of symmetry undoubtedly is Ariadne's ball of thread used in all natural sciences, including chemistry.

1.2. Predecessors. Historically, the English chemist E. Frankland was the first who in a 1852 paper developed the theory of combining power of the elements, called rays of atomicity, or lines of connection, or valency, or valence (f. LL: "power"). He introduced "latent valence" for free bond. In the paper [2, p. 348], which is a letter to the mathematician J. J. Sylvester, Frankland insisted that he had discovered the theory of molecule structure.

In the period 1857–58, the German organic chemist F. A. Kekulé also formulated the theory of the structure of an organic molecule, stressing on the tetravalence of the carbon atom and the ability of carbon atoms to link to each other. His most famous paper from 1865 studied the structural formula of benzene. In order to explain why benzene always has one monosubstituted derivative, three di-substituted homogeneous and three di-substituted heterogeneous derivatives, he supposed that the six carbon atoms form a regular planar hexagon with alternating single and double bonds. In other words, he introduced the hexagonal symmetry of the molecule of benzene that yields the desired numbers and thus was forerunner of Lunn–Senior's theory of isomerism.

During that time, in a series of papers, starting from his work on algebraic forms and determinants, J. J. Sylvester added his own ideas to others, in what is called Invariant Theory (then Invariative Theory). In his paper [35], he denoted the univalent atoms (H, Cl, Br, K, ...) with binary linear forms, bivalent atoms (O, Zn, Mg, ...) – with binary quadrics, trivalent atoms (B, Tl, Au, ...) – with binary cubics, etc. Further, he considered any invariant of a form, or system of forms, as representing a saturated system of atoms. Thus, "... O_2 will represent a quadratic invariant of a quadric ..., KOH ... will represent the invariant to a system of one quadratic and two linear forms, which is linear in each set of coefficients. This is in fact the *Connective* between the given quadratic and another obtained by taking the product of the two linear forms" (see [35, p. 65]). Thus, J. J. Sylvester gives a model of skeletal isomerism, which is the prototype of the modern version of Frankland's valence bond theory — this is the so-called spin-coupled theory of molecular electronic structure. It was the first time Sylvester introduced the mathematical idea of symmetry in chemistry in the full sense of this word by using invariants of the special linear group $SL_2(\mathbb{R})$ as models of molecules. He also was the first who used graphs for the representation of a molecule and especially noted that "Chemical graphs, at all events, for the present are to be regarded as mere translations into geometrical forms of trains of priorities and sequences having their proper *habitat* in the sphere of order and existing quite outside the world of space. Were it otherwise, we might indulge in some speculations as to the directions of the lines of emission or influence or radiation or whatever else the bond might then be supposed to represent as dependent on the manner of the atoms entering into combination to form chemical substances" (see [35, p. 79]).

The above quotation describes very well the philosophy of chemistry before the birth of stereochemistry. The structure of molecule consists of its connectivity data and its space configuration is irrelevant. Thus, a material phenomenon — molecule — is represented by a scheme, by an idea, form, which is said to be its chemical graph and which works as its model and interacts with other forms. Note that sometimes these forms possess symmetry like Kekulé's structural formula of benzene with its hexagonal symmetry.

The three-dimensional Euclidian space as receptacle of all material things arises in the works of J. H. van't Hoff and of J. A. Le Bel. Both chemists are credited with giving an explanation of chirality (enantiomerism, optical activity). In 1874 they independently assumed that the existence of chiral pairs is an effect of (up to terminology) the existence of two different orientations of the three-dimensional space, thus giving birth to stereoisomerism and stereochemistry. According to van't Hoff's doctrine of "the asymmetric carbon atom", there exists exactly one stereoisomer of methane with composition CXYZA, which is a chiral pair regardless of the nature of the univalent substituents X, Y, Z, A. Van't Hoff explained this phenomenon with the space arrangement of the substituents at the apices of a regular tetrahedron with center C. The two univalent substitution isomers — members of this chiral pair — can be obtained from one another via mirror symmetry, and, in particular, possess the two different orientations in the three-dimensional space. Van't Hoff insists that the chiral pair is unique because the four valences of the carbon atom C are chemically equivalent. This uniqueness is a type property of the molecule, that is, a property which does not depend on the nature of the substituents.

1.3. Lunn and Senior. The nature of the above equivalence is elucidated by Lunn–Senior's theory of isomerism (see [25]). Lunn and Senior arrange the permutations of X, Y, Z, A, in two classes which are the two orbits of the alternating group A_4 in the set S_4 of all permutations of four objects, and these two classes are supposed to represent the two members of the chiral pair. Lunn and Senior explain van't Hoff's equivalence of the four bonds of carbon as a result of the action of a symmetry group, the permutation group A_4, which they attach to the molecule of methane divided into a skeleton C and the four univalent substituents. Any odd permutation, for instance the transposition (XY), can act the part of the space mirror symmetry: the multiplication by (XY) turns any one of the A_4-orbits onto the other. Thus, the arrangement of the substituents in the three-dimensional Euclidian space becomes superfluous, or, as Lunn-Senior note in [25, p. 1030], “Connexity is a relation of order independent of considerations of space. The “structural” relations treated by chemists are relations of just this sort, and it is unfortunate that the word structure as used by engineers, etc., should carry with it geometrical connotations which are too special for chemistry. Throughout the present article “connexity” and “structure” are used as synonyms, and the former expression is introduced here merely to emphasize the fact that the relations indicated by both terms are independent of space limitations, except perhaps the vague one implied in the word vicinity.”

2. Lunn–Senior’s theory.

2.1. Lunn–Senior’s theory and the idea of symmetry. Lunn–Senior’s theory is a wide generalization of the above setup, which philosophically goes back to the tradition before van’t Hoff’s and Le Bel’s use of tetrahedra as spatial models of the carbon atom, that is, before the birth of the stereochemistry, which was painful and controversial, see for instance [24], [29], [36]. As the example of methane indicates, this theory of isomerism also is based on the idea of symmetry: for some types of isomerism the authors introduce finite permutation groups associated with a given parent molecule and similar to the above A_4. Lunn–Senior’s groups reflect the internal symmetry of these molecules by producing certain orbits that model their derivatives, and show, in particular, why the number of these derivatives with given composition is an invariant when changing the nature of the substituents.

In the book [21] and in our doctoral dissertation [22], which is a translation of this book (with immaterial changes), we present, continue, generalize and trace out the framework of the theory of isomerism developed by A. C. Lunn and J. K. Senior in their paper [25]. Below, we will follow the structure of the dissertation in order to make a review in English of this work, which is written in Bulgarian. We note that these results were initially published in the papers [5]–[25] and [37].

In section II.1 we introduce notation and define precisely the notions that will be used further. Here we identify the structural formulae of chemical compounds with labelled connected multi-graphs without loops, which, with an abuse of the language, are said to be graphs.

2.2. Skeletons and substituents. Lunn-Senior’s theory is based on fixing a division of the molecule under consideration into a skeleton and several, let us say d, univalent substituents. A molecule is said to be Lunn–Senior’s if there is no univalent substituent which is also a part of the skeleton. We clarify these notions by the examples of ethane and bromoethane below.

(a) Ethane C_2H_6. Suppose that the skeleton chosen is its carbon skeleton C — C. Then the number d of univalent substituents is 6, and this is a Lunn-Senior structural formula.

($a_{(5,1)}$) The number of all chloroethanes C_2H_5Cl is 1, the number of all bromoethanes C_2H_5Br is 1, etc.; in general, the number of all derivatives of ethane of type $(5,1)$ is 1, so we obtain a type property of ethane, that is, a property which does not depend on the nature of the univalent substituents.

($a_{(4,2)}$) The number of all dichloroethanes $C_2H_4Cl_2$, the number of all difluoroethanes $C_2H_4F_2$, the number of all dibromoethanes $C_2H_4Br_2$, etc., is 2, and we get another type property of ethane.

($a_{(4,1^2)}$) The number of bromochloroethanes C_2H_4ClBr is 3, etc., the number of all derivatives of ethane of type $(4,1,1)$ is 3, so we have a type property of ethane.

($a_{(3^2)}$) The number of all tribromoethanes $C_2H_3Br_3$ is 2, and, in general, this is the number of all products of ethane of type $(3,3)$, so this number also is a type property.

($a_{(3,2,1)}$) The number of all dichlorobromoethanes $C_2H_3Cl_2Br$ is 4, the number of all dibromochloroethanes $C_2H_3ClBr_2$ is 4, and, in general, this is the number of all products of ethane of type $(3,2,1)$, so this number also is a type property.

(b) Bromoethane C_2H_5Br. We choose the skeleton to be C — C — Br. Then the number d of univalent substituents is 5.

($b_{(4,1)}$) When the five substituents consist of four H and one Cl, the number of all different products of bromoethane is 3 — see ($a_{(4,1^2)}$). When the five substituents consist of four H and one Br, the number of all different products of bromoethane is 2 — see ($a_{(4,2)}$). The number of all derivatives of bromoethane of type $(4,1)$ is 3 under the restriction that all five substituents are different from Br (the corresponding structural formulae are Lunn-Senior's), and this is a type

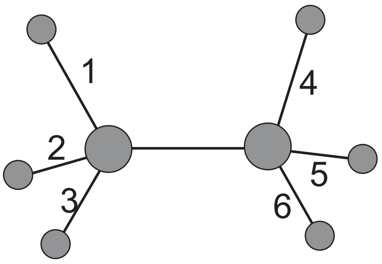

Fig. 1. Ethane

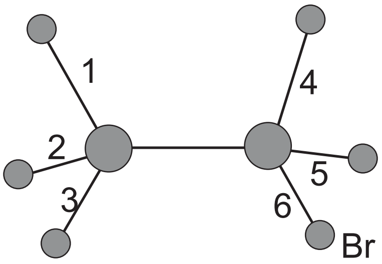

Fig. 2. Bromoethane

property of bromoethane.

($b_{(3,2)}$) In case the five substituents consist of three H and two Cl, the number of all different products of bromoethane is 4 — see ($a_{(3,2,1)}$). On the other hand, when the five constituents consist of three H and two Br, we obtain 2 derivatives — see ($a_{(3^2)}$). The number of all derivatives of bromoethane of type $(3,2)$ is 4 under the restriction that all five substituents are different from Br (the corresponding structural formulae are Lunn–Senior's), and this is a type property of bromoethane.

The intrinsic reason for these variations is that we got a structural formula which is not Lunn-Senior's: Br is among the univalent substituents and in the same time — a constituent of the skeleton.

The differences among the substituents (but not their nature) are reflected by the model in the following way. The d free bonds of the skeleton are numbered with the elements of the integer-valued interval $[1,d]$, and any attachment of univalent substituents at these bonds produces a dissection of $[1,d]$ into several disjoined subsets A_1, A_2, $\dots$, via the rule: A_k consists of the numbers of the positions of the ligants of type x_k, $k=1,2,\dots$. Here by x_k we denote any univalent substituent or group, for instance, Cl, Br, I, K, $\dots$, COOH, NH_2, N_3, ... We may assume that these subsets are ordered from largest to smallest, and then we obtain a tabloid $A=(A_1,A_2,\dots)$, and a partition $\lambda=(\lambda_1,\lambda_2,\dots)$ of d, $\lambda_k=|A_k|$, $k=1,2,\dots$. The tabloid A represents the structural formula of the univalent part of the molecule under consideration, and the partition λ represents its molecule formula $x_1^{\lambda_1}x_2^{\lambda_2}\dots x_d^{\lambda_d}$ in Berzelius notation.

Let us denote by P_d the set of all partitions λ of d, by T_d — the set of all tabloids (structural formulae) with d nodes, and by T_λ — those of them with molecular formula λ. The symmetric group S_d (and any of its subgroups) acts naturally on the set T_d and on any of its subsets of the form T_λ, $\lambda\in P_d$.

2.3. Types of isomerism: groups and orbit spaces. Lunn–Senior's theory studies three types of isomerism: univalent substitution isomerism, stereoisomerism, and structural isomerism. These three types of isomerism define three equivalence relations in the set of all structural formulae T_λ with fixed molecule formula λ, each of them is finer than the next one, and any equivalence class is identified with an isomer. Lunn and Senior postulated that the equivalence classes of these relations are produced as orbits of three permutation groups $G\leq G'\leq G''\leq S_d$, specific for the considered molecule, and such that: any univalent substitution isomer can be identified with a G-orbit in T_λ; any stereoisomer can be identified with a G'-orbit in T_λ; any structural isomer can be identified with a G''-orbit in T_λ. With an abuse of the language, we can also call these orbits structural formulae of the corresponding isomers.

The groups G and G' are related as follows: $G = G'$, in case there are no chiral pairs among the univalent substitution isomers, and $G \leq G'$ with $|G' : G| = 2$, in case there are such pairs. In the first case, the G- and G'-orbits coincide and represent the diamers. In the last case, each G'-orbit contains either two G-orbits, and the members of any chiral pair are represented by such a couple of G-orbits, or, coincide with one G-orbit, and any diamer is represented by such a G-orbit.

Let us denote the corresponding orbit spaces by $T_{\lambda;G}$, $T_{\lambda;G'}$, and $T_{\lambda;G''}$, respectively, and their sizes by $\nu_{\lambda;G}$, $\nu_{\lambda;G'}$, and $\nu_{\lambda;G''}$. Let $N_{\lambda;\Sigma}$ (respectively, $N'_{\lambda;\Sigma}$, $N''_{\lambda;\Sigma}$) be the number of actually existing univalent substitution isomers (respectively, stereoisomers, structural isomers) of the given molecule with skeleton Σ and molecule formula λ. In particular, as far as Lunn-Senior's thesis is valid, for any $\lambda \in P_d$ we obtain the following inequalities:

$$N_{\lambda;\Sigma} \leq \nu_{\lambda;G},\ N'_{\lambda;\Sigma} \leq \nu_{\lambda;G'},\ N''_{\lambda;\Sigma} \leq \nu_{\lambda;G''}.$$

Thus, the numbers $\nu_{\lambda;G}$, $\nu_{\lambda;G'}$, and $\nu_{\lambda;G''}$ are upper bounds for the corresponding numbers of experimentally found isomers, and, moreover, are type properties of the molecule, that is, properties which do not depend on the nature of the univalent substituents under the condition that this molecule is Lunn–Senior's.

The above inequalities can be used to find the group which corresponds to the particular type of isomerism, as Lunn-Senior's thesis asserts: if one of the inequalities is false for a particular subgroup W of the symmetric group S_d, then this subgroup has to be rejected. On the other hand, the family $(\nu_{\lambda;W})_{\lambda \in P_d}$ of non-negative integers defines the permutation group W up to combinatorial equivalence, see [30, Ch. 1, Sec. 25].

The group G (respectively, G', G'') is said to be Lunn–Senior's group of univalent substitution isomerism (respectively, stereoisomerism, structural isomerism).

2.4. Substitution (genetic) reactions. The substitution (genetic) reactions among the derivatives of the given molecule are reflected by the model in the following way:

(a) On the level of molecule formulae a simple substitution reaction has the form

$$x_1^{\mu_1} \ldots x_i^{\mu_i} \ldots x_j^{\mu_j} \ldots \longrightarrow x_1^{\lambda_1} \ldots x_i^{\lambda_i} \ldots x_j^{\lambda_j} \ldots$$

(falling simple substitution reaction), or the form

$$x_1^{\lambda_1} \ldots x_i^{\lambda_i} \ldots x_j^{\lambda_j} \ldots \longrightarrow x_1^{\mu_1} \ldots x_i^{\mu_i} \ldots x_j^{\mu_j} \ldots$$

(rising simple substitution reaction), where $\lambda, \mu \in P_d$, and $\mu_1 = \lambda_1, \dots, \mu_i = \lambda_i + 1, \dots, \mu_j = \lambda_j - 1, \dots, \mu_d = \lambda_d$, with $1 \leq i < j \leq d$. The above two substitution reactions mean respectively: "a ligant of type x_j takes the place of a ligant of type x_i" and "a ligant of type x_i takes the place of a ligant of type x_j", and in both cases we write $\mu = \varrho_{i,j}\lambda$ and $\lambda < \mu$.

(b) On the level of structural formulae the simple substitution reaction from (a) have either the form

$$B = (B_1, B_2, \dots, B_i, \dots, B_j, \dots) \longrightarrow A = (A_1, A_2, \dots, A_i, \dots, A_j, \dots)$$

(falling simple substitution reaction), or the form

$$A = (A_1, A_2, \dots, A_i, \dots, A_j, \dots) \longrightarrow B = (B_1, B_2, \dots, B_i, \dots, B_j, \dots)$$

(raising simple substitution reaction), where B can be obtained from A via moving an element $s \in A_j$ into the set A_i, and in both cases we write $B = R_{i,s}A$ and $A < B$.

(c) In general, we write $\lambda \leq \mu$ if μ can be obtained from λ via several rising simple substitution reactions of the form (a) — this is the famous dominance order on the set P_d, which plays an important role in the representation theory of the symmetric group; we write $A \leq B$ where B can be obtained from A via several rising simple substitution reactions of the form (b); an equivalent definition of the last partial order is: $A \leq B$ if $A_1 \cup \dots \cup A_k \subset B_1 \cup \dots \cup B_k$ for all $k = 1, \dots, d$.

(d) We factor the partial order from (c) and get a partial order on the space $T_{d;G}$ of all G-orbits via the rule: $a \leq b$ if there exist $A \in a$ and $B \in b$ such that $A \leq B$.

We note that $\varrho_{i,j}$ and $R_{i,s}$ from (a) and (b), respectively, are said to be raising operators.

The relation $a \leq b$, written in the form $b \geq a$ means that the derivative corresponding to a can be obtained from the derivative corresponding to b via several consecutive falling simple substitution reactions. The relation $a \leq b$ means that the derivative corresponding to b can be obtained from the derivative corresponding to a via several consecutive raising simple substitution reactions. Thus, the partially ordered set $(T_{d;G}, \leq)$ represents the univalent substitution isomers and all possible genetic relations among them.

Below, the dominance order on P_6 is graphically portrayed.

$$\begin{tikzcd}
 & (6) \arrow[d] & \\
 & (5,1) \arrow[d] & \\
 & (4,2) \arrow[dl] \arrow[dr] & \\
(4,1^2) \arrow[dr] & & (3^2) \arrow[dl] \\
 & (3,2,1) \arrow[dl] \arrow[dr] & \\
(3,1^3) \arrow[dr] & & (2^3) \arrow[dl] \\
 & (2^2,1^2) \arrow[d] & \\
 & (2,1^4) \arrow[d] & \\
 & (1^6) &
\end{tikzcd}$$

2.5. Substitution reactions and partitions. Neighbourhood. In II.2 we study the properties of the dominant order on the wider set M_d consisting of all d-tuples $m = (m_1, \dots, m_d)$ of non-negative integers whose sum is d, and present statements concerning the neighbourhood in M_d and its subset P_d. The definitions of the order and the raising operators are given in II.2.1. Here we modify the definition of a raising operator from [27, Ch. I, Sec. 1] in order to adjust it for our purposes.

In II.2.2 we consider the relations "adjacency" and "neighbourhood" in the sets M_d and P_d, and borrow the corresponding propositions from [23] and [27]. We note that Lemma II.2.2.1 is a significant reinforcement of the corresponding statements from [27, Ch. I, Sec. 1]. The relation "adjacency" models the simple substitution reactions from (a), that is, a reaction during which a ligant take the place of another ligant. In the language of this mathematical model, $\lambda \leq \mu$ are neighbours if the open interval (λ, μ) is empty. The translation in to the language of chemistry is that there are no intermediate products between λ and μ, when the experimenter wants to get one of them from the other via substitution reaction.

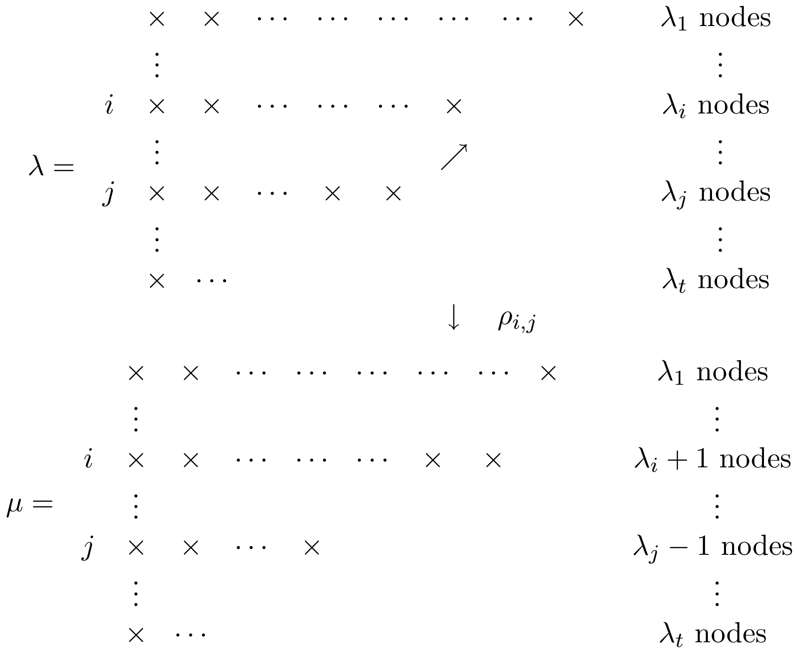

Fig. 3. The rising operator $\rho_{i,j}$ acting on $\lambda \in P_d$

2.6. Substitution reactions and tabloids. Neighbourhood. Section II.3 is devoted to a study of the dominant order (proposed by us) in the set T_d of all tabloids with d nodes, which model the structural formulae. Along with this, we study the partial order defined by the same rule on the bigger set Δ_d, consisting of all dissections $A = (A_1, \dots, A_d)$ of the set $[1, d]$ and such that if we consider the dominant order on the set M_d, the map

$$\varphi\colon \Delta_d \to M_d,\ (A_1, \dots, A_d) \to (|A_1|, \dots, |A_d|).$$

is a homomorphism of partially ordered sets.

We prove criteria for adjacency and neighbourhood in the partially ordered sets Δ_d and T_d, and study the equation $\varphi(X) = n$ for a fixed $n \in M_d$ (respectively, $n \in P_d$), where the unknown X varies in an interval $[A, B]$ in Δ_d (respectively, in T_d). This is done by a systematic use of raising operators.

We define the dominant order on the set Δ_d and restrict it to a partial order on T_d in II.3.1. Here we also define raising operators on Δ_d and prove two useful statements.

In II.3.2 we define and study the relation “adjacency” in the set Δ_d. The

$$A = \begin{array}{llllll|l} a_{1,1}, & a_{1,2}, & \cdots & \cdots & \cdots & a_{1,\lambda_1} & \text{component } A_1 \\ a_{2,1}, & a_{2,2}, & \cdots & \cdots & a_{2,\lambda_2} & & \text{component } A_2 \\ & & \vdots & & & & \vdots \\ a_{t,1}, & \cdots & & & & & \text{component } A_t \end{array}$$

$$\downarrow \quad \varphi$$

$$\lambda = \begin{array}{llllll|l} \times & \times & \cdots & \cdots & \cdots & \times & \lambda_1 \text{ nodes} \\ \times & \times & \cdots & \cdots & \times & & \lambda_2 \text{ nodes} \\ & & \vdots & & & & \vdots \\ \times & \cdots & & & & & \lambda_t \text{ nodes} \end{array}$$

Fig. 4. A tabloid, its shape, and the corresponding partition

main result here is Theorem II.3.2.3 which asserts that if $A, B \in \Delta_d$ with $A \leq B$, then B can be obtained from A by applying a specific raising operator.

Let $A, B \in \Delta_d$ with $A \leq B$ and let $\ell = \varphi(A)$, $m = \varphi(B)$. The image of the interval $[A, B]$ via the map φ is contained in the interval $[\ell, m]$. In II.3.3 we study the equation $\varphi(X) = n$, where $X \in [A, B]$, and $n \in [\ell, m]$ is fixed. Theorem II.3.3.2, which implies the surjectivity of the map

$$\varphi\colon [A, B] \to [\ell, m],$$

is proven by induction and the possibility of the inductive step is established in Lemma II.3.3.1. The detailed investigation of the above map and its restriction on T_d is finished in Theorem II.3.3.3. The equivalence of the relation $A \leq B$ with the existence of a raising operator R such that $RA = B$ is proven in Theorem II.3.3.4 and means that there are no superfluous relations, that is, for every relation $A \leq B$ the structural formula B can be gotten from the structural formula A via applying several simple raising operators, or, which is the same, via several rising simple substitution reactions.

In II.3.4 we find necessary and sufficient conditions for A, B with $A \leq B$ to be neighbours in Δ_d and in T_d — this is the content of Theorem II.3.4.1.

2.7. Isomers as orbits. Neighbourhood. Every type of isomerism produces an equivalence relation in the set T_d of structural formulae. The roughest "isomerism" corresponds to the dissection $T_d = \cup_{\lambda \in P_d} T_\lambda$ into disjoint subsets, so the compounds with different molecule formulae are "isomers" in this sense. Every other relation of equivalence is finer than the above one.

In this dissertation we (together with Lunn-Senior) consider three types of isomerism: (a) univalent substitution isomerism; (a′) stereoisomerism; (a″)

$$A = \begin{array}{lllllllll}
a_{1,1}, & * & \dots & * & \dots & * & * & a_{1,\lambda_1} & \text{component } A_1 \\
\vdots & & & & & & & & \vdots \\
a_{i,1}, & * & \dots & * & \dots & a_{i,\lambda_i} & & & \text{component } A_i \\
\vdots & & & & & \nearrow & & & \vdots \\
a_{j,1}, & * & \dots & * & s & & & & \text{component } A_j \\
\vdots & & & & & & & & \vdots \\
a_{t,1}, & \dots & & & & & & & \text{component } A_t
\end{array}$$

$$\downarrow \quad R_{i,s}$$

$$B = \begin{array}{lllllllll}
a_{1,1}, & * & \dots & * & \dots & * & * & a_{1,\lambda_1} & \text{component } B_1 \\
\vdots & & & & & & & & \vdots \\
a_{i,1}, & * & \dots & * & \dots & a_{i,\lambda_i}, & s & & \text{component } B_i \\
\vdots & & & & & & & & \vdots \\
a_{j,1}, & * & \dots & * & & & & & \text{component } B_j \\
\vdots & & & & & & & & \vdots \\
a_{t,1}, & \dots & & & & & & & \text{component } B_t
\end{array}$$

Fig. 5. A simple rising operator acting on a tabloid

structural isomerism. In [25, III] Lunn and Senior suppose that for every isomeric relation (a) - (a$''$) and for every skeleton Σ there exists a permutation group $W \leq S_d$ such that the corresponding isomeric classes can be identified with the W-orbits in T_d, that is, with the elements of the orbit spaces $T_{d;W} = W\backslash T_d$. After this identification, the W-orbits are said to be structural formulae. Moreover, $T_{d;W} = \cup_{\lambda \in P_d} T_{\lambda;W}$, where $T_{\lambda;W} = W\backslash T_\lambda$; in particular, we say that the isomer $a \in T_{\lambda;W}$ has the molecule formula λ. In particular, the molecule formulae, as represented by elements of the orbit space $T_{d;S_d} = S_d\backslash T_d$, are prototypes of the structural formulae. Lunn and Senior underline that this group W can be chosen among the subgroups of S_d, using considerations that have nothing in common with the three-dimensional configuration of the corresponding molecule.

Section II.4 has three purposes: representation of isomers via elements of the orbit spaces $T_{d;W}$, definition of the factor-order on $T_{d;W}$, and formulation of the main postulates of Lunn-Senior from [25], grouped in the fundamental Lunn-Senior's Thesis II.4.2.1. The partial order on $T_{d;W}$ is a wide and natural generalization of the adjacency relations considered in [25, VI], and models the

$$
A = \begin{array}{cccccccccl}
a_{1,1}, & a_{1,2}, & * & * & \dots & * & * & * & a_{1,\lambda_1} & A_1 \\
\vdots & & & & & & & & & \vdots \\
a_{i,1}, & a_{i,2}, & * & * & \dots & * & a_{i,\lambda_i} & & & A_i \\
\vdots & & & & & & & & & \vdots \\
 & * & * & * & * & \dots & * & * & & \quad A_{i_r} \\
 & \vdots & & \nwarrow & & & & & & \\
a_{j,1}, & * & * & s_r, & \dots & * & a_{j,\lambda_j} & & & A_j \\
\vdots & & & & & & & & & \vdots \\
 & a_{t,1}, & \dots & & & & & & & \quad A_t
\end{array}
$$

$$\downarrow R_{i_r,s_r}$$

$$
\begin{array}{cccccccccl}
a_{1,1}, & a_{1,2}, & * & * & \dots & * & * & * & a_{1,\lambda_1} & A_1 \\
\vdots & & & & & & & & & \vdots \\
a_{i,1}, & a_{i,2}, & * & * & \dots & * & a_{i,\lambda_i} & & & A_i \\
\vdots & & & & & & & & & \vdots \\
* & * & * & * & \dots & * & * & & & A_{i_{r-1}} \\
\vdots & & & \nearrow & & & & & & \vdots \\
* & s_r, & s_{r-1}, & * & \dots & * & * & * & & A_{i_r} \cup \{s_r\} \\
\vdots & & & & & & & & & \\
a_{j,1}, & * & * & \hat{s_r}, & \dots & a_{j,\lambda_j} & & & & A_j \backslash \{s_r\} \\
\vdots & & & & & & & & & \vdots \\
a_{t,1}, & \dots & & & & & & & & A_t
\end{array}
$$

$$\downarrow \quad R_{i_{r-1},s_{r-1}}$$

$$\vdots$$

$$\downarrow$$

$$
B = \begin{array}{cccccccccl}
a_{1,1}, & a_{1,2}, & * & * & \dots & * & * & * & a_{1,\lambda_1} & A_1 \\
\vdots & & & & & & & & & \vdots \\
a_{i,1}, & a_{i,2}, & * & * & \dots & * & a_{i,\lambda_i}, & s_1 & & A_i \cup \{s_1\} \\
\vdots & & & & & & & & & \vdots \\
a_{j,1}, & * & * & \hat{s_r}, & \dots & a_{j,\lambda_j} & & & & A_j \backslash \{s_r\} \\
\vdots & & & & & & & & & \vdots \\
a_{t,1}, & \dots & & & & & & & & A_t
\end{array}
$$

(A hat over an elements means its absence)

Fig. 6. A rising operator acting on a tabloid

substitution (genetic) reactions among isomers in organic chemistry.

Because of the fact that the language of chemistry and the language of mathematics are talking at cross-purposes, in Remark II.4.2.5 we give the definitions of some chemical terms, using the language of this mathematical model.

Section II.5 has two subsections where we study the relation between the partial order in Δ_d (respectively, in T_d) and its factorization to a partial order in $\Delta_{d;W} = W\backslash\Delta_d$ (respectively, $T_{d;W}$), and the relations "adjacency" and "neighbourhood" in the sets $\Delta_{d;W}$ (respectively, $T_{d;W}$). The main results are Theorem II.5.1.2, Theorem II.5.2.1, and Theorem II.5.2.2. The second part (ii) of the last theorem presents a necessary and sufficient condition for the lack of intermediate products in the reaction $a < b$.

2.8. Distinguishability via substitution reactions. Automorphisms. Let W is one of the two Lunn-Senior groups of isomerism G, $G' \leq S_d$. A disadvantage of the original Lunn-Senior model of isomerism is that there are no enough immanent tools for two W-orbits to be distinguished. In section II.6 we present a mathematical formalism, which includes Lunn–Senior's model as particular case and uses the one-dimensional characters of the group W and the one-dimensional characters of the group $S_\lambda = S_{\lambda_1} \times S_{\lambda_2} \times \cdots \leq S_d$, which reflects the molecule formula $\lambda \in P_d$, in order to choose some special W-orbits. The starting point of our considerations is the following observation. Let us suppose that there are chiral pairs among the stereoisomers of a given molecule with molecule formula $\lambda \in P_d$. Then the group G is a (normal) subgroup of G' with $|G' : G| = 2$. Let $\chi_e \colon G' \to \{1, -1\}$ be the homomorphism of groups, which attains the value 1 at any element of G and the value -1 at any element of the complement $G'\backslash G$. Every G'-orbit (which represents a stereoisomer) either coincides with the corresponding G-orbit (and represents a diamer), or is a union of two G-orbits (thus representing a chiral pair). The G'-orbits O, which consists of two G-orbits, can be distinguished from the other G'-orbits in the following way. Let $A \in O$ be a tabloid and let G'_A be the stabilizer of A in G'. We can consider χ_e as one-dimensional character $\chi_e \colon G' \to \mathbb{C}$. Then O is a union of two G-orbits if and only if the character χ_e is identically 1 on the subgroup G'_A. We can find the number of these G'-orbits (let us call them χ_e-orbits) by using the machinery developed in chapter III. Thus, the one-dimensional character χ_e of the group G' produces a type property of the molecule under consideration.

This situation can be generalized in the following way. Given a permutation group $W \leq S_d$ and a one-dimensional character χ on W, in II.6.1 we define the subset $T_{\lambda;\chi} \subset T_{\lambda;W}$, consisting of all W-orbits O such that the character χ is identically 1 on a stabilizer W_A, where $A \in O$. The W-orbits from $T_{\lambda;\chi}$ are said to be χ-orbits. In particular, when $W = G'$ and $\chi = \chi_e$, the elements of the set $T_{\lambda;\chi}$ represent chiral pairs and the elements of the difference $T_{\lambda;W} \backslash T_{\lambda;\chi}$ represent diamers.

Proposition II.6.2.2 gives a combinatorial interpretation of the χ-orbits via an extremum property: if $W_\chi \leq W$ is the kernel of the character χ, then the χ-orbits are exactly those W-orbits which contain $|W \colon W_\chi|$ (that is, a maximal number) W_χ-orbits.

An important problem which can be solved, at least partially, within the boundaries of Lunn-Senior's model is as follows: given a univalent substitution isomer, how to find a structural formula (that is, G-orbit) which corresponds to this isomer? The classical Körner relations show how this problem is solved for the di-substitution homogeneous derivatives of benzene C_6H_6 (para, ortho, and meta) and its tri-substitution homogeneous derivatives (asymmetrical, vicinal, and symmetrical).

On the other hand, the members of the pair consisting of the structurally identical di-substitution homogeneous derivatives of ethene C_2H_4 and the members of the pair of its di-substitution heterogeneous derivatives can-not be identified with their structural formulae using only substitution reactions.

The internal reason for the above impossibility is the existence of an automorphism of the mathematical structure of the model which maps one of the members of any of this pairs onto the other. Contrariwise, the success of the famous Körner relations is due to the fact that in the case of benzene the automorphism group of the appropriate fragment of the mathematical structure of the model is trivial.

Let us suppose that several univalent substitution isomers with molecule formula $x_1^{\lambda_1} x_2^{\lambda_2} \ldots$ of the substituents have to be identified with the corresponding structural formulae. Below, we suppose that we know the set of the corresponding structural formulae (that is, G-orbits) but do not know the correspondence. These isomers are called indistinguishable via substitution reactions if for any couple of elements of the corresponding set of structural formulae $\{a, b, \ldots\} \subset T_{\lambda;G}$, say a, b, there exists an automorphism $\alpha \colon T_{d;G} \to T_{d;G}$ of the partially ordered set $T_{d;G}$ such that: (i) $\alpha(T_{\mu;G}) = T_{\mu;G}$ for every $\mu \in P_d$, (ii) α maps any chiral pair onto a chiral pair, (iii) c and $\alpha(c)$ are structurally identical for any $c \in T_{d;G}$, and (iv) $\alpha(a) = b$. Otherwise they are called distinguishable via substitution reactions.

Let us consider the group $Aut_{pos}(T_{d;G})$ of automorphisms of the partially ordered set $T_{d;G}$ (that is, bijections $u \colon T_{d;G} \to T_{d;G}$ such that the inequalities $a \leq b$ and $u(a) \leq u(b)$ are equivalent for any pair $a, b \in T_{d;G}$)). The automorphisms which satisfy (i) form a subgroup $Aut_0(T_{d;G})$ of $Aut_{pos}(T_{d;G})$, and those of them which satisfy (ii) form a subgroup $Aut'(T_{d;G}) \leq Aut_0(T_{d;G})$. In order to take into account the structural isomerism, we add (iii). The automorphisms which satisfy conditions (i) - (iii) constitute a subgroup $Aut(T_{d;G})$ of $Aut'(T_{d;G})$, called Lunn–Senior's group of automorphisms.

The group $Aut(T_{d;G})$ acts naturally on the set $T_{d;G}$, and all of its subgroups inherit this action. The elements of a set of univalent substitution isomers with molecule formula $x_1^{\lambda_1} x_2^{\lambda_2} \dots$ are indistinguishable via substitution reactions iff the corresponding set of structural formulae $\{a, b, \dots\} \subset T_{\lambda;G}$ is contained in an $Aut(T_{d;G})$-orbit in $T_{d;G}$.

In case there are chiral pairs among the derivatives of the molecule under consideration with molecule formula $\lambda \in P_d$ we get $|G' : G| = 2$ and then every element $\tau \in G' \backslash G$ produces an involution $\hat{\tau} \in Aut(T_{d;G})$ (called chiral involution), which permutes the members of the chiral pairs and leaves the diamers invariant. In this case the Lunn-Senior automorphism group $Aut(T_{d;G})$ contains the cycle group $\langle \hat{\tau} \rangle$ of order 2, so its order is even. In particular, this group is not trivial.

For example, Lunn-Senior's automorphism group of ethane $Aut(T_{6;G})$ has the form

$$Aut(T_{6;G}) = \langle z_1, z_2, z_3, z_4, z_5 \rangle \simeq C_2 \times C_2 \times C_2 \times C_2 \times C_2,$$

where z_1, z_2, z_3, z_4, z_5, are involutions, and one of them is the chiral involution. Here by C_2 we denote the cyclic group of order 2 (see Theorem VI.1.3.1, (ix)).

Unfortunately, chemists have synthesized enough products with given molecule formula of the substituents only for a small number of partitions $\lambda \in P_d$ — usually we know the mono-substitution derivatives ($\lambda = (d-1, 1)$), di-substitution derivatives ($\lambda = (d-2, 2), (d-2, 1^2)$), tri-substitution derivatives ($\lambda = (d-3, 3), (d-3, 2, 1), (d-3, 1^3)$), and so on. Thus, in most of the cases we have information not for the whole partially ordered set $T_{d;G}$, but for parts of it — for subsets of the type $T_{D;G} = \cup_{\mu \in D} T_{\mu;G}$, where $D \subset P_d$, with the induced partial order.

The greater part of section II.7 is devoted to a generalization of the above considerations and to a study of the relation between the partially ordered sets $T_{D;W}$ and $T_{D;W'}$ for three groups $W \leq W' \leq W'' \leq S_d$ with $|W' : W| \leq 2$, which are not necessarily Lunn–Senior's groups of some molecule. We study as well the formal behaviour of the groups $Aut_0(T_{D;W})$, $Aut'(T_{D;W})$, and $Aut(T_{D;W})$, which can be obtained via restriction of the conditions (i) – (iii) on D.

We note that the group $Aut(T_{6;G})$ of ethane is a group of exponent 2 and this also is true for Lunn-Senior's automorphism group of ethene, cyclopropane, benzene, etc. see chapter VI.

Conjecture 1. *Lunn–Senior's automorphism group* $Aut(T_{D;G})$, $D \subset P_d$, *of any compound has exponent* 2.

In II.7.1 we define when several univalent substitution isomers with molecule formula $x_1^{\lambda_1} x_2^{\lambda_2} \ldots$, $\lambda \in D$, of the substituents are indistinguishable via substitution reactions among the elements of $T_{D;G}$.

The renumberings of the d free bonds of the skeleton, which leave the group G of symmetries of the molecule invariant, are exactly the elements ς of the normalizer N of G in S_d, and any such renumbering ς induces an automorphism $\hat{\varsigma} \in Aut_0(T_{D;G})$, $D \subset P_d$. In addition, if $\varsigma \in N'$ ($\varsigma \in N''$), where N' (respectively, N'') is the intersection of N with the normalizer of G' in S_d (respectively, in G''), then $\hat{\varsigma} \in Aut'(T_{D;G})$ (respectively, $\hat{\varsigma} \in Aut(T_{D;G})$). Following A. Kerber (see [28, 1.5]), we call the permutations $\varsigma \in N''$ hidden permutations and the automorphisms $\hat{\varsigma}$, where $\varsigma \in N''$, hidden symmetries of the molecule under consideration, or hidden automorphisms of the model. The properties of the hidden automorphisms after changing the group G with any permutation group $W \leq S_d$ are considered in II.7.2. Theorem II.7.2.2 shows that under some constraint on the set D of molecule formulae, the group $Aut_0(T_{D;W})$ contains the factor-group N/W. On the other hand, the group N'' acts naturally on the group X_W of one-dimensional characters χ of the group W and we denote its action by $\chi \mapsto \varsigma\chi$. Given $\chi \in X_W$ and $\lambda \in P_d$, any hidden automorphism $\hat{\varsigma}$, $\varsigma \in N''$, maps the set $T_{\lambda;\chi}$ of all χ-orbits onto the set $T_{\lambda;\varsigma\chi}$ of all $\varsigma\chi$-orbits. A generalization of this statement is proven in Theorem II.7.2.4.

In II.7.3 we suppose that $W \leq W' \leq W'' \leq S_d$ is a triple of permutation groups such that $|W' : W| \leq 2$, that is, we generalize the chiral situation. In the statements from this subsection we discuss the transition from W to W' and back, and study the relation between the groups $Aut'(T_{D;W})$ and $Aut_0(T_{D;W'})$.

In II.7.4 we examine under which restraints upon the permutations from the group N they induce hidden symmetries from the groups $Aut'(T_{D;W})$ and $Aut(T_{D;W})$. For any subset $D \subset P_d$ and for any permutation $\varsigma \in N'$ (respectively, $\varsigma \in N''$) Theorem II.7.4.1 yields $\hat{\varsigma} \in Aut'(T_{D;W})$ (respectively, $\hat{\varsigma} \in Aut(T_{D;W})$), and, in particular, shows that the hidden symmetries form a subgroup $Aut^h(T_{D;W})$ of $Aut(T_{D;W})$, which is isomorphic to the factor-group N''/W in case $(1^d) \in D$. Since $W'/W \leq N''/W$, when $|W' : W| = 2$ the group $Aut^h(T_{D;W})$ contains a copy of the factor-group W'/W generated by the chiral involution (see Corollary II.7.4.3). As a consequence we obtain that the members of a chiral pair are indistinguishable via substitution reactions — this is the content of the fundamental Theorem II.7.4.5.

2.9. Distinguishability via characters. Next, in II.7.5, we consider all $\varsigma\chi$-orbits, where $\chi \in X_W$, $\varsigma \in N''$, as equivalent and define so called χ-property, or χ-chirality. We note that we work in the more general case of (χ, θ)-orbits defined in II.6.1 by considering as equivalent all $(\varsigma\chi, \theta)$=orbits and define the so-called (χ, θ)-property, or, (χ, θ)-chirality. Here θ is a one-dimensional character of the group $S_\lambda = S_{\lambda_1} \times \cdots \times S_{\lambda_d} \leq S_d$. Using this property, we define indistinguishability of the derivatives which correspond to the structural formulae $a, b \in T_{\lambda;G}$, $\lambda \in P_d$ via pairs of characters if a and b are structurally identical and if both possess or both do not possess the (χ, θ)-property for every couple of characters $(\chi, \theta) \in X_W \times X_{S_\lambda}$. In particular, we get the definition of indistinguishability via characters. The central results are Theorem II.7.5.2 and Corollary II.7.5.3, which assert that the members of a chiral pair can not be distinguished via pairs of characters and via characters, respectively.

In II.7.6 we extend Lunn-Senior's Thesis II.4.2.1 by adding the hypothesis that the (χ, θ)-property defined in II.7.5 is a type property of the molecule under consideration.

3. Enumeration of isomers.

3.1. Explicit formulae. Chapter III is devoted to counting of isomers. In Section III.1 we use theory of symmetric groups and theory of symmetric functions in order to prove explicit formulae for the numbers $\nu_{\lambda;\chi,\theta}$ and, in particular, for the numbers $\nu_{\lambda;\chi}$. Theorem III.1.1.5 and its Corollary III.1.1.6 are the central results here. In Corollary III.1.1.7 we give an alternative proof of Ruch's formula which is an explicit expression for the numbers $\nu_{\lambda;W}$ (see [33]).

In III.1.2 we study the family of non-negative integers $(\nu_{\lambda;\chi})_{\lambda \in P_d}$. In Theorem III.1.2.1 we prove that the map $\lambda \to \nu_{\lambda;\chi}$ is decreasing. As a direct corollary we obtain a beautiful result of E. Ruch: if a distribution of ligands according to the partition μ amounts to a chiral molecule, and if $\lambda < \mu$, then also a distribution according to λ yields a chiral molecule.

In III.1.3 we prove Theorem III.1.3.2 which generalizes Ruch's theorem for χ-chiral molecules.

A new proof of Kauffmann formulae for the number of the derivatives of naphthalene $C_{10}H_8$ is given in III.1.4.

3.2. A generalization of Pólya's theorem. Section III.2 is devoted to a conceptual proof of the generalized Pólya theorem within the boundaries of Schur-Macdonald's theory of "invariant matrices" . This theory was developed in the doctoral dissertation of I. Schur [34], and generalized by I. G. Macdonald in [26]. The main result of Schur-Macdonald's theory is Theorem III.2.1.1 which establishes equivalence of two categories: the category of finite-dimensional $\mathbb{C}$-linear representations of the symmetric group S_d and the category of polynomial homogeneous degree d functors on the category $\mathcal{L}$ of finite-dimensional $\mathbb{C}$-linear spaces.

A natural background for generalization of Pólya theory are the induced monomial representations of S_d, which correspond via this equivalence to so-called semi-symmetric powers. Both objects can be defined by fixing a permutation group $W \leq S_d$ and a one-dimensional $\mathbb{C}$-valued character χ on W. Then the representation $Ind_W^{S_d}(\chi)$ corresponds to the d-th semi-symmetric power $[\chi]^d(-)$. In particular, when $W = S_d$ and χ is the signature or the unit character, we get the exterior power $\bigwedge^d(-)$ or the symmetric power $S^d(-)$, respectively. If W is the unit group, then the regular representation of S_d corresponds to the tensor power $T^d(-)$.

A substantial part of problems of combinatorial analysis deals with a set of objects, often called figures, and the number of figures is usually irrelevant, provided that it is large enough. For convenience, we may suppose that the set of figures coincides with the set N of positive integers. The figures form configurations, that is, elements $(j_1, \ldots, j_d)$ of the free monoid $Mo(N)$ generated by N. Any configuration $j = (j_1, \ldots, j_d)$ can be identified with an ordered dissection $A = (A_1, A_2, \ldots)$ of the set $[1, d]$, via the rule $A_k = \{i \in [1, d] \mid j_i = k\}$, $k = 1, 2, \ldots$. If $c_k(j) = |A_k|$, $k = 1, 2, \ldots$, then $\sum_k c_k(j) = d$ and after eventual permutation of $c_k(j)$ we obtain a partition $\lambda = \lambda(j)$ of d.

Let $(x_i)_{i\in N}$ be a family of independent variables. Sometimes, for more flexibility, we identify N with the set $\{x_1, x_2, \ldots\}$, via the bijection $k \mapsto x_k$, $k = 1, 2, \ldots$. Now, we are able to specialize the variables x_k to numbers, to some variables or expressions, or simply, to elements of an appropriate set, for instance, the set of all univalent substituents. The above bijection induces a surjective homomorphism of monoids

$$w\colon Mo(N) \to \mathbb{C}[(x_k)_{k\in N}],\ (j_1, \ldots, j_d) \mapsto x_{j_1} \ldots x_{j_d},$$

called weight function, where the target of w is the commutative algebra of polynomials in $x_1, x_2, \ldots$ over the field $\mathbb{C}$, considered to be a monoid with respect to multiplication. The other weight functions can be obtained by appropriate specialization of the variables x_k. The monomial $x_{j_1} \ldots x_{j_d}$ is called weight of the configuration $(j_1, \ldots, j_d)$.

The group S_d acts on the set N^d via the rule $\zeta j = (j_{\zeta^{-1}(1)}, \ldots, j_{\zeta^{-1}(d)})$, the weight function w is S_d-invariant ($w(\zeta j) = j$ for any $\zeta \in S_d$ and any $j \in N^d$), and induces a bijection between the orbit space $S_d\backslash N^d$ and the set of degree d monomials in $x_1, x_2, \ldots$. In this case of maximal symmetry of the positions $1, 2, \ldots, d$

(S_d-symmetry, when all positions are indistinguishable), the weight $x_{j_1} \dots x_{j_d}$ of the configuration $(j_1, \dots, j_d)$ and all of its specializations, carry the whole information, the whole knowledge, about any of the configurations $\zeta(j_1, \dots, j_d)$, $\zeta \in S_d$. The disregarding of the nature (that is, the value) of the figures $1, 2, \dots$ and keeping only their distinguishability within our scope, gives rise to another symmetry: the action of the infinite symmetric group S_∞ (consisting of permutations ω of N with finite support) on N^d: $\omega j = (\omega(j_1), \dots, \omega(j_d))$; this action commutes with the action of S_d on the positions, and, in turn, produces for any S_d-orbit $O = O_{S_d}(j)$ an S_∞-invariant, that is, a symmetric function: the monomial symmetric function m_λ, where $\lambda = \lambda(j)$. The whole information for O is carried by the symmetric function m_λ, and the whole information for the orbit space $S_d \backslash N^d$ is carried by the complete symmetric function $h_d = \sum_{\lambda \in P_d} m_\lambda$, see [27, Ch. I, Sec. 2].

Now, consider the S_∞-orbit of the configuration $j = (j_1, \dots, j_d)$ which is identified with the ordered dissection $A = (A_1, A_2, \dots)$ of the set $[1, d]$. In terms of dissections the above action of the group S_∞ can be written as

$$\omega(A_1, A_2, \dots) = (A_{\omega^{-1}(1)}, A_{\omega^{-1}(2)}, \dots).$$

In the S_∞-orbit of the dissection $A = (A_1, A_2, \dots)$ there is a tabloid $B = (B_1, B_2, \dots)$ of shape $\lambda = \lambda(j) = (\lambda_1, \lambda_2, \dots)$, and then the weight $x_1^{\lambda_1} x_2^{\lambda_2} \dots$ is the molecular formula of the substituents part of the molecule that has a structural formula represented by B.

More generally, when the symmetry of the positions $1, 2, \dots, d$ is not maximal, we identify only the configurations that are in a W-orbit $O_W(j)$, where W is a subgroup of the symmetric group S_d, which inherits its action from S_d. The main objects in Pólya's theory are the orbit spaces $W \backslash N^d$, and it turns out that there exist bijections of certain orbit subspaces, including the whole orbit space, onto some index sets which arise naturally within the framework of the semi-symmetric powers. Given a $\mathbb{C}$-linear space E with basis $(v_i)_{i \in N}$, we can construct a basis $(v_j)_{j \in J(N^d, \chi)}$ for $[\chi]^d(E)$. Here $J(N^d, \chi)$ is a system of distinct representatives of a set of W-orbits in N^d, and the corresponding orbit subspace depends on the character $\chi \colon W \to \mathbb{C}$. In particular, if χ is the unit character 1_W, then $J(N^d, 1_W)$ is a transversal for all W-orbits in N^d.

The formal infinite sum of monomials

$$g(W; x_1, x_2, \dots) = \sum_{j \in J(N^d, 1_W)} x_{j_1} \dots x_{j_d}$$

is a homogeneous degree d symmetric function that counts the W-orbits in N^d

provided with weights, and carries the whole information for the orbit space $W\backslash N^d$. By the fundamental theorem on symmetric functions and by Newton's formulae

$$g(W; x_1, x_2, \ldots) = Z(W; p_1, \ldots, p_d),$$

where $p_k = \sum_{i \in N} x_i^k$ are the power sums and $Z(W; p_1, \ldots, p_d)$ is an uniquely defined isobaric polynomial in $p_1, \ldots p_d$ with rational coefficients. Pólya's enumeration theorem asserts that this polynomial in the free variables $p_1, \ldots p_d$ coincides with the cycle index of the group W (see [21, Ch. 1, Sec. 10, (1.5)]). By the specialization $x_{n+1} = x_{n+2} = \cdots = 0$ in the above equality we establish the finite version of Pólya's theorem, where the symmetric polynomial $g(W; x_1, x_2, \ldots, x_n, 0, 0, \ldots)$ in n variables counts the weighted W-orbits in the integer-valued hypercube $[1, n]^d$.

The left-hand side of the above equality is *a fortiori* the characteristic of the polynomial functor $[1_W]^d(-)$ while the cycle index $Z(W; p_1, \ldots, p_d)$ of the group W, where p_k are the power sums, is the characteristic of the induced monomial representation $Ind_W^{S_d}(1_W)$. The coincidence of these characteristics (that is, Pólya's theorem) is a consequence of Schur-Macdonald's equivalence.

In general, the characteristic of the polynomial functor $[\chi]^d(-)$ is a symmetric function $g(\chi; x_0, x_1, x_2, \ldots)$ which inventories the weighted W-orbits O in N^d subject to the maximum condition "O contains $|W : H|$ in number H-orbits" where $H \leq W$ is the kernel of χ and $|W : H|$ is the index of H in W. Again, the symmetric function $g(\chi; x_0, x_1, x_2, \ldots)$ encodes the whole knowledge for the orbits O that satisfy the above maximum condition (so called χ-orbits). On the other hand, the characteristic $ch(ind_W^{S_d}(\chi))$ is equal to the generalized cycle index $Z(\chi; p_1, \ldots, p_d)$ of the group W, corresponding to the character χ. Schur-Macdonald's equivalence yields the identity

$$g(\chi; x_1, x_2, \ldots) = Z(\chi; p_1, \ldots, p_d),$$

which turns into Pólya's theorem in case $\chi = 1_W$.

For instance, let W be the whole symmetric group S_d and let χ be the alternating character ε_d. Then $g(\varepsilon; x_1, x_2, \ldots) = ch(\bigwedge^d(-))$ is the d-th elementary symmetric function e_d which inventories the S_d-orbits in N^d consisting of sequences $(i_1, \ldots, i_d)$ with pairwise distinct components. By a tradition dating back to Pólya, the formal expression $Z(A_d - S_d; p_1, \ldots, p_d)$ is widely used in combinatorial literature for denoting the generalized cycle index $Z(\varepsilon_d; p_1, \ldots, p_d)$. Since $\varepsilon_d = Ind_{A_d}^{S_d}(1_{A_d}) - 1_{S_d}$ in the appropriate Grothendieck group, we have

$$Z(\varepsilon_d; p_1, \ldots, p_d) = Z(A_d; p_1, \ldots, p_d) - Z(S_d; p_1, \ldots, p_d).$$

Thus, in the present context, the "old" notation $Z(A_d - S_d; p_1, \ldots, p_d)$ can be viewed as an archetype.

In III.2.2 we define the semi-symmetric powers as polynomial functors and prove Theorem III.2.2.1 which asserts that the semi-symmetric powers correspond to induced monomial representations via Schur-Macdonald's equivalence from Theorem III.2.1.1.

Some functorial properties of the semi-symmetric powers are considered in III.2.3. It turns out that not only the tensor power $T^d(E)$, the symmetric power $S^d(E)$, and the exterior power $\bigwedge^d(E)$ of a $\mathbb{C}$-linear space E, but also the general semi-symmetric power $[\chi]^d(E)$ is a representing object of a functor of the form $Mult_{\mathbb{C}}(E^d, -)_{\chi^{-1}} : \mathcal{L} \to \mathcal{L}$, and reduces the poly-linear maps with appropriate symmetry to linear ones. This is proved in Proposition III.2.3.1 and its Corollary III.2.3.2. The same is true for the tensor product of two semi-symmetric powers, see Proposition III.2.3.3 and Corollary III.2.3.4.

In III.2.4 we bring up the definition and the main properties of the monomial modules. Proposition III.2.4.3 presents a special basis of a monomial module. A specialization of this proposition allows us to build a basis for the semi-symmetric power $[\chi]^d(E)$, starting from a basis for the $\mathbb{C}$-linear space E, see Proposition III.2.4.4.

Theorem III.2.5.2 is the central result which generalizes Pólya's theorem from [30, Ch. 1, Sec. 16]. In Remark III.2.5.6 we interpret Theorem III.2.5.2 in combinatorial terms.

Propositions III.2.6.1 and III.2.6.2 show that the set of all semi-symmetric powers is closed with respect to tensor product and composition of polynomial functors — see [27, Ch. I, A6]. The corresponding canonical isomorphisms of functors generalize Pólya's rules from [30, Ch. 1, Sec. 27].

We note that Williamson's generalizations of Pólya's enumeration theorem ([38, (13)]) and of the substitution rule ([38, (25)]) are equivalent to Theorem III.2.5.2 and Proposition III.2.6.2, (iii), respectively, but our approach has conceptual advantages.

Pólya's generalized theorem III.2.5.2 is used in III.2.7 in order to enumerate the univalent substitution isomers, stereoisomers, and structural isomers of ethene, ethane, cyclopropane, benzene, and the linear alkanes, as well as some of their χ-isomers.

III.2.9 shows that the polynomial functors can be used as a tool for making an inventory of some graphs, and that the labelled graphs, multi-graphs, pseudographs, and so on, with given number of edges are "natural" combinatorial objects according to the popular thesis "combinatorial analysis = representation theory of the symmetric group".

3.3. A generalization of Redfield's theorem. In section III.3 we prove a generalization of Redfield's master theorem as a direct consequence of the decomposition of the tensor product of several induced monomial representations of the symmetric group into its transitive summands (see [32]). The underlying permutation representations give rise to Redfield's original group-reduced distributions, or, equivalently, to Read's equivalence relation of "T-similarity" and superpositions. The most important examples of superpositions are those of several graphs $\Gamma_1, \dots, \Gamma_m$, each on the same number of vertices. A superposition of $\Gamma_1, \dots, \Gamma_m$ is a graph that is obtained by superposing every graph Γ_k on the same set of vertices and by keeping their edges apart. The superposition theorem counts the number of superpositions of the graphs Γ_k in terms of their automorphism groups $W_k \leq S_d$. The corresponding generalization enables us to count the superpositions whose automorphism groups have certain properties in case one of the automorphism groups W_k, $k = 1, \dots, m$, has a one-dimensional character of special type.

In Proposition III.3.1.3 we prove that the tensor product of several induced monomial representations of the symmetric group S_d is monomial. We show that there exists a canonical bijection between the orbit space of the corresponding permutation representation and the set of Read's equivalence classes from [31, Sec. 3].

Theorem III.3.2.1 describes the induced monomial summands of the above monomial representation. Theorem III.3.2.2 can be obtained as a result of applying the characteristic map on the equality from Theorem III.3.2.1. In particular, the two theorems are equivalent and generalize Redfield's master theorem. Theorem III.3.2.3 follows from Theorem III.3.2.2, and is a generalization of Redfield's superposition theorem.

4. Characterization of some Lunn–Senior's groups. In [25] Lunn and Senior find their groups of univalent substitution isomerism of benzene, ethene, ethane, cyclopropane, and many other compounds by using the experimentally known numbers of isomers with fixed compositions, as well as the tables of subgroups of the corresponding symmetric group, and all of their orbital numbers. In [3] W. Hässelbarth gives a conceptual proof of the theorem that describes up to conjugation in S_6 the famous group G of benzene by using only three equalities: $\nu_{(5,1);G} = 1$, $\nu_{(4,2);G} = 3$, and $\nu_{(4,1^2);G} = 3$.

Section IV.1 is devoted to proofs of a series of statements that prepare the ground for finding the above Lunn–Senior's groups under certain weaker conditions. Here we use systematically a graph $\Gamma = \Gamma(W, H, \lambda)$, which corresponds to a permutation group $W \leq S_d$, its subgroup H, and a partition λ of d, as well as Ruch's formula from Corollary III.1.1.7.

In section IV.2 we use the results from section IV.1 and give similar conceptual proofs for Lunn–Senior's groups of univalent substitution isomerism of ethane, cyclopropane, as well as another proof for the group of benzene. We get also characterizations up to conjugation of Lunn–Senior's groups of stereoisomerism and structural isomerism of these compounds.

In IV.2.4 we generalize the cases of benzene and cyclopropane by considering molecules that can be divided into a skeleton and six univalent substituents, and which have one mono-substitution derivative and at least three di-substitution homogeneous derivatives. Lunn–Senior's group of univalent substitution isomerism is characterized in Theorem IV.2.4.1, and this helps us to find upper bounds for their homogeneous di-substitution and tri-substitution derivatives.

In [25, IV] Lunn and Senior postulate the form of the group G_n of univalent substitution isomerism of n-th linear alkane. Under certain conditions that reflect the common properties and the differences of the members of the homologous series of linear alkanes, in Theorem IV.2.6.4 we characterize the group G_n up to conjugation in the symmetric group S_{2n+2}. In Corollary IV.2.6.5, for every linear alkane we find the number of its mono-substitution, di-substitution, and tri-substitution derivatives as a linear, quadratic, and cubic polynomial, respectively. We note that there are no obstacles to establish such a polynomial for every given composition.

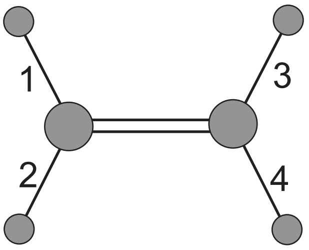

Fig. 7. Ethene

5. Description of some isomers. Chapter V is devoted to the description of all isomers of ethene, ethane, and some isomers of cyclopropane and benzene, as well as the substitution reactions among them. We hope that the corresponding meticulous lists will help the chemists to synthesize these isomers, to throw aside *a priori* "forbidden" substitution reactions, that is, "reactions"

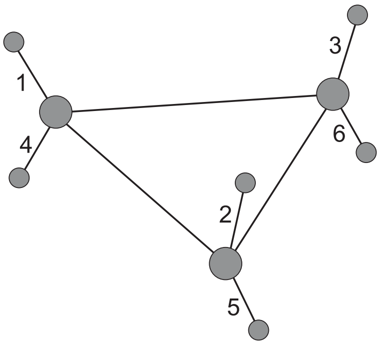

Fig. 8. Cyclopropane

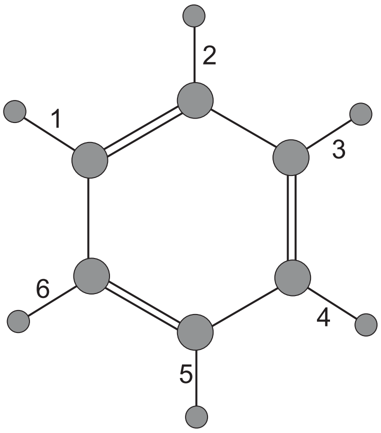

Fig. 9. Benzene

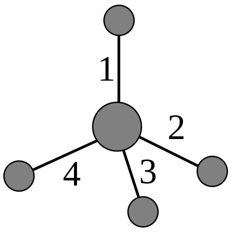

Fig. 10. Methane

$A \longrightarrow B$ for which neither $A < B$ nor $B < A$ is satisfied, as well as to predict the reactions $A \longrightarrow B$ such that $A < B$ or $B < A$. This description is also necessary for chapter VI where we make exhaustive analysis of all structurally identical derivatives of the above compounds that can and that can not be distinguished via substitution reactions.

6. Certain Lunn–Senior's automorphism groups. In chapter VI we give an account of Lunn–Senior's automorphism groups $Aut(T_{D;G})$ of ethene, ethane, and cyclopropane for some sets $D \subset P_6$ of molecule formulae.

Proposition VI.1.1.1, its Corollary VI.1.1.2, as well as a series of *ad hoc* lemmas (Lemma VI.1.1.3 – Lemma VI.1.1.13) contain properties of the partially

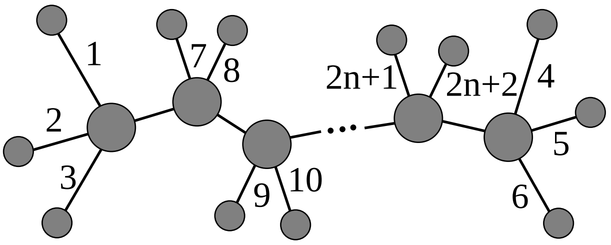

Fig. 11. Linear alkane

$$\begin{tikzcd}
(4) \arrow[d] & & & a_{(4)} \arrow[d] & & \\
(3,1) \arrow[d] & & & a_{(3,1)} \arrow[dl] \arrow[d] \arrow[dr] & & \\
(2^2) \arrow[d] & & a_{(2^2)} \arrow[dl] \arrow[r, leftrightarrow, "u_{(2^2)}"] & b_{(2^2)} \arrow[d] & c_{(2^2)} \arrow[dr] & \\
(2,1^2) & a_{(2,1^2)} \arrow[rr, leftrightarrow, "u_{(2,1^2)}"] & & b_{(2,1^2)} & & c_{(2,1^2)}
\end{tikzcd}$$

Fig. 12. Derivatives of ethene

ordered set $T_{d;G}$, which are used in order to find some Lunn–Senior's automorphism groups.

Theorem VI.1.2.1 presents descriptions of Lunn–Senior's groups $Aut(T_{D;G})$ for $D = D_k$, $k = 1, \ldots, 3$, and $Aut(T_{4;G})$, where

$$D_1 = \{(4), (3,1)\},\ D_2 = D_1 \cup \{(2^2)\},\ D_3 = D_2 \cup \{(2,1^2)\},$$

and G is Lunn–Senior's group of univalent substitution isomerism of ethene. In Corollaries VI.1.2.2–VI.1.2.4 we list all structurally identical di-substitution derivatives (homogeneous or heterogeneous) of ethene as well as all of its derivatives with composition CXYZA, that can not be distinguished via substitution reactions. In Propositions VI.1.2.5–VI.2.2.7 we show that the above derivatives of ethene can not be distinguished via characters either.

Theorem VI.1.3.1, Theorem VI.1.3.4, and Theorem VI.1.3.7 clarify the structure of Lunn–Senior's automorphism groups $Aut(T_{D;G})$ of ethane for $D = D_k$, $k = 1, \ldots, 8$, where

$$D_1 = \{(6), (5,1), (4,2)\},\ D_2 = \{(6), (5,1), (4,2), (4,1^2)\},$$

$$D_3 = \{(6), (5,1), (4,2), (4,1^2), (3^2)\},$$

$$D_4 = \{(6),(5,1),(4,2),(4,1^2),(3^2),(3,2,1)\},$$
$$D_5 = \{(6),(5,1),(4,2),(4,1^2),(3^2),(3,2,1),(3,1^3)\},$$
$$D_6 = \{(6),(5,1),(4,2),(4,1^2),(3^2),(3,2,1),(3,1^3),(2^3)\},$$
$$D_7 = \{(6),(5,1),(4,2),(4,1^2),(3^2),(3,2,1),(3,1^3),(2^3),(2^2,1^2)\},$$
$$D_8 = \{(6),(5,1),(4,2),(4,1^2),(3^2),(3,2,1),(3,1^3),(2^3),(2^2,1^2),(2,1^4)\},$$

and for $D = P_6$, as well as for $D = \{(2^3),(2^2,1^2)\}$ and $D = \{(2^2,1^2),(2,1^4)\}$.

In Corollaries VI.1.3.2 and VI.1.3.3 we make an inventory of all structurally identical chiral pairs with compositions $(2,1^4)$ and (1^6) that can (not) be distinguished via substitution reactions among the elements of different $T_{D;G}$, where D is from the list above.

Corollary VI.1.3.5 shows that the two structurally identical chiral pairs of ethane with composition $(2^2,1^2)$ can be distinguished via substitution reactions among the elements of the set $T_{D';G}$.

Corollary VI.1.3.8 asserts that the two couples of structurally identical chiral pairs of ethane with composition $(2,1^4)$ can be distinguished via substitution reactions among the elements of the set $T_{D'_8;G}$.

In Propositions VI.1.3.10 – VI.3.3.12 we list all couples of structurally identical chiral pairs of ethane that can- (not) be distinguished via characters.

Theorem VI.1.4.1 is devoted to a complete description of Lunn–Senior's automorphism groups $Aut(T_{D;G})$ of cyclopropane for the sets $D = D_k$, $k = 1,\ldots,6$.

In Corollaries and Remarks VI.1.4.2–VI.1.4.18 we list all structurally identical derivatives of cyclopropane, which can (not) be distinguished via substitution reactions among the elements of different $T_{D;G}$, where D is from the list above.

In Propositions VI.1.4.19–VI.1.4.23 we describe all couples of structurally identical derivatives of cyclopropane, which can (not) be distinguished via characters.

In VI.1.5 we prove Körner relations among the homogeneous di-substitution and tri-substitution derivatives of benzene and note that these relations can be generalized for compounds with one mono-substitution, at least three di-substitution derivatives, and Lunn–Senior's group of univalent substitution isomerism of order 12. The intrinsic reason for the complete identification of the homogeneous di-substitution derivatives as para, ortho, and meta, and its tri-substitution homogeneous derivatives as asymmetrical, vicinal, and symmetrical, is that the group $Aut_{pos}(T_{D;G})$ of automorphisms of the partially ordered set $T_{D;G}$, where $D = \{(4,2),(3^2)\}$, is the trivial group.

$$\begin{tikzcd}
a_{(4,2)} \arrow[d] & & b_{(4,2)} \arrow[dl] \arrow[d] & & c_{(4,2)} \arrow[dl] \arrow[d] \arrow[dr] & \\
a_{(3^2)} & a_{(3^2)} & b_{(3^2)} & a_{(3^2)} & b_{(3^2)} & c_{(3^2)}
\end{tikzcd}$$

Fig. 13. Körner relations

Chapter VII gives very brief information on the creative work of some chemists and mathematicians who have contributions to the theory of chemical structure and to the theory of isomerism of chemical compounds.

In chapter VIII we make an attempt to outline a biography of Arthur Constant Lunn who, beyond question, is the author of the ideas underlying this theory of isomerism.

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