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On the Inverse Problem of Isomer Enumeration: Part I, Case of Ethane

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ABSTRACT

In their fundamental paper from 1929, Lunn and Senior show that the groups of substitution isomerism and stereoisomerism of ethane can be reconstructed up to conjugation if one knows the numbers of its mono-substitution, di-substitution, and tri-substitution homogeneous derivatives. The proof is an exhaustive quest through the list of orbit numbers for all subgroups of the symmetric group of degree 6. Here we present more conceptual proofs of these statements.

1. INTRODUCTION

1.1. In the pioneering paper [6], A. C. Lunn and J. K. Senior stated explicitly that, in general, there is no agreement between the symmetry group of a given molecule's skeleton Σ with d free valences, thought of as a rigid space configuration, and the family $(N_{\lambda;\Sigma})_\lambda$ of the numbers of experimentally known isomers obtained by distributing univalent substituents among the free valences of Σ by virtue of the partitions λ of d. If the idea of representing isomers as orbits of a finite group is correct, then one has to look for a group which is generally different from the 3-dimensional symmetry group. Lunn and Senior define their symmetry groups as those permutation groups on the univalent substituents, which are in accordance with the above-mentioned experimental data.
In [6, IV], via an exhaustive search, is proved that the Lunn-Senior's symmetry group responsible for the substitution isomerism of ethane is a permutation group $G \leq S_6$ of order 18, defined up to conjugacy. In compliance with the classification of the point groups of finite order, there is no rigid space configuration whose symmetry group is isomorphic to G. In these cases the euphemism "non-rigid space configuration" was introduced in order for similar "pathological" situations to continue to be in keeping with the traditional (rigid) concept of configuration.
Lunn and Senior assert ([6, III]) that "such a group has much the same relation to a space configuration as the mathematical law of inverse squares has to the physical laws of gravitation (Newtonian form), the Coulomb law of electrostatic attractions and repulsions, the law of the attractions and repulsions of magnetic poles, etc.", and that "a

space configuration (rigid or non-rigid) is likely to be available for use as an illustration of the permutation group in question; ... and the continued adherence to a particular mode of representation, instead of clarifying the situation, is apt to result in confusion between the properties of the phenomena observed and the properties of the particular method of representation adopted".
The inverse problem of isomer enumeration consists of finding the Lunn-Senior's symmetry group G provided that enough numbers $N_{\lambda;\Sigma}$ are experimentally known. Besides Lunn and Senior, this problem was also addressed by J. H. Redfield in his lecture given at the University of Pennsylvania in 1937 (see [8]). In his significant paper [2], W. Hasselbarth presents a conceptual treatment of the inverse problem for the classical case of benzene.

1.2. Let Σ be a molecule's skeleton with d univalent substituents. Each permutation group $W \leq S_d$ acts naturally on the set $[1,d] = \{1,\dots,d\}$ of the free valences of the skeleton Σ, thus producing an action on the set T_λ of all tabloids of shape λ where $\lambda = (\lambda_1, \lambda_2, \dots)$ is a partition of d (see 2.1). Any tabloid $A = (A_1, A_2, \dots) \in T_\lambda$ can be identified with a distribution of ligands among the unsatisfied valences of Σ via the rule: Attach λ_1 identical ligands of type x_1 to the valences from A_1, attach λ_2 identical ligants of type x_2 to the valences from A_2, and so on. In other words, the tabloids $A \in T_\lambda$ represent the structural formulae of the derivatives of the parent substance ΣH_d, whose univalent substituents have empirical formula $x_1^{\lambda_1} x_2^{\lambda_2} \dots$. In general however, several tabloids (structural formulae) represent one and the same chemical compound. In [6], Lunn and Senior assert that there exists a permutation group $G \leq S_d$ such that the set of all tabloids (structural formulae) which represent the same compound, coincides with a G-orbit in T_λ, and the action of the group G is induced by the action

$$\zeta A = (\zeta(A_1), \zeta(A_2), \dots, \zeta(A_d)). \tag{1.2.1}$$

of the symmetric group S_d on T_λ.

REMARK 1.2.2. There is another, well known representation of the structural formulae of the isomers with a given skeleton Σ, and with d univalent substituents whose empirical formula is $x_1^{\lambda_1} x_2^{\lambda_2} \dots$ — the representation via double cosets (see [5, Ch. 3, 3.4]. In fact, these two mathematical models are isomorphic. Indeed, let $G \leq S_d$ be the symmetry group corresponding to the skeleton Σ. The set T_λ contains the tabloid I with components $I_1 = [1, \lambda_1], I_2 = [\lambda_1 + 1, \lambda_1 + \lambda_2], \dots$, and its stabilizer with respect to the action (1.2.1) of S_d is the Young subgroup $S_\lambda = S_{\lambda_1} \times \cdots \times S_{\lambda_d} \leq S_d$. Thus

$$S_d/S_\lambda \simeq T_\lambda, \tag{1.2.3}$$

$$vS_\lambda \mapsto vI,$$

is an isomorphism of S_d-sets. Now, consider the action of the permutation group $G \leq S_d$ on T_λ, which is induced by the action (1.2.1). The isomorphism (1.2.3) of S_d-sets can also be considered as an isomorphism of G-sets, and moreover, it factors out to a bijection

$$G\backslash S_d/S_\lambda \simeq G\backslash T_\lambda.$$

$$GvS_\lambda \mapsto vI,$$

between the set of double cosets of S_d modulo (G, S_λ), and the set of G-orbits in T_λ.

Let $n_{\lambda;G}$ be the number of all G-orbits in T_λ, and let $N_{\lambda;\Sigma}$ be the number of all experimentally known substitution isomers with empirical formula $x_1^{\lambda_1} x_2^{\lambda_2} \ldots$ of their univalent substituents. As a consequence of Lunn-Senior's thesis (see [6, IV], [3, 1.5.1]) we obtain for any partition λ of d the inequality

$$N_{\lambda;\Sigma} \leq n_{\lambda;G}. \tag{1.2.4}$$

The differences $n_{\lambda;G} - N_{\lambda;\Sigma}$ give an account of the theoretically possible isomers which have not been synthesized yet. However, for mono-substitution and di-substitution derivatives, and sometimes for tri-substitution homogeneous derivatives (that is, for $\lambda = (d-1,1)$, $(d-2,2)$, $(d-2,1^2)$, and sometimes for $\lambda = (d-3,3)$) it may safely be said that

$$N_{\lambda;\Sigma} = n_{\lambda;G}. \tag{1.2.5}$$

In the ideal situation, when the equality (1.2.5) holds for all partitions λ of d, the permutation group $G \leq S_d$ is defined up to *literal conformality* (see [6, IV], [7, Ch. I, Sec. 25], [3, Theorem 5.2.5]). We remind that each permutation group $G \leq S_d$ is a disjoint union of its subsets G_λ, where G_λ consists of all elements of G of cycle type λ, and thus G produces a sequence $(g_{\lambda;G})_\lambda$ of non-negative integers, where $g_{\lambda;G} = |G_\lambda|$. Two groups G, $G' \leq S_d$ are said to be *literally conformal* if their sequences $(g_{\lambda;G})_\lambda$ and $(g_{\lambda;G'})_\lambda$ coincide. This is an equivalence relation which is weaker than the conjugacy in S_d. The group G is uniquely determined (up to literal conformality) by its sequence $(n_{\lambda;G})_\lambda$ because the two sequences $(n_{\lambda;G})_\lambda$ and $(g_{\lambda;G})_\lambda$ are related via the equalities

$$|G| n_{\lambda;G} = \sum_{\mu \in P_6} M_{\lambda\mu} g_{\mu;G}, \ \lambda \in P_6, \tag{1.2.6}$$

where $(M_{\lambda\mu})$ is an invertible matrix with integer entries (see [2, II]).

1.3. The considerations in Subsection 1.2 show that, in general, the situation is not consolatory because the chemists feel practically certain that all derivatives of a given chemical compound are synthesized only in the mono-substitution, di-substitution, and sometimes — in tri-substitution homogeneous case. Fortunately, for small d this information, as a rule, is sufficient for the group G to be recovered even up to conjugation. In this case the equalities (1.2.5) for $\lambda = (d-1,1)$, $(d-2,2)$, $(d-2,1^2)$, and $\lambda = (d-3,3)$ impose enough restrictions upon the structure of (the subgroups of) G, so that $|G_\mu| = g_{\mu;G} = 0$ for sufficiently many partitions μ. The latter commonly allows us to find the group G. This is the case with the group of ethane.

1.4. Let us consider the two carbon atoms of ethane C_2H_6, which are united by a single bond, as a skeleton Σ with 6 univalent substituents. The following numbers of substitution isomers of ethane are experimentally known:

$$N_{(5,1);\Sigma} = 1 \text{ (mono-substitution derivatives)},$$

$$N_{(4,2);\Sigma} = 2 \text{ (di-substitution homogeneous derivatives)},$$

$$N_{(4,1^2);\Sigma} = 3 \text{ (di-substitution heterogeneous derivatives)},$$

$$N_{(3^2);\Sigma} = 2 \text{ (tri-substitution homogeneous derivatives)}.$$

The aim of this paper is to present the proofs of the next theorem, and its two corollaries:

THEOREM 1.4.1. *Let $G \leq S_6$ be a permutation group. The equalities*

$$n_{(5,1);G} = 1,\ n_{(4,2);G} = 2,\ n_{(4,1^2);G} = 3, \text{and } n_{(3^2);G} = 2, \tag{1.4.2}$$

hold if and only if G is conjugated in S_6 to the group

$$\langle(123), (456), (14)(25)(36)\rangle$$

of order 18.

COROLLARY 1.4.3. *The group $G \leq S_6$ of substitution isomerism of ethane coincides up to conjugacy with the group*

$$\langle(123), (456), (14)(25)(36)\rangle$$

of order 18.

COROLLARY 1.4.4. *The group $G' \leq S_6$ of stereoisomerism of ethane coincides up to conjugacy with the group*

$$\langle(123), (456), (14)(25)(36), (12)(45)\rangle$$

of order 36.

The above statements are proved in [6] by brute force, that is, the list of all subgroups G of S_6, and their sequences $(n_{\lambda;G})_{\lambda \in P_6}$, was used. We have employed [2] as an example to follow, but our methods are different.

1.5. In Section 2 we introduce the terminology and notation which are used further. Section 3 is the body of the paper. We prove there a series of lemmas which state that certain $g_{\mu;G}$ are zeroes, so the linear system (1.2.6) for the $n_{\lambda;G}$'s on hand can be solved with respect to remaining $g_{\mu;G}$, and with respect to $|G|$. The latter is done in Lemma 3.2.3. Section 4 contains proofs of Theorem 1.4.1, and of Corollaries 1.4.3, and 1.4.4. The technique of the proofs is mainly based on Sylow's theorems as well as on systematical use of a graph $\Gamma(G, H, \lambda)$ which models the orbit spaces $G\backslash T_\lambda$ and $H\backslash T_\lambda$, where H is a subgroup of G. The graph $\Gamma(G, H, \lambda)$ for an appropriate H which contains an element of G of cycle type μ, is an efficient tool for proving the equality $g_{\mu;G} = 0$.

2. PRELIMINARIES

2.1. Given a positive integer d, by a *partition* of d we mean a sequence $\lambda = (\lambda_1, \lambda_2, \ldots)$ of non-negative integers with $\lambda_1 \geq \lambda_2 \geq \cdots$, and $\lambda_1 + \lambda_2 + \cdots = d$. *Length* $|\lambda|$ of a partition λ is the number of its non-zero terms. Sometimes we denote a partition λ also by $(1^{m_1}, 2^{m_2}, \ldots)$, where m_k is the number of k's in the sequence $\lambda = (\lambda_1, \lambda_2, \ldots)$, $k = 1, 2, \ldots, d$.

Let λ be a partition of d. *Tabloid of shape* λ is a sequence $A = (A_1, A_2, \ldots)$ of disjoint subsets of the integer-valued interval $[1, d]$ with $|A_1| = \lambda_1$, $|A_2| = \lambda_2, \ldots$ (cf. [4, Ch. 2, 2.2]). Let T_λ be the set of all tabloids of shape λ. Any subgroup G of the symmetric group S_d acts on T_λ via the rule (1.2.1). We denote by $n_{\lambda;G}$ the number of the G-orbits in T_λ.

Given a partition λ of d, we use notation G_λ for the subset of the permutation group $G \le S_d$, consisting of all elements of cycle type λ. We set $g_{\lambda;G} = |G_\lambda|$. In particular, if $\lambda = (1^{m_1}, 2^{m_2}, \dots)$, then the conjugate class $(S_d)_\lambda$ of the symmetric group S_d contains

$$g_{\lambda;S_d} = d!/z_\lambda \tag{2.1.1}$$

permutations, where $z_\lambda = 1^{m_1} m_1! 2^{m_2} m_2! \dots$.

2.2. For any triple consisting of a permutation group $G \le S_d$, its subgroup H, and a partition λ of d, we define a graph $\Gamma = \Gamma(G, H, \lambda)$ in the following way: The set of vertices of Γ is the set of H-orbits in T_λ; two different vertices a and b are joined by an edge if and only if there exist $A \in a$, $B \in b$, and $\sigma \in G$, such that $\sigma(A) = B$. The H-orbits that are contained in a particular G-orbit in T_λ form a complete graph which is connected component of Γ. Therefore, Γ is a disjoint union of $n_{\lambda;G}$ complete graphs Γ_1, $\Gamma_2, \dots$. If ν_i is the number of the vertices of Γ_i, then $\sum_i \nu_i = n_{\lambda;H}$, and after eventual renumbering of Γ_i, we can suppose that $\nu = (\nu_1, \nu_2, \dots)$ is a partition of $n_{\lambda;H}$. Thus, each triple G, H, λ produces a partition $\nu = \nu(G, H, \lambda)$ of $n_{\lambda;H}$ with length $|\nu| = n_{\lambda;G}$. Moreover, the degree of each vertex of the connected component Γ_i is equal to $\nu_i - 1$.

3. The cycle type statistics of the group of ethane

3.1. Since we can identify the set $T_{(5,1)}$ of all tabloids $A = (A_1, A_2)$ of shape $(5,1)$ with the integer-valued interval $[1, 6]$ via the rule $A_2 = \{i\}$, $1 \le i \le 6$, the number $n_{(5,1)}$ of G-orbits in $T_{(5,1)}$ is equal to the number of sets of transitivity of G. Therefore, the next lemma follows.

LEMMA 3.1.1. *Let $G \le S_6$. One has $n_{(5,1);G} = 1$ if and only if G is transitive.*

Throughout the paper, we represent the elements of the set $T_{(4,1^2)}$, that is, the tabloids $A = (A_1, A_2, A_3)$ of shape $(4, 1^2)$, as ordered pairs (i, j), $1 \le i \ne j \le 6$, via the rule: $A_2 = \{i\}$, $A_3 = \{j\}$.

LEMMA 3.1.2. *Let $G \le S_6$ be a transitive permutation group. Then the inequality $n_{(4,1^2);G} \ge 2$ implies $g_{(5,1);G} = 0$.*

PROOF: Let us suppose that $g_{(5,1);G} \ge 1$. Then the group G contains a 5-cycle. Up to conjugation in S_6 we can suppose that $(12345) \in G$. We set $H = \langle (12345) \rangle$. There are 6 H-orbits in $T_{(4,1^2)}$:

(I)	(II)	(III)	(IV)	(V)	(VI)
$(1,2)$	$(2,1)$	$(1,3)$	$(3,1)$	$(1,6)$	$(6,1)$
$(2,3)$	$(3,2)$	$(2,4)$	$(4,2)$	$(2,6)$	$(6,2)$
$(3,4)$	$(4,3)$	$(3,5)$	$(5,3)$	$(3,6)$	$(6,3)$
$(4,5)$	$(5,4)$	$(4,1)$	$(1,4)$	$(4,6)$	$(6,4)$
$(5,1)$	$(1,5)$	$(5,2)$	$(2,5)$	$(5,6)$	$(6,5)$

The group G is a transitive, so there exists $\sigma \in G$ with $\sigma(1) = 6$. Let us consider the graph $\Gamma = \Gamma(G, H, (5,1))$ with vertices $(I), \dots, (VI)$ (see 2.2). Since $\sigma(1,2) = (6, \sigma(2))$, and $\sigma(1,3) = (6, \sigma(3))$, the vertices (I), (III), and (VI) form a triangle in Γ. Since $\sigma(2,1) = (\sigma(2), 6)$, and $\sigma(3,1) = (\sigma(3), 6)$, the vertices (II), (IV), and (V) form another triangle in Γ. The equality $\sigma(1,5) = (6, \sigma(5))$ connects the vertices (II) and (VI), so Γ is the complete graph with vertices $(I), \dots, (VI)$. In particular, $n_{(4,1^2);G} = 1$, which is a contradiction.

LEMMA 3.1.3. *Let $G \leq S_6$ be a transitive permutation group. If one has $n_{(4,1^2);G} \geq 3$, then $g_{(4,2);G} = g_{(4,1^2);G} = g_{(3,2,1);G} = 0$.*

PROOF: Let $g_{(4,2);G} \geq 1$. Then, after eventual conjugation in S_6, we can suppose that the group G contains the cyclic group $H = \langle(1234)(56)\rangle$.
We have 8 H-orbits in $T_{(4,1^2)}$:

(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	$(VIII)$
$(1,2)$	$(2,1)$	$(1,3)$	$(1,5)$	$(5,1)$	$(1,6)$	$(6,1)$	$(5,6)$
$(2,3)$	$(3,2)$	$(2,4)$	$(2,6)$	$(6,2)$	$(2,5)$	$(5,2)$	$(6,5)$
$(3,4)$	$(4,3)$	$(3,1)$	$(3,5)$	$(5,3)$	$(3,6)$	$(6,3)$	
$(4,1)$	$(1,4)$	$(4,2)$	$(4,6)$	$(6,4)$	$(4,5)$	$(5,4)$	

The transitivity of the group G yields the existence of a $\sigma \in G$, such that $\sigma(1) = 6$. We consider the graph $\Gamma = \Gamma(G, H, (4, 1^2))$ with vertices $(I), \ldots, (VIII)$.
The equalities $\sigma(1,2) = (6, \sigma(2))$, and $\sigma(4,1) = (\sigma(4), 6)$, imply that the degrees $deg(I)$ and $deg(II)$ are at least 2.
In case $\sigma(3) = 5$ we have: $\sigma(1,3) = (6,5)$, and $\sigma(3,1) = (5,6)$, so $deg(III) \geq 1$, and $deg(VIII) \geq 1$; $\sigma(1,5) = (6, \sigma(5))$, $\sigma(3,5) = (5, \sigma(5))$, and $\sigma(2,6) = (\sigma(2), \sigma(6))$, where $\sigma(2), \sigma(5), \sigma(6) \in \{1,2,3,4\}$, so $deg(IV) \geq 3$, and $deg(V) \geq 3$; $\sigma(1,6) = (6, \sigma(6))$, $\sigma(3,6) = (5, \sigma(6))$, and $\sigma(2,5) = (\sigma(2), \sigma(5))$, where $\sigma(2), \sigma(5), \sigma(6) \in \{1,2,3,4\}$, so $deg(VI) \geq 3$, and $deg(VII) \geq 3$.
Now, suppose that $\sigma(3) \in \{1,2,3,4\}$. We have: $\sigma(1,3) = (6, \sigma(3))$, $\sigma(3,1) = (\sigma(3), 6)$, so $deg(III) \geq 2$; $\sigma^{-1}(5,6) = (\sigma^{-1}(5), 1)$, $\sigma^{-1}(6,5) = (1, \sigma^{-1}(5))$, where $\sigma^{-1}(5) \neq 3$, therefore $deg(VIII) \geq 2$; $\sigma(1,5) = (6, \sigma(5))$, $\sigma(3,5) = (\sigma(3), \sigma(5))$, hence $deg(IV) \geq 2$, and $deg(V) \geq 2$; $\sigma(1,6) = (6, \sigma(6))$, $\sigma(3,6) = (\sigma(3), \sigma(6))$, hence $deg(VI) \geq 2$, and $deg(VII) \geq 2$.
Since $n_{(4,1^2);G} \geq 3$, the graph Γ has at least 3 connected components, that is, the corresponding partition $\nu = \nu(G, H, \lambda)$ of 8 has length ≥ 3. In case $\sigma(3) = 5$, degree's sequence of Γ yields that there exists a connected component with at least 4 vertices, there are no isolated vertices, and at most one component has exactly 2 vertices. Now, it is obvious that there is no partition $\nu = (\nu_1, \nu_2, \nu_3, \ldots)$ of 8 with $\nu_1 \geq 4$, $\nu_2 \geq 3$, and $\nu_3 \geq 2$. When $\sigma(3) \in \{1,2,3,4\}$ all degrees of the vertices of Γ are ≥ 2, so $\nu_1 \geq 3$, $\nu_2 \geq 3$, and $\nu_3 \geq 3$, which is a contradiction.
Let $g_{(4,1^2);G} \geq 1$. Then, up to conjugation in S_6, we can assume that the group G contains the cyclic group $H = \langle(1234)\rangle$.
We have 9 H-orbits in $T_{(4,1^2)}$:

(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	$(VIII)$	(IX)
$(1,2)$	$(2,1)$	$(1,3)$	$(1,5)$	$(5,1)$	$(1,6)$	$(6,1)$	$(5,6)$	$(6,5)$
$(2,3)$	$(3,2)$	$(2,4)$	$(2,5)$	$(5,2)$	$(2,6)$	$(6,2)$		
$(3,4)$	$(4,3)$	$(3,1)$	$(3,5)$	$(5,3)$	$(3,6)$	$(6,3)$		
$(4,1)$	$(1,4)$	$(4,2)$	$(4,5)$	$(5,4)$	$(4,6)$	$(6,4)$		

Since the group G is transitive, there exist σ, τ, $\eta \in G$ such that $\sigma(1) = 6$, $\tau(1) = 5$, and $\eta(5) = 6$.
Let us consider the graph $\Gamma = \Gamma(G, H, (4, 1^2))$ with vertices $(I), \ldots, (IX)$.
The equalities $\sigma(1,2) = (6, \sigma(2))$, $\sigma(4,1) = (\sigma(4), 6)$, $\tau(1,2) = (5, \tau(2))$, and $\tau(4,1) = (\tau(4), 5)$, yield that the degrees $deg(I)$ and $deg(II)$ of the vertices (I) and (II) are at least 3.

The equalities $\sigma(1,3) = (6, \sigma(3))$, and $\sigma(3,1) = (\sigma(3), 6)$, imply that $deg(III) \geq 2$.
Further, we have $\sigma(1,5) = (6, \sigma(5))$, and $\tau(1,5) = (5, \tau(5))$. We can choose $2 \leq i \leq 4$ such that $\tau(i) \notin \{5,6\}$. Then $\tau(i,5) = (\tau(i), \tau(5))$ yields that $deg(IV) \geq 3$, and $deg(V) \geq 3$. Similarly, we obtain $deg(VI) \geq 3$, and $deg(VII) \geq 3$.
The equalities $\eta(5,6) = (6, \eta(6))$, and $\eta(6,5) = (\eta(6), 6)$, imply $deg(VIII) \geq 1$, and $deg(IX) \geq 1$.
In particular, $deg(I) + \cdots + deg(IX) \geq 22$, hence the graph Γ has at least 11 edges. According to the above inequalities, there are neither isolated vertices nor more than one component with exactly two vertices in Γ. Therefore, if $\nu_k \neq 0$, then $\nu_k \geq 2$, and there is at most one k with $\nu_k = 2$. Since the corresponding partition $\nu = \nu(G, H, (4, 1^2))$ of 9 has length ≥ 3, this yields only two possibilities: $\nu = (4,3,2)$, or $\nu = (3,3,3)$. In the first case Γ has 10 edges and in the second — 9 edges, which in both cases is a contradiction.
Now, suppose that $g_{(3,2,1);G} \geq 1$. Then, after eventual conjugation in S_6, we can assume $(123)(45) \in G$, and let $H = \langle(123)(45)\rangle$.
We have 9 H-orbits in $T_{(4,1^2)}$:

(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	$(VIII)$	(IX)
$(1,2)$	$(1,3)$	$(1,4)$	$(4,1)$	$(1,6)$	$(6,1)$	$(4,6)$	$(6,4)$	$(4,5)$
$(2,3)$	$(2,1)$	$(2,5)$	$(5,2)$	$(2,6)$	$(6,2)$	$(5,6)$	$(6,5)$	$(5,4)$
$(3,1)$	$(3,2)$	$(3,4)$	$(4,3)$	$(3,6)$	$(6,3)$			
		$(1,5)$	$(5,1)$					
		$(2,4)$	$(4,2)$					
		$(3,5)$	$(5,3)$					

Since the group G is a transitive, there exist $\sigma \in G$ such that $\sigma(1) = 6$, and $\tau \in G$ with $\tau(5) = 6$. We consider the graph $\Gamma = \Gamma(G, H, (4, 1^2))$ with vertices $(I), \ldots, (IX)$. The equalities $\sigma(1,2) = (6, \sigma(2))$, and $\sigma(3,1) = (\sigma(3), 6)$, yield $deg(I) \geq 2$. Similarly, since $\sigma(1,3) = (6, \sigma(3))$, and $\sigma(2,1) = (\sigma(2), 6)$, we obtain $deg(II) \geq 2$; since $\sigma(1,6) = (6, \sigma(6))$, and $\sigma(2,6) = (\sigma(2), \sigma(6))$, we obtain $deg(V) \geq 2$ and $deg(VI) \geq 2$; since $\sigma^{-1}(4,6) = (\sigma^{-1}(4), 1)$, and $\tau^{-1}(5,6) = (\tau^{-1}(5), 5)$, we get $deg(VII) \geq 2$, and $deg(VIII) \geq 2$; since $\sigma(4,5) = (\sigma(4), \sigma(5))$, and $\sigma(5,4) = (\sigma(5), \sigma(4))$, we obtain $deg(IX) \geq 2$. For the vertices (III) and (IV) we have $\sigma(1,4) = (6, \sigma(4))$, $\tau(1,5) = (\tau(1), 6)$, and $\sigma(2,5) = (\sigma(2), \sigma(5))$, so $deg(III) \geq 3$, and $deg(IV) \geq 3$.
The degree's sequence of Γ implies $\nu_k \geq 3$ for all $k = 1, 2, 3, \ldots$. Moreover, Γ has at least 3 connected components. The only possible partition ν of 9, which satisfies these restrictions is $\nu = (3,3,3)$. Therefore Γ consists of three disjoint triangles, and this contradicts the inequality $deg(III) \geq 3$. The proof of Lemma 3.1.3 is finished.

3.2. According to [2] or [9], and taking into account (2.1.1), we rewrite (1.2.6) in the form

$$n_{\lambda;G} = \frac{1}{|G|\lambda_1!\lambda_2!\cdots} \sum_{\mu \in P_6} |(S_\lambda)_\mu| z_\mu g_{\mu;G}, \ \lambda \in P_6. \tag{3.2.1}$$

LEMMA 3.2.2. *Let $G \leq S_6$ be a transitive permutation group. If $n_{(4,1^2);G} \geq 3$, and $n_{(3^2);G} \leq 2$, then one has:*
(i) $g_{(3,1^3);G} \geq 2$;

(ii) $g_{(2,1^4);G} = g_{(2^2,1^2);G} = 0$.

PROOF: (i) Obviously, we have $g_{(1^6);G} = 1$. According to Lemmas 3.1.2 – 3.1.3, $g_{(5,1);G} = 0$, $g_{(4,2);G} = 0$, $g_{(4,1^2);G} = 0$, and $g_{(3,2,1);G} = 0$. We write down (3.2.1) for $\lambda = (5,1), (3^2)$, and taking into account Lemma 3.1.1, we get

$$\begin{array}{llllll} 4g_{(2,1^4);G} + 2g_{(2^2,1^2);G} & + 3g_{(3,1^3);G} & & - & (|G|-6) & = 0 \\ 8g_{(2,1^4);G} + 4g_{(2^2,1^2);G} & + 2g_{(3,1^3);G} & + 2g_{(3^2);G} & - & (n_{(3^2);G}|G|-20) & = 0. \end{array}$$

This system yields $4g_{(3,1^3);G} - 2g_{(3^2);G} = (2-n_{(3^2);G})|G|+8$, and our statement follows.
(ii) Let us suppose that the group G contains a transposition. After eventual conjugation in S_6 we can assume $(12) \in G$. Since G is transitive, it also contains transpositions of the type $(k_i i)$ for $i = 3,4,5,6$. If the sequence (k_i) is identically equal to some $k \in [1,6]$, then k is either 1 or 2, and in both cases $G = S_6$, which is a contradiction. Otherwise, among (12) and $(k_i i)$, $i = 3,4,5,6$, we can find two transpositions with disjoint supports. We can suppose $(12) \in G$ and $(34) \in G$. In particular, $(12)(34) \in G$, and hence $g_{(2,1^4);G} \geq 1$ implies $g_{(2^2,1^2);G} \geq 1$.
Now, let us assume the opposite of (ii), that is, $(12)(34) \in G$. Part (i) yields that the group G contains a 3-cycle. We consider the subgroup $H \leq G$ with generators $(12)(34)$ and this 3-cycle. There are four substantially different cases:

$$H = \langle(12)(34),(125)\rangle,\ \langle(12)(34),(123)\rangle,\ \langle(12)(34),(135)\rangle,\ \text{or}\ \langle(12)(34),(156)\rangle.$$

We have $n_{(4,1^2);G} \geq 3$, so the graph $\Gamma = \Gamma(G,H,(4,1^2))$ has at least 3 connected components.
Case 1. $H = \langle(12)(34),(125)\rangle$. We have

$$H = \{(1),(12)(34),(125),(152),(25)(34),(15)(34)\}.$$

There are 8 H-orbits in $T_{(4,1^2)}$:

(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	$(VIII)$
$(1,2)$	$(1,3)$	$(3,1)$	$(1,6)$	$(6,1)$	$(3,4)$	$(3,6)$	$(6,3)$
$(2,1)$	$(2,3)$	$(3,2)$	$(2,6)$	$(6,2)$	$(4,3)$	$(4,6)$	$(6,4)$
$(5,2)$	$(5,4)$	$(4,5)$	$(5,6)$	$(6,5)$			
$(2,5)$	$(2,4)$	$(4,2)$					
$(1,5)$	$(1,4)$	$(4,1)$					
$(5,1)$	$(5,3)$	$(3,5)$					

Since the group G is a transitive, there exist $\sigma, \tau \in G$ such that $\sigma(1) = 6$, and $\tau(3) = 6$. Let us consider the graph $\Gamma = \Gamma(G,H,(4,1^2))$ with vertices $(I),\ldots,(VIII)$. The equalities $\sigma(1,2) = (6,\sigma(2))$, and $\sigma(2,1) = (\sigma(2),6)$ show that $deg(I) \geq 2$. The two pairs of equalities $\sigma(1,3) = (6,\sigma(3))$, $\sigma(2,3) = (\sigma(2),\sigma(3))$, and $\sigma(1,6) = (6,\sigma(6))$, $\sigma(2,6) = (\sigma(2),\sigma(6))$, imply $deg(II) \geq 2$, $deg(III) \geq 2$, and $deg(IV) \geq 2$, $deg(V) \geq 2$, respectively.
Moreover, $\tau(3,4) = (6,\tau(4))$, $\tau(4,3) = (\tau(4),6)$, and $\tau(3,6) = (6,\tau(6))$, $\tau(4,6) = (\tau(4),\tau(6))$, yield $deg(VI) \geq 2$, and $deg(VII) \geq 2$, $deg(VIII) \geq 2$, respectively.
The above inequalities imply that each connected component of Γ contains at least 3 vertices. Now, it is obvious that there is no partition $\nu = (\nu_1,\nu_2,\nu_3,\ldots)$ of 8 with $\nu_1 \geq 3$, $\nu_2 \geq 3$, and $\nu_3 \geq 3$.

Case 2. $H = \langle(12)(34),(123)\rangle$. We have $(12)(34)(213)(12)(34) = (124)$, so $H = \langle(123),(124)\rangle = A_4$.
There are 7 H-orbits in $T_{(4,1^2)}$:

(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)
$(1,2)$	$(1,5)$	$(5,1)$	$(1,6)$	$(6,1)$	$(5,6)$	$(6,5)$
$(1,3)$	$(2,5)$	$(5,2)$	$(2,6)$	$(6,2)$		
$(1,4)$	$(3,5)$	$(5,3)$	$(3,6)$	$(6,3)$		
$(2,1)$	$(4,5)$	$(5,4)$	$(4,5)$	$(6,4)$		
$(3,1)$						
$(4,1)$						
$(2,3)$						
$(2,4)$						
$(3,2)$						
$(4,2)$						
$(3,4)$						
$(4,3)$						

Since the group G is a transitive, there exists $\sigma \in G$ such that $\sigma(1) = 6$.
We consider the graph $\Gamma = \Gamma(G, H, (4,1^2))$ with vertices $(I), \dots, (VII)$. The equalities $\sigma(1,2) = (6, \sigma(2))$, and $\sigma(2,1) = (\sigma(2), 6)$ show that $deg(I) \geq 2$. Further, for $k = 5, 6$ we have $\sigma(1,k) = (6, \sigma(k))$, and $\sigma(2,k) = (\sigma(2), \sigma(k))$, so $deg(II) \geq 2$, $deg(III) \geq 2$, $deg(IV) \geq 2$, and $deg(V) \geq 2$. Moreover, $\sigma^{-1}(5,6) = (\sigma^{-1}(5), 1)$, implies $deg(VI) \geq 1$, and $deg(VII) \geq 1$.
The above inequalities yield that each connected component of Γ, except possibly one, contains at least 3 vertices. The possible exception contains at least two vertices. Now, it is obvious that there is no partition $\nu = (\nu_1, \nu_2, \nu_3, \dots)$ of 7 with $\nu_1 \geq 3$, $\nu_2 \geq 3$, and $\nu_3 \geq 2$.
Case 3. $H = \langle(12)(34),(135)\rangle$. We have $(12)(34)(135) = (14352)$, so H contains an element of cycle type $(5,1)$, and this contradicts Lemma 3.1.2.
Case 4. $H = \langle(12)(34),(156)\rangle$. Since $(12)(34)(156) = (1562)(34)$, the group H contains an element of cycle type $(4,2)$. The latter contradicts Lemma 3.1.3.

LEMMA 3.2.3. *If $G \leq S_6$ is a permutation group such that*

$$n_{(5,1);G} = 1,\ n_{(4,2);G} = 2,\ n_{(4,1^2);G} = 3, \text{and } n_{(3^2);G} = 2,$$

then the order of G is 18 and $g_{(3,1^3);G} = 4$, $g_{(3^2);G} = 4$, and $g_{(2^3);G} = 3$.

PROOF: We write down (3.2.1) for $\lambda = (5,1), (4,2), (4,1^2), (3^2)$, and taking into account Lemmas 3.1.2 – 3.1.3, and Lemma 3.2.2, (ii), we obtain

$$\begin{aligned}
3g_{(3,1^3);G} \qquad\qquad & - (|G| - 6) = 0 \\
3g_{(2^3);G} + 3g_{(3,1^3);G} \qquad\qquad & - (2|G| - 15) = 0 \\
6g_{(3,1^3);G} \qquad\qquad & - (3|G| - 30) = 0 \\
g_{(3,1^3);G} + g_{(3^2);G} & - (|G| - 10) = 0.
\end{aligned}$$

Therefore, $|G| = 18$ and $g_{(3,1^3);G} = 4$, $g_{(3^2);G} = 4$, and $g_{(2^3);G} = 3$.

4. The group of ethane

4.1. We have collected enough information in order to prove our main Theorem 1.4.1, stated in the Introduction. We shall start with the formulation of the following obvious

LEMMA 4.1.1. *Let* $B_1 = \{1,2,3\}$ *and* $B_2 = \{4,5,6\}$, *and suppose that the permutation* $\sigma \in S_6$ *of cycle type* (2^3) *maps* B_1 *onto* B_2. *Then* $\sigma \in \Omega$, *where*

$$\Omega = \{(14)(25)(36), (15)(26)(34), (16)(24)(35), (14)(26)(35), (15)(24)(36), (16)(25)(34)\}.$$

Let $H \leq G$ be a Sylow's 3-subgroup of G. According to Sylow's theorems (see [1, Ch. 4, 4.2]) the number of Sylow's 3-subgroups of G is a divisor of 18 of the type $3k+1$, so H is a normal subgroup of G. Since $|H| = 3^2$, [1, Ch. 4, 4.4] yields that the group H is elementary Abelian of type $(3,3)$. After eventual conjugation in S_6, we can suppose $H = \langle (123), (456) \rangle$. By virtue of Lemma 3.2.3, there are three elements of cycle type (2^3) in G. If ι is one of them, then $G = H\langle \iota \rangle$, so it remains to find their form. Lemma 3.2.3 yields that the elements of cycle type $(3,1^3)$ in G are (123), (132), (456), and (465), so $\iota\langle (123) \rangle \iota = \langle (456) \rangle$. In particular, $\iota B_1 = B_2$, and Lemma 4.1.1 implies $\iota \in \Omega$. The cyclic group $C = \langle (123) \rangle$ acts on the set Ω by conjugation, and dissects it into two C-orbits:

$$\Omega_1 = \{(14)(25)(36), (15)(26)(34), (16)(24)(35)\},$$

and

$$\Omega_2 = \{(14)(26)(35), (15)(24)(36), (16)(25)(34)\}.$$

We have either $\Omega_1 \subset G$, or $\Omega_2 \subset G$, hence we can set $\iota = (14)(25)(36)$, or $\iota = (14)(26)(35)$. Thus, $G = H\langle (14)(25)(36) \rangle$, or $G = H\langle (14)(26)(35) \rangle$. Since the last two groups are conjugated in S_6 via the transposition (56), we are done.
In the end, we note that the group $G = \langle (123), (456), (14)(25)(36) \rangle$ satisfies the equations (1.4.2).

4.2. Proof of Corollary 1.4.3.
Theorem 1.4.1 yields immediately the form of the group G of substitution isomerism of ethane, as well as the equalities (1.4.2) for this G. The numbers $n_{\lambda;G}$ for the remaining λ can be calculated directly, and a comparison with the experimental data show that the inequalities (1.2.4) hold for any partition λ of 6.

4.3. Proof of Corollary 1.4.4.

LEMMA 4.3.1. *If a group* $G' \leq S_6$ *of order* 36 *contains the group*

$$G = \langle (123), (456), (14)(25)(36) \rangle,$$

then

$$G' = \langle (123), (456), (14)(25)(36), (12)(45) \rangle. \qquad (4.2.2)$$

PROOF: The dihedral group $D_4 = \langle (1425)(36), (14)(25)(36) \rangle$ of order 8 normalizes the group $H = \langle (123), (456) \rangle$ in S_6. Therefore the normalizer $N_{S_6}(H)$ contains the group $N = D_4 H$ of order 72. In particular, the index n_3 of $N_{S_6}(H)$ in S_6 divides 10. Since H is a Sylow 3-subgroup of S_6, according to Sylow's theorems (see [1, Ch. 4, 4.2]) n_3 is the number of all Sylow's 3-subgroups of S_6, $n_3 > 1$, and $n_3 \equiv 1 (mod\ 3)$. Hence $n_3 = 10$, or, equivalently, $N_{S_6}(H) = N$. This yields $G \leq N_{S_6}(G) \leq N$. Since $(12)(45)G(12)(45) = G$, the normalizer $N_{S_6}(G)$ contains the group $G\langle(12)(45)\rangle$ of order 36. On the other hand, $(45) \in D_4$, and $(45)(14)(25)(36)(45) \notin G$, so $(45) \notin N_{S_6}(G)$. Therefore $N_{S_6}(G) = G\langle(12)(45)\rangle$. If a group $G' \leq S_6$ of order 36 contains G, then it normalizes G, so $G' = \langle(123), (456), (14)(25)(36), (12)(45)\rangle$.

The following numbers of stereoisomers of ethane are experimentally established:

$$N'_{(5,1);\Sigma} = 1,\ N'_{(4,2);\Sigma} = 2,\ N'_{(4,1^2);\Sigma} = 2,\ N'_{(3^2);\Sigma} = 2.$$

Both the experiment and the equality $N_{(4,1^2);\Sigma} - N'_{(4,1^2);\Sigma} = 1$ yield that there is a chiral pair among the di-substitution heterogeneous derivatives of ethane. Therefore the order of the group $G' \leq S_6$ of stereoisomerism of ethane is 36, and G' contains G. Now, Lemma 4.3.1 implies (4.2.2), and for this particular G' the equalities

$$n_{(5,1);G'} = 1,\ n_{(4,2);G'} = 2,\ n_{(4,1^2);G'} = 2,\ n_{(3^2);G'} = 2,$$

hold. Finally, a straightforward calculation of the numbers $n_{\lambda;G'}$, and the experimental data yield the inequalities (1.2.4) for any partition λ of 6, so Corollary 1.4.4 is proved.

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