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On the Inverse Problem of Isomer Enumeration: Part II, Case of Cyclopropane

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ABSTRACT

In their fundamental paper from 1929, Lunn and Senior show that the groups of substitution isomerism and stereoisomerism of cyclopropane can be reconstructed up to conjugation if one knows the numbers of its mono-substitution and di-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.

5. INTRODUCTION

5.1. We consider the three carbon atoms of cyclopropane C_3H_6, which are united by single bonds, as a skeleton Σ with 6 univalent substituents. The following numbers of substitution isomers of cyclopropane are experimentally known:

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

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

This paper contains proofs of the next theorem, and its two corollaries:

THEOREM 5.1.1. *Let $G \leq S_6$ be a permutation group. The equalities*

$$n_{(5,1);G} = 1,\ n_{(4,2);G} = 4, \tag{5.1.2}$$

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

$$\langle (123)(456), (14)(26)(35) \rangle$$

of order 6, which is isomorphic to the dihedral group of order 6.

COROLLARY 5.1.3. *The group $G \leq S_6$ of substitution isomerism of cyclopropane coincides up to conjugacy with the group*

$$\langle(123)(456),(14)(26)(35)\rangle$$

of order 6, *which is isomorphic to the dihedral group of order* 6.

COROLLARY 5.1.4. *The group* $G' \leq S_6$ *of stereoisomerism of cyclopropane coincides up to conjugacy with the group*

$$\langle(123)(456),(14)(26)(35),(14)(25)(36)\rangle$$

of order 12, *which is isomorphic to the dihedral group of order* 12.

In Lunn-Senior's paper [6, V], the previous statements are proved by using only the list of the orbit numbers of all subgroups of the symmetric group S_6. In the present paper we give conceptual proofs of these results.

5.2. In Section 6 we establish the cycle type statistics of the group G of cyclopropane. Here we use the graph $\Gamma = \Gamma(G, H, (4,2))$ which was introduced in [3, 2.2], in order to show that G contains neither transpositions nor 3-cycles. Since the partition $(4, 1^2)$ is less than the partition $(4,2)$ with respect to the dominance order, the inequalities [2, 5.3.2] allow us to use the results from [3, Section 3], and this makes possible for the linear system [3, 1.2.6] to be solved. Section 7 is devoted to proofs of Theorem 5.1.1, and its Corollaries 5.1.3, and 5.1.4. As in Part I of this paper (see [3]), the main tools used in these proofs are Sylow's theorems.

6. THE CYCLE TYPE STATISTICS OF THE GROUP OF CYCLOPROPANE

6.1. We can identify the set $T_{(4,2)}$ of all tabloids $A = (A_1, A_2)$ of shape $(4,2)$ (see [4, Ch. 2, 2.2]) with the set of all two-element subsets $\{i,j\}$ of the integer-valued interval $[1,6]$, via the rule $A_2 = \{i,j\}$, $1 \leq i < j \leq 6$.

LEMMA 6.1.1. *Let* $G \leq S_6$ *be a transitive permutation group. Then the inequality* $n_{(4,2);G} \geq 3$ *implies* $g_{(2,1^4);G} = g_{(3,1^3);G} = 0$.

PROOF: For, since the inequality $n_{(4,2);G} \geq 3$ holds, the graph $\Gamma = \Gamma(G, H, (4,2))$ has at least 3 connected components, that is, the corresponding partition $\nu = \nu(G, H, \lambda)$ has length ≥ 3 for any subgroup $H \leq G$ (see [3, 2.2]).
Since the group G is transitive, for any pair i, j, $1 \leq i \neq j \leq 6$, there exists an element $\sigma_{ij} \in G$, such that $\sigma_{ij}(i) = j$.
Let us suppose that $g_{(2,1^4);G} \geq 1$. The transitivity of G yields the existence of two transpositions in G with disjoint supports (see the proof of [3, 3.2.2, (ii)]). After eventual conjugation in S_6, we can assume $(12) \in G$, and $(34) \in G$. We set $H = \langle(12),(34)\rangle$.
There are 8 H-orbits in $T_{(4,2)}$:

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

We consider the graph $\Gamma = \Gamma(G, H, (4,2))$ with vertices $(I), \ldots, (VIII)$, and the corresponding partition $\nu = \nu(G, H, (4,2))$ of 8. (see [3, 2.2]).

The triples of equalities $\sigma_{16}\{1,2\} = \{6, \sigma_{16}(2)\}$, $\sigma_{15}\{1,2\} = \{5, \sigma_{15}(2)\}$, $\sigma_{14}\{1,2\} = \{4, \sigma_{14}(2)\}$, and $\sigma_{36}\{3,4\} = \{6, \sigma_{36}(4)\}$, $\sigma_{35}\{3,4\} = \{5, \sigma_{35}(4)\}$, $\sigma_{31}\{3,4\} = \{1, \sigma_{31}(4)\}$, yield $deg(I) \geq 2$ and $deg(III) \geq 2$, respectively.
Since at least one of the two-element subsets $\sigma_{16}\{1,3\} = \{6, \sigma_{16}(3)\}$ and $\sigma_{16}\{1,4\} = \{6, \sigma_{16}(4)\}$ does not coincide with $\{5,6\}$, the equality $\sigma_{15}\{1,3\} = \{5, \sigma_{15}(3)\}$ implies $deg(II) \geq 2$.
We have $\sigma_{54}\{1,5\} = \{\sigma_{54}(1), 4\}$, $\sigma_{54}\{2,5\} = \{\sigma_{54}(2), 4\}$, and $\sigma_{56}\{1,5\} = \{\sigma_{56}(1), 6\}$. If we assume that these three two-element subsets belong to the same H-orbit, then this is necessarily orbit (VII), so $\sigma_{54}(1) = \sigma_{54}(2) = 6$ — a contradiction. Therefore $deg(IV) \geq 2$.
Similarly, the equalities $\sigma_{64}\{1,6\} = \{\sigma_{64}(1), 4\}$, $\sigma_{64}\{2,6\} = \{\sigma_{65}(2), 4\}$, and $\sigma_{65}\{1,6\} = \{\sigma_{64}(1), 5\}$, yield $deg(V) \geq 2$.
Transposing 1 and 3, and 2 and 4, we replace the vertices (IV) and (V) with the vertices (VI) and (VII), respectively. Hence the above considerations yield $deg(VI) \geq 2$ and $deg(VII) \geq 2$.
Finally, it is obvious that $deg(VIII) \geq 1$. If the connected component of Γ that contains the vertex $(VIII)$, consists of two vertices, we would get a contradiction with the above inequalities. Hence this connected component consists of at least three vertices; in particular, $deg(VIII) \geq 2$.
If $\nu = (\nu_1, \nu_2, \nu_3, \ldots)$, then the degree sequence of Γ yields $\nu_1 \geq 3$, $\nu_2 \geq 3$, and $\nu_3 \geq 3$, which contradicts the equality $\nu_1 + \nu_2 + \nu_3 + \ldots = 8$.
Now, suppose that $g_{(3,1^3);G} \geq 1$. Then, up to conjugation in S_6, we can assume $(123) \in G$. Set $H = \langle (123) \rangle$. There are 7 H-orbits in $T_{(4,2)}$:

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

We consider the graph $\Gamma = \Gamma(G, H, (4,2))$ with vertices $(I), \ldots, (VII)$, and the corresponding partition $\nu = \nu(G, H, (4,2))$ of 7.
Because of $\sigma_{16}\{1,2\} = \{6, \sigma_{16}(2)\}$, $\sigma_{15}\{1,2\} = \{5, \sigma_{15}(2)\}$, and $\sigma_{14}\{1,2\} = \{4, \sigma_{14}(2)\}$, we obtain $deg(I) \geq 2$.
At least one of the sets $\sigma_{46}\{1,4\} = \{\sigma_{46}(1), 6\}$, and $\sigma_{46}\{2,4\} = \{\sigma_{46}(2), 6\}$, contain an element i with $1 \leq i \leq 4$. Then the equality $\sigma_{45}\{1,4\} = \{\sigma_{45}(1), 5\}$, implies $deg(II) \geq 2$.
If we transpose 4 and 5 (respectively, 4 and 6), we get vertex (III) (respectively, (IV)), instead of vertex (II); hence $deg(III) \geq 2$ and $deg(IV) \geq 2$.
The inequalities $deg(V) \geq 1$, $deg(VI) \geq 1$, and $deg(VII) \geq 1$, are obvious.
Since the connected components of Γ are complete graphs, the above inequalities yield that at least one of the vertices (V), (VI), and (VII), has degree ≥ 2. Therefore all non-zero components of the partition $\nu = (\nu_1, \nu_2, \nu_3, \ldots)$, except possibly one, are ≥ 3. The remaining component is ≥ 2. Thus, $\nu_1 \geq 3$, $\nu_2 \geq 3$, and $\nu_3 \geq 2$, which contradicts the equality $\nu_1 + \nu_2 + \nu_3 + \ldots = 7$.

LEMMA 6.1.2. *Let $G \leq S_6$ be a transitive permutation group. Then the inequality $n_{(4,2);G} \geq 3$ implies*

$$g_{(5,1);G} = g_{(4,2);G} = g_{(4,1^2);G} = g_{(3,2,1);G} = 0.$$

PROOF: In accordance with [2, 5.3.2], the inequality $(4,1^2) < (4,2)$ with respect to the dominance order (see [5, Ch. 6, 6.1]) implies $n_{(4,1^2);G} \geq n_{(4,2);G}$. In particular, $n_{(4,1^2);G} \geq 3$, which in turn yields: $g_{(5,1);G} = 0$, after [3, 3.1.2], and $g_{(4,2);G} = 0$, $g_{(4,1^2);G} = 0$, and $g_{(3,2,1);G} = 0$, after [3, 3.1.3].

6.2. In the next lemma we establish the cycle type statistics of any transitive group $G \leq S_6$ with $n_{(4,2);G} = 4$.

LEMMA 6.2.1. *Let $G \leq S_6$ be a permutation group such that*

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

Then one has:
(i) The order of G is 6 and $g_{(2^3);G} = 3$, $g_{(3^2);G} = 2$;
(ii) The group G is isomorphic to the dihedral group of order 6.

PROOF: (i) We write down the linear equations [3, 3.2.1] for $\lambda = (1^6), (5,1), (4,2)$. Then Lemmas 6.1.1 – 6.1.2, and [3, 3.1.1] yield

$$\begin{array}{llll} g_{(2^2,1^2)} & + g_{(2^3);G} & + g_{(3^2)} + g_{(6)} & - (|G|-1) = 0 \\ 2g_{(2^2,1^2);G} & & & - (|G|-6) = 0 \\ 3g_{(2^2,1^2)} & + 3g_{(2^3);G} & & - (4|G|-15) = 0. \end{array} \tag{6.2.2}$$

Therefore, $3(g_{(3^2)} + g_{(6)}) = 12 - |G|$, so, in particular, $|G| \leq 12$. The transitivity of the group $G \leq S_6$ implies that 6 divides $|G|$. Hence, $|G|$ equals 6, or 12. If we suppose that $|G| = 12$, then $g_{(3^2)} = g_{(6)}) = 0$, and unless the identity, the group G contains only elements of cycle type $(2^2, 1^2)$, and (2^3). In particular, there can be no elements of order 3, which contradicts Sylow's theorems (see [1, Ch. 4, 4.2]). Thus, we have $|G| = 6$. Then the system (6.2.2) yields $g_{(2^2,1^2)} = 0$, and $g_{(2^3)} = 3$.
On the other hand, if we assume that $g_{(6)} \geq 1$, then we would obtain $g_{(6)} \geq 2$, and $g_{(3^2)} \geq 2$, which would contradict the equality $g_{(3^2)} + g_{(6)} = 2$. Therefore, $g_{(6)} = 0$, and $g_{(3^2)} = 2$.
(ii) We remind that each group of order 6 is either cyclic or dihedral, and since G does not contain elements of order 6, we are done.

7. THE GROUP OF CYCLOPROPANE

7.1. In this Subsection we present a proof of our main Theorem 5.1.1.
In compliance with Lemma 6.2.1 and after eventual conjugation in S_6, we can suppose that $(123)(456) \in G$. The cyclic group $H = \langle(123)(456)\rangle$ is a normal subgroup of G, so if ι is one of the three elements of cycle type (2^3) in G, then $G = H\langle\iota\rangle$. Now, we shall find the form of ι. Let us denote $B_1 = \{1,2,3\}$ and $B_2 = \{4,5,6\}$. Since $\iota(123)(456)\iota \in H$, we have $\iota B_1 = B_2$. By virtue of [3, 4.1.1], we have $\iota \in \Omega$, where

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

The group H acts on the set Ω by conjugation and dissects it into four H-orbits:

$$\Omega_1 = \{(14)(25)(36)\},\ \Omega_2 = \{(15)(26)(34)\},\ \Omega_3 = \{(16)(24)(35)\},$$

and

$$\Omega_4 = \{(14)(26)(35), (15)(24)(36), (16)(25)(34)\}.$$

If $\Omega_i \subset G$, for some $1 \leq i \leq 3$, then G would be Abelian which contradicts (6.2.1), (ii). Thus, $\Omega_4 \subset G$, so we can set $\iota = (14)(26)(35)$. It remains to note that the group $G = \langle (123)(456), (14)(26)(35) \rangle$ is isomorphic to the dihedral group of order 6, and satisfies the equations (5.1.2).

7.2. Proof of Corollary 5.1.3.

Corollary 5.1.3 is a direct consequence of Theorem 5.1.1, if we take into account that the experimental data confirm the equalities 5.1.2, as well as the inequalities [3, 1.2.4].

7.3. Proof of Corollary 5.1.4

LEMMA 7.3.1. *If a group $G' \leq S_6$ of order 12 contains the group*

$$G = \langle (123)(456), (14)(26)(35) \rangle,$$

then G' is conjugated to the group

$$\langle (123)(456), (14)(26)(35), (14)(25)(36) \rangle, \tag{7.2.2}$$

which is isomorphic to the dihedral group of order 12.

PROOF: The group $H = \langle (123)(456) \rangle$ is the only Sylow's 3-subgroup of G, and since G is normal in G', then H is normal in G'. In particular, H is the only Sylow's 3-subgroup of G'. Let K be a Sylow's 2-subgroup of G'. If K were a normal subgroup of G', then G' would be the product group $H \times K$ which is Abelian, and this would contradict the fact that G is the dihedral group. Thus, in accord with Sylow's theorems, there are three subgroups of G' of order 4: $K_1 = K$, K_2, K_3. Any pair from the three involutions of G generate the group G, so we can suppose $(14)(26)(35) \in K_1$, $(15)(24)(36) \in K_2$, and $(16)(25)(34) \in K_3$. The group K is the Klein four group because if $K \leq S_6$ were cyclic, then it would not contain elements of cycle type (2^3). The group K acts on H by conjugation, and since $G' = KH$ is not Abelian, this action is not the trivial one. The group H has only two automorphisms, so we can choose $a \in K$, $a \neq (1)$, and $s \in K$, with $a(123)(456)a^{-1} = (123)(456)$, and $s(123)(456)s^{-1} = (132)(465)$. In particular, the element $v = a(123)(456) \in G'$ has order 6. The relations $v^6 = 1$, $s^2 = 1$, and $svs = v^{-1}$, yield that G' is isomorphic to the dihedral group of order 12.

In case there exists a pair of Sylow's 2-subgroups K_i with trivial intersection we have $K_1 \cap K_2 \cap K_3 = \{(1)\}$, and then besides the identity (1) the group G' consists of two elements of order 3 and nine elements of order 2, which is a contradiction. Thus, $K_1 \cap K_2 = \langle b_3 \rangle$, $K_2 \cap K_3 = \langle b_1 \rangle$, and $K_3 \cap K_1 = \langle b_2 \rangle$, where the involutions b_i are not elements of G.

Since the group H acts transitively on the set $\{K_1, K_2, K_3\}$ via conjugation, this action permutes transitively the intersections $K_1 \cap K_2$, $K_2 \cap K_3$, and $K_3 \cap K_1$ which form an H-orbit O of subgroups of G'. Then their generators b_1, b_2, and b_3 constitute an H-orbit in G'.

If O consists of three elements, then b_1, b_2, and b_3 are pairwise different, and this yields

$$K_1 = \{(1), x_1, b_2, b_3\}, \; K_2 = \{(1), x_2, b_3, b_1\}, \; K_3 = \{(1), x_3, b_1, b_2\},$$

where $x_1 = (14)(26)(35)$, $x_2 = (15)(24)(36)$, and $x_3 = (16)(25)(34)$. In this case the remaining three elements must be all elements of order 6 in G', which is a contradiction. Otherwise, $b_1 = b_2 = b_3 = b$, and $b(123)(456)b = (123)(456)$, so the permutation b has cycle type (2^3), and $bB_1 = B_2$. As a consequence of both [3, 4.1.1], and the description of the action of H on the set Ω (see 7.1), we obtain $b = (14)(25)(36)$, $b = (15)(26)(34)$, or $b = (16)(24)(35)$. Hence

$$G' = \langle (123)(456), (14)(26)(35), (14)(25)(36) \rangle,$$

$$G' = \langle (123)(456), (14)(26)(35), (15)(26)(34) \rangle,$$

or,

$$G' = \langle (123)(456), (14)(26)(35), (16)(24)(35) \rangle.$$

The last three groups form a $\langle (456) \rangle$-orbit with respect to conjugation.
The experiment establishes the following numbers of stereoisomers of cyclopropane:

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

The equality $N_{(4,2);\Sigma} - N'_{(4,2);\Sigma} = 1$ yields that there is a chiral pair among the disubstitution homogeneous derivatives of cyclopropane, and this also is confirmed experimentally. Hence the order of the group $G' \leq S_6$ of stereoisomerism of ethane is 12, and G' contains G. Now, Lemma 7.3.1 implies (7.3.2), and for this particular G' the equalities

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

hold. A direct calculation of the numbers $n_{\lambda;G'}$, and the experimental data yield the inequalities [3, 1.2.4] for any partition λ of 6, so Corollary 5.1.4 is proved.

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