On Lunn-Senior’s Mathematical Model of Isomerism in Organic Chemistry. Part II

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7. Introduction

This paper is a continuation of [3], and we shall use all terminology and notation introduced there.

7.1. Let a molecule’s skeleton with $d$ unsatisfied single valences is fixed. Lunn-Senior’s thesis 1.5.1 asserts that for any type of isomerism of the molecule with that skeleton (univalent substitution isomerism, stereoisomerism, or structural isomerism) there exists a permutation group $W \leq S_d$ such that each isomer of that type can be identified with a $W$-orbit in the set $T_d$, that is, with an element of the set $T_{d,W}$ of $W$-orbits. If $W = G$, where $G$ is Lunn-Senior’s group of substitution isomerism, then the members of the set $T_{d,G}$ represent the corresponding univalent substitution isomers, and the inequalities $a \prec b$, $a, b \in T_{d,G}$, represent the substitution reactions $b \rightarrow a$ among them. We denote by $G'$ and $G''$ the groups of stereoisomerism and structural isomerism, respectively, of the molecule under question. The group $G'$ either coincides with $G$ (there are no chiral pairs), or $G \leq G'$ and $|G' : G| = 2$ (otherwise) — see [7, V] or 1.5.1.

The aim of the paper is to consider a mathematical model in which the following statement from chemistry becomes a well formed formula: the derivatives that correspond to the structural formulae $a, b \in T_{d,G}$ cannot be distinguished via substitution reactions. The present approach gives a conceptual basis of the Lunn-Senior’s ad hoc considerations in [7, VI] (see also 6.4) on the diamers of ethene and of our statements in [5, Sections 3,4,5] concerning the identification of the isomers of certain compounds with one mono-substitution and at least three di-substitution homogeneous derivatives (for instance, benzene and cyclopropane).

It is natural to suppose that $a$ and $b$ are identical as structural isomers, that is, $a$ and $b$ are contained in one and the same $G''$-orbit, — otherwise they are trivially distinguishable; thus they also have the same empirical formula: $a, b \in T_{\lambda,G}$, $\lambda \in P_d$. Since the substitution reactions are modeled by the inequalities in $T_{d,G}$, and since

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the symmetries are the automorphisms of the corresponding algebraic structure — the partially ordered set \( T_{d;G} \) — we define that the products corresponding to \( a \) and \( b \) are indistinguishable via substitution reactions if \( a \) and \( b \) are identical as structural isomers and if there exists an automorphism \( \alpha: T_{d;G} \to T_{d;G} \) of the partially ordered set \( T_{d;G} \), such that: (a) \( \alpha(T_{\mu;G}) = T_{\mu;G} \) for any \( \mu \in P_d \), (b) \( \alpha \) maps any chiral pair onto a chiral pair, and (c) \( \alpha(a) = b \). Otherwise, they are called distinguishable via substitution reactions. The automorphisms \( \alpha \) of \( T_{d;G} \), which satisfy condition (a) form a group \( \text{Aut}_0(T_{d;G}) \) that acts naturally on the set \( T_{d;G} \). The elements \( \alpha \in \text{Aut}_0(T_{d;G}) \) that obey (b) form a subgroup \( \text{Aut}_0'(T_{d;G}) \leq \text{Aut}_0(T_{d;G}) \).

In practice, however, the chemists know experimentally enough derivatives as well as enough substitution reactions among them only for a small number of \( \lambda \in P_d \) (mono-substitution, di-substitution, tri-substitution homogeneous, etc., derivatives). Thus, we are forced to consider subsets of \( T_{d;G} \) consisting of several \( T_{\mu;G} \), \( \mu \in P_d \), with the induced partial order. For any subset \( D \subset P_d \) we define the partially ordered set \( T_{D;G} = \cup_{\mu \in D} T_{\mu;G} \) and generalize the above definition in the following natural way: the products corresponding to \( a, b \in T_{\lambda;G}, \lambda \in D \), are indistinguishable via substitution reactions among the elements of \( T_{D;G} \) if \( a \) and \( b \) are identical as structural isomers, and if there exists an automorphism \( \alpha: T_{d;G} \to T_{D;G} \) of the partially ordered set \( T_{D;G} \), such that (aD) \( \alpha(T_{\mu;G}) = T_{\mu;G} \) for any \( \mu \in D \), (bD) \( \alpha \) maps any chiral pair onto a chiral pair, and (cD) \( \alpha(a) = b \). Otherwise, they are said to be distinguishable via substitution reactions among the elements of \( T_{D;G} \). The automorphisms \( \alpha \) of \( T_{D;G} \) possessing property (aD) form a group \( \text{Aut}_0(T_{D;G}) \), and those \( \alpha \in \text{Aut}_0(T_{D;G}) \) which obey (bD) form a subgroup \( \text{Aut}_0'(T_{D;G}) \leq \text{Aut}_0(T_{D;G}) \). The elements of the group \( \text{Aut}_0'(T_{D;G}) \) could be called chiral automorphisms of the partially ordered set \( T_{D;G} \).

Obviously, if \( D \subset D' \), then any automorphism from the group \( \text{Aut}_0'(T_{D';G}) \) induces by restriction an automorphism from the group \( \text{Aut}_0'(T_{D;G}) \), and we obtain a homomorphism of groups \( \text{Aut}_0'(T_{D';G}) \to \text{Aut}_0'(T_{D;G}) \). The fact that this homomorphism is, in general, not surjective reflects the plain observation that the products corresponding to \( a, b \in T_{\lambda;G}, \lambda \in D \), can be indistinguishable via substitution reactions among the elements of \( T_{D;G} \), but distinguishable via substitution reactions among the elements of (the wider set) \( T_{D';G} \).

7.2. In the beginning of Section 8 we study the relation between the partially ordered sets \( T_{d;W} \) and \( T_{d';W'} \), for a couple of groups \( W \leq W' \leq S_d \) with \( |W' : W| = 2 \), and the formal behaviour of the group \( \text{Aut}_0^{W'}(T_{D;W}) \) of chiral automorphisms of \( T_{d;W} \). Thus, when \( W = G, W' = G' \) we have \( \text{Aut}_0^{W'}(T_{D;W}) = \text{Aut}_0'(T_{D;W}) \), and we generalize the “chiral” situation.

The renumberings of the \( d \) unsatisfied valences of the skeleton, which do not affect the group \( G \) of symmetries of the molecule, are exactly the elements \( \nu \) of the normalizer \( N \) of \( G \) in \( S_d \), and any such renumbering \( \nu \) induces an automorphism \( \nu \in \text{Aut}_0(T_{D;G}) \), \( D \subset P_d \). In addition, if \( \nu \in N' \), where \( N' \) is the intersection of \( N \) with the normalizer of \( G' \) in \( S_d \), then \( \nu \in \text{Aut}_0'(T_{D;G}) \). After A. Kerber (see [6, 1.5]), we call the automorphisms \( \nu \), where \( \nu \in N' \), hidden symmetries of the molecule under consideration, or hidden automorphisms of the partially ordered set \( T_{D;W} \).

In the formal treatment, Theorem 8.2.2 yields \( \nu \in \text{Aut}_0^{W'}(T_{D;W}), D \subset P_d \), and, in particular, shows that the hidden symmetries form a subgroup \( \text{Aut}_0^{h;W'}(T_{D;W}) \) of \( \text{Aut}_0^{W'}(T_{D;W}) \), isomorphic to the factor-group \( N'/W \) when \( (1^d) \in D \). In case \( W = G, W' = G' \) we denote \( \text{Aut}_0^{h;W'}(T_{D;W}) \) by \( \text{Aut}_0^h(T_{D;G}) \). Under certain condition, chemically
equivalent to existence of chiral pairs among the derivatives with empirical formulae from $D$, the group $Aut^h_{0,W'}(T_{D,W})$ contains a copy of the factor-group $W'/W$, generated by the so-called chiral involution $\hat{\tau}$ that permutes the members of any chiral pair and leaves invariant the diamers (Corollary 8.2.4). In particular, the members of a chiral pair are indistinguishable via substitution reactions, which is the content of Theorem 8.2.6.

On the other hand, the normalizer $N$ acts in a natural way on the set $X_W$ of all one-dimensional characters $\chi$ of the group $W$, $\chi \mapsto \nu\chi$, and this action induces actions of both the factor-group $N/W$ and, under some condition on $D$, of the group $Aut^h_{0,W'}(T_{D,W})$ of hidden automorphisms, on the set $X_W$. Given $\theta \in X_{S_\lambda}$, $\lambda \in P_d$, any automorphism $\hat{\nu}$, $\nu \in N$, maps the set of all $(\chi,\theta)$-orbits onto the set of all $(\nu\chi,\theta)$-orbits in $T_d$, and, in particular, any hidden symmetry $\alpha \in Aut^h_{0,W'}(T_{D,W})$ does the same. This is proved in Theorem 9.1.1. As Corollary 9.1.2 we get that any automorphism $\hat{\nu}$, $\nu \in N$, transforms the set of all $\chi$-orbits onto the set of all $\nu\chi$-orbits.

The Extended Lunn-Senior’s thesis 1.6.1, hypothesis 5, asserts that for any $(\chi,\theta)$-orbit $(\chi',\theta)$ of the molecule. Moreover, the automorphism $\hat{\nu}$, $\nu \in N'$, of our algebraic structure transforms the set $T_{\lambda,\nu\chi,\theta}$ onto the set $T_{\lambda,\nu\chi,\theta}$, so the type properties $(\chi,\theta)$ and $(\nu\chi,\theta)$ are not distinguishable. Thus, it is natural to define that the derivatives which correspond to the structural formulae $a, b \in T_{\lambda,G}$, $\lambda \in P_d$, are indistinguishable via pairs of characters if $a$ and $b$ are structurally identical, if for any pair of characters $(\chi,\theta) \in X_G \times X_{S_\lambda}$ with $a \in T_{\lambda,\nu\chi,\theta}$ and $b \notin T_{\lambda,\nu\chi,\theta}$, there exists a $\nu \in N' \cup \{\mu\}$ such that $b \in T_{\lambda,\nu\chi,\theta}$ and $a \notin T_{\lambda,\nu\chi,\theta}$, and if for any pair of characters $(\chi,\theta) \in X_G \times X_{S_\lambda}$ with $b \in T_{\lambda,\nu\chi,\theta}$ and $a \notin T_{\lambda,\nu\chi,\theta}$, there exists a $\nu \in N' \cup \{\mu\}$ such that $a \in T_{\lambda,\nu\chi,\theta}$ and $b \notin T_{\lambda,\nu\chi,\theta}$. By the specialization $\theta = 1_{S_\lambda}$, we obtain the definition of indistinguishability via characters. Otherwise, these derivatives are called distinguishable via pairs of characters, respectively, via characters. The central results here are Theorem 9.2.1 and Corollary 9.2.2, which assert that the members of a chiral pair are indistinguishable via pairs of characters and via characters.

In Section 10 we illustrate these ideas by several molecules: those ethene $C_2H_4$, benzene $C_6H_6$, and cyclopropane $C_3H_6$. The results on the last two are valid in a more general situation described in [5]. Since there are no chiral pairs among the derivatives of ethene, its group of “chiral” automorphisms is relatively big — it is described in Theorem 10.1.1. In Proposition 10.1.2 the group of the hidden symmetries of ethene is described.

Corollary 10.1.3 gives a rigorous treatment of Lunn-Senior’s considerations in [7, VI], concerning the indistinguishability of the diamic pairs $\{a_{(22)}, b_{(22)}\}$, $\{a_{(2,12)}, b_{(2,12)}\}$ of ethene. Proposition 10.1.4 and Corollary 10.1.5 specify their indistinguishability via (pairs of) characters, mentioned in 6.4. The group of chiral automorphisms $Aut^t_0(T_{D,G})$ of benzene for $D = \{(4,2), (3^2)\}$ is the unit group, so we get once again that the Körner relations identify completely the $(4,2)$- and $(3^2)$-derivatives of benzene — see Theorem 10.2.1 and Corollary 10.2.2. Theorem 10.3.5 asserts that the group of chiral automorphisms $Aut^t_0(T_{D,G})$ of cyclopropane for $D = \{(6), (5,1), (4,2), (4,1^2), (3^2)\}$ is direct product of two cyclic groups of order 2. Corollary 10.3.6 yields that for this $D$ all chiral pairs and all diamers are pairwise distinguishable via substitution reactions.

8. Automorphisms

8.1. Let $W \leq S_d$ be a permutation group. We set $T_D = \cup_{\mu \in D} T_\mu$, $T_{D;W} = \cup_{\mu \in D} T_{\mu;W}$, and consider the partial order on $T_{D;W}$, induced from $T_{d;W}$. By definition, a map
Let $W \leq W' \leq S_d$ be a pair of permutations groups such that $|W' : W| = 2$. In particular, $W$ is a normal subgroup of $W'$ and the factor-group $W'/W$ has order 2. We denote by $\chi_\epsilon$ the one-dimensional complex-valued character of $W'$ with kernel $W$ (cf. 6.2). In keeping with 6.2, for any $\lambda \in \tau$ we denote by $\psi\lambda (\psi)$ the $\lambda$-orbits. Let us set $T_{\lambda; \chi_\epsilon} = \cup_{\mu \in D} T_{\lambda; \mu \chi_\epsilon}$. We fix a $\tau \in W'/W$, so $\tau^2 \in W$. Then we have $W'/W = \langle \bar{\tau} \rangle$, where $\bar{\tau} = \tau W$. The factor-group $W'/W$ acts on the set $T_{d,W}$ via the rule $(\eta W) O_W(A) = O_W(\eta A)$.

We remind that for any $W \leq S_d$ the canonical projection $T_d \rightarrow T_{d,W}$ is denoted by $\psi_W$ (see 4.1); its restriction on $D$ is the canonical projection $\psi_{D,W}: T_D \rightarrow T_{D,W}$. The following technical lemma is obvious.

**Lemma 8.1.1.** Let $D \subset P_d$.

(i) The surjective map

$$\psi_D: T_{D,W} \rightarrow T_{D,W'}, \ O_W(A) \mapsto O_{W'}(A),$$

where $A \in T_D$, is the unique map such that $\psi_D \psi_{D,W} = \psi_{D,W'}$;

(ii) the canonical map

$$(W'/W) \setminus T_{D,W} \rightarrow T_{D,W'}, \ O_{W'/W}(O_W(A)) \mapsto \cup_{\eta \in W'}(\eta W)O_W(A)$$

is a bijection;

(iii) after the identification of the orbit space $(W'/W) \setminus T_{D,W}$ with $T_{D,W'}$ via the canonical bijection from (ii), the map $\psi_D$ coincides with the canonical projection $T_{D,W} \rightarrow (W'/W)/T_{D,W}$;

(iv) for $a' \in T_{D,W'}$ one has $\#\psi_D^{-1}(a') = 2$ if $a' \in T_{D; \chi_\epsilon}$ and $\#\psi_D^{-1}(a') = 1$ if $a' \in T_{D,W'} \setminus T_{D; \chi_\epsilon}$;

(v) for any $W'/W$-invariant map $\alpha: T_{D,W} \rightarrow T_{D,W}$ there is a unique map $\alpha': T_{D,W'} \rightarrow T_{D,W'}$, such that $\alpha' \psi_D = \psi_D \alpha$;

(vi) for any two $W'/W$-invariant maps $\alpha: T_{D,W} \rightarrow T_{D,W}$ and $\beta: T_{D,W} \rightarrow T_{D,W}$, one has $(\alpha \beta)' = \alpha' \beta'$.

We denote by $Aut_0^{W'}(T_{D,W})$ the subgroup of $Aut_0(T_{D,W})$ consisting of the $W'/W$-invariant automorphisms $\alpha$, that is, $\alpha(\iota a) = \iota \alpha(a)$ for any $\iota \in W'/W$ and for any $a \in T_{D,W}$.

The lemma below shows, that here we use correctly the notation $Aut_0^{W'}(T_{D,W})$ for the group of chiral automorphisms introduced in Section 7.

**Lemma 8.1.2.** Let $\alpha \in Aut_0(T_{D,W})$. The following three statements are equivalent:

(i) one has $\alpha \in Aut_0^{W'}(T_{D,W})$;

(ii) there exists an automorphism $\alpha' \in Aut_0(T_{D,W'})$, such that $\psi_D \alpha = \alpha' \psi_D$.

(iii) for any $a' \in T_{D; \chi_\epsilon}$ with $\psi^{-1}(a') = \{a, a_1\}$, $a \neq a_1$, there exists $a'' \in T_{D; \chi_\epsilon}$ such that $\psi_D^{-1}(a'') = \{\alpha(a), \alpha(a_1)\}$;

**Proof:** (i) implies (ii). In compliance with Lemma 8.1.1, (v), any $W'/W$-invariant map $\alpha: T_{D,W} \rightarrow T_{D,W}$ produces a unique map $\alpha': T_{D,W'} \rightarrow T_{D,W'}$, such that $\alpha' \psi_D = \psi_D \alpha'$;
\(\psi_D \alpha\). The functoriality of this dependence (Lemma 8.1.1, (vi)) implies that since \(\alpha\) is a bijection, then \(\alpha'\) is a bijection. Now, we shall show that \(\alpha' \in \text{Aut}_0(T_{D;W'})\). Obviously, \(\alpha'(T_{\mu;W'}) = T_{\mu;W'}\) for all \(\mu \in P_d\). Suppose that \(\alpha' \leq \bar{a}\) in \(T_{D;W'}\). Equivalently, there are \(a, \bar{a} \in T_{D;W}\) such that \(a \subset a', \bar{a} \subset \bar{a}'\), and \(a \leq \bar{a}\). The last inequality is equivalent to \(\alpha(a) \leq \alpha(\bar{a})\), and since \(\alpha(a) \subset \alpha'(a)\), \(\alpha(\bar{a}) \subset \alpha'(\bar{a})\), we obtain \(\alpha'(a') \leq \alpha'(\bar{a}')\). Conversely, the definition of \(\alpha'\) and the previous inequality imply the existence of \(a, \bar{a} \in T_{D;W}\) such that \(\alpha(a) \leq \alpha(\bar{a})\). Hence the two inequalities \(\alpha'(a') \leq \alpha'(\bar{a}')\) and \(a' \leq \bar{a}'\) are equivalent.

(ii) implies (iii). Suppose that \(\alpha' \in T_{D;\chi}\). Then we have \(\psi^{-1}_D(\alpha') = \{a, a_1\}\), where \(a \neq a_1\). We set \(a'' = \alpha'(a')\). Thus, \(a'' = \psi_D(\psi_D(a)) = \psi_D(\alpha(a))\), and, by analogy, \(a'' = \psi_D(\alpha(\{a\}))\), so \(\psi_D^{-1}(a'') = \{\alpha(a), \alpha(\{a\})\}\). In particular, \(a'' \in T_{D;\chi}\).

(iii) implies (i). Suppose that (iii) holds. Then \(\alpha\) maps the set \(\psi^{-1}_D(T_{D;\chi})\) and its complement onto themselves. We want to show that \(\alpha(\mu a) = \mu \alpha(a)\) for any \(\mu \in W'/W\) and for any \(a \in T_{D;W}\). If \(\mu\) is the unit element of \(W'/W\), our equality is trivial. Now, let \(\mu = \bar{\tau}\). If \(a = \bar{\tau} a\), then \(\psi^{-1}_D(\alpha') = \{a, \bar{\tau} a\}\), where \(\alpha' = \psi_D(a)\). Therefore \(\psi^{-1}_D(a'') = \{\alpha(a), \alpha(\bar{\tau} a)\}\), and hence \(\alpha(\bar{\tau} a) = \bar{\tau} \alpha(a)\). If \(a = \bar{\tau} a\), then \(\bar{\tau} \alpha(a) = \alpha(a)\), and we have again \(\alpha(\bar{\tau} a) = \bar{\tau} \alpha(a)\).

8.2. We remind that via the rule (1.1.1) any permutation \(\zeta \in S_d\) induces a bijection \(\zeta: T_d \to T_d\), \(A \mapsto \zeta A\), of the set of all tabloids with \(d\) nodes, and its restriction on \(T_\mu\) is a bijection of \(T_\mu\) onto itself for all \(\mu \in P_d\).

Let \(L \leq W' \leq S_d\) be a pair of permutation groups such that \(|W' : W| = 2\). We denote by \(N\) the normalizer of the group \(W\) in \(S_d\), and by \(N'\) the intersection of \(N\) with the normalizer of \(W'\) in \(S_d\). Plainly, \(W' \leq N'\).

**Lemma 8.2.1.** For any \(\nu \in N\) the bijection \(\nu\) can be factored out to a bijection \(\nu: T_{d;W} \to T_{d;W'}, a \mapsto \nu(a)\): if \(a \in a\), then \(\nu(a)\) is the \(W\)-orbit of \(\nu A\). Moreover, the bijection \(\nu\) maps the set \(T_{\chi;W}\) onto itself for any \(\chi \in P_d\).

**Proof:** Given \(\nu \in N\) and \(\sigma \in W\), there exists \(\sigma_1 \in W\), such that \(\nu \sigma = \sigma_1 \nu\). Therefore \(O_W(\nu \sigma A) = O_W(\sigma_1 \nu A) = O_W(\nu A)\), so the rule in the condition yields a map \(\nu\). We have \((\nu)^{-1} = \nu^{-1}\), hence \(\nu\) is a bijection of \(T_{d;W'}\) onto itself, and plainly any set \(T_{\chi;W}\) is \(\nu\)-stable.

**Theorem 8.2.2.** (i) Given \(\nu \in N\) and \(D \subset P_d\), the bijection \(\nu\) induces an automorphism from \(\text{Aut}_0(T_{D;W})\);

(ii) the map \(\nu \mapsto \nu\) is a homomorphism of the group \(N\) into the group \(\text{Aut}_0(T_{D;W})\), whose kernel contains \(W\); if \((1^d) \in D\), then its kernel coincides with \(W\);

(iii) the map \(\nu \mapsto \nu\) is a homomorphism of the group \(N'\) into the group \(\text{Aut}_0^{W'}(T_{D;W})\), whose kernel contains \(W\); if \((1^d) \in D\), then its kernel coincides with \(W\).

**Proof:** (i) According to Lemma 8.2.1, \(\nu\) induces a bijection of the set \(T_{D;W'}\) onto itself. Let \(a, b \in T_{D;W}, A \in a, B \in b\). The inequality \(a \leq b\) means that there exists a \(\sigma \in W\), such that \(\sigma A \leq B\), or, equivalently, \(\sigma A \leq \nu B\). The inequality \(\nu(a) \leq \nu(b)\) means that there exists a \(\sigma_1 \in W\), such that \(\sigma_1 \nu A \leq \nu B\). Since \(\nu W = W\nu\), the last two conditions are equivalent.

(ii) Let \(\nu_1, \nu_2 \in N\), and let \(a \in T_{D;W}, a = O_W(A)\). We have

\[\nu_1 \nu_2(a) = O_W(\nu_1 \nu_2 A) = O_W(\nu_1(\nu_2 A)) = \nu_1(O_W(\nu_2 A)) = \nu_1(\nu_2(a)) = (\nu_1 \nu_2)(a),\]

so \(\nu_1 \nu_2 = \nu_1 \nu_2\).
Plainly, if \( \sigma \in W \), then \( \hat{\sigma}(a) = a \) for any \( a \in T_{D; W} \), hence \( W \) is a subgroup of the kernel. Now, suppose \( (1^d) \in D \), and let \( \nu \in N \) be such that \( \hat{\nu}(a) = a \) for any \( a \in T_{D; W} \). The last condition can also be written as \( O_W(\nu A) = O_W(A) \) for any \( A \in T_D \). In other words, for any \( A = (A_1, A_2, \ldots) \in T_D \) there exists a \( \sigma \in W \) such that \( \nu A = \sigma A \), that is, \( \nu(A_1) = \sigma(A_1), \nu(A_2) = \sigma(A_2), \ldots \). In particular, if \( A = (A_1, A_2, \ldots, A_d) \) with \( A_1 = \{1\}, A_2 = \{2\}, \ldots, A_d = \{d\} \), then \( \nu = \sigma \in W \).

(iii) Part (i) applied for the group \( W' \) yields that any \( \nu \in N' \) induces an automorphism \( \hat{\nu}' \in \text{Aut}_0(T_{D; W'}) \). It is obvious that \( \psi_D \hat{\nu} = \hat{\nu}' \psi_D \). Then Lemma 8.1.2 implies \( \hat{\nu} \in \text{Aut}_{0}^{h,W'}(T_{D; W}) \). Now, since \( N' \) is a subgroup of \( N \) that contains \( W', \) part (ii) finishes the proof.

**Theorem 8.2.2.** (ii), yields information concerning the subgroup \( \text{Aut}_{0}^{h,W'}(T_{D; W}) \) of the group \( \text{Aut}_{0}^{W'}(T_{D; W}) \), consisting of all hidden symmetries.

**Corollary 8.2.3.** If \( (1^d) \in D \), then there exists a natural embedding of the factor-group \( N'/W \) into the group \( \text{Aut}_{0}^{W'}(T_{D; W}) \) with image \( \text{Aut}_{0}^{h,W'}(T_{D; W}) \).

We set \( D_e = \varphi_W(T_{d;X_e}) \), where \( \varphi_W : T_{d; W} \rightarrow P_d \) is the restriction of the projection defined in the beginning of Subsection 4.1. Theorem 5.3.1 yields immediately that the subset \( D_e \subseteq P_d \) is an order ideal (see [1, Section 2]) of the partially ordered set \( P_d \). Moreover, \( D_e \neq \emptyset \) because at least \( T_{(1^d); W} \subset T_{d;X_e} \).

**Corollary 8.2.4.** For any \( D \subseteq P_d \) there exists a natural homomorphism of the factor-group \( W'/W \), the automorphism \( \hat{\tau} \in \text{Aut}_{0}^{W'}(T_{D; W}) \) maps the fiber \( \psi^{-1}(a') \) onto itself in the following way: if \( a' \in T_{D; W}\setminus T_{d;X_e} \), then \( \hat{\psi}^{-1}(a') = \{a\} \) and \( \hat{\tau}(a) = a \), and if \( a' \in T_{d;X_e} \), then \( \hat{\psi}^{-1}(a') = \{a, a_1\} \) and \( \hat{\tau}(a) = a_1, \hat{\tau}(a_1) = a \). If \( D \cap D_e = \emptyset \), then \( \hat{\tau} \) is the identity. If \( D \cap D_e \neq \emptyset \), then \( \hat{\tau} \) is an involution and the above homomorphism is an embedding \( W'/W \simeq \langle \hat{\tau} \rangle \subseteq \text{Aut}_{0}^{h,W'}(T_{D; W}) \).

**Proof:** Because of \( W' \leq N' \), the homomorphism from Theorem 8.2.2, (iii), induces a homomorphism \( W'/W \rightarrow \text{Aut}_{0}^{W'}(T_{D; W}) \), \( \hat{\tau} \rightarrow \tilde{\tau} \), where \( \tilde{\tau} = \eta W, \eta \in W' \). In particular, since \( \tilde{\tau} a = \hat{\tau}(a) \) for any \( a \in T_{D; W}, \eta \in W' \), Lemma 8.1.1, (iv), yields the prescribed action on the fibers of \( \psi \). If \( D \cap D_e = \emptyset \), then for all \( a' \in T_{D; W} \), the fiber \( \psi^{-1}(a') \) consist of one inverse image \( a: \psi^{-1}(a') = \{a\} \), and this yields \( \tilde{\tau}(a) = a \), so \( \hat{\tau} \) is the identity automorphism. The condition \( D \cap D_e \neq \emptyset \) implies that there exists at least one \( a' \in T_{D; W} \) with two inverse images: \( \psi^{-1}(a') = \{a, a_1\} \). Then \( \hat{\tau}(a) = a_1, \hat{\tau}(a_1) = a \), and as a consequence the automorphism \( \hat{\tau} \) is an involution. Therefore we get the desired embedding.

In accord with Lemma 8.1.1, (v), and Lemma 8.1.2, for any \( \alpha \in \text{Aut}_{0}^{W}(T_{d; W}) \) there exists a unique automorphism \( \alpha' \in \text{Aut}_{0}(T_{d; W'}) \), such that \( \alpha \psi = \alpha' \psi \).

**Proposition 8.2.5.** For any \( D \subseteq P_d \) the map

\[
\text{Aut}_{0}^{W'}(T_{D; W}) \rightarrow \text{Aut}_{0}(T_{D; W'}), \quad \alpha \mapsto \alpha',
\]

is a homomorphism of groups and the group \( \langle \hat{\tau} \rangle \) is contained in its kernel.

**Proof:** Let \( \alpha, \beta \in \text{Aut}_{0}^{W'}(T_{D; W}) \). Lemma 8.1.1, (vi), yields \( (\alpha \beta)' = \alpha' \beta' \). Moreover, \( (\hat{\tau})' \) is the identity.
The elements of the group $\text{Aut}_{0}^{W}(T_{D;W})$ are called *chiral automorphisms* of the partially ordered set $T_{D;W}$. In case $D \cap D_{c} \neq \emptyset$ the involution $\hat{\tau} \in \text{Aut}_{0}^{W}(T_{D;W})$ is said to be the *chiral involution* of the group $\text{Aut}_{0}^{W}(T_{D;W})$.

When $W = G$ and $W' = G'$, where $G$ and $G'$ are the groups of substitution isomerism and stereoisomerism, respectively, of the molecule under consideration, and when a distribution of ligands amounts to a chiral molecule, then in compliance with (1.5.1), (2a), we have $|G' : G| = 2$ and denote the group $\text{Aut}_{0}^{G'}(T_{D;G})$ by $\text{Aut}_{0}^{G}(T_{D;G})$.

Taking into account Lunn-Senior’s thesis 1.5.1, (2b), we can reformulate (8.2.4) in the following way:

**Theorem 8.2.6.** The members of a chiral pair are indistinguishable via substitution reactions.

9. Characters

9.1. Here we continue to use notations, introduced in Section 8. Let $X_{W}$ be the Abelian group of the one-dimensional characters of the group $W$. The normalizer $N$ of $W$ in $S_{d}$ acts on $X_{W}$ by the rule

$$(\nu\chi)(\sigma) = \chi(\nu^{-1}\sigma\nu),$$

where $\chi \in X_{W}$, $\sigma \in W$, $\nu \in N$. Since $\sigma\chi = \chi$ for each $\sigma \in W$, we obtain an action of the factor-group $N/W$ on $X_{W}$, defined by the rule

$$(\nu W\chi)(\sigma) = \chi(\nu^{-1}\sigma\nu),$$

where $\chi \in X_{W}$, $\nu \in N$. In particular, since $N'/W$ is a subgroup of $N/W$, and because of Corollary 8.2.3, in case $(1^d) \in D$ we obtain an action of the group $\text{Aut}_{0}^{h;W'}(T_{D;W})$ of hidden symmetries on the set $X_{W}$:

$$(\alpha\chi)(\sigma) = \chi(\nu^{-1}\sigma\nu),$$

where $\chi \in X_{W}$, $\alpha \in \text{Aut}_{0}^{h;W'}(T_{D;W})$, $\alpha = \hat{\nu}$, $\nu \in N'$.

Now, we refer to the notations from Subsection 5.1. Let $\lambda$ be a partition of the number $d$ and let $\theta$ be a one-dimensional character of the group $S_{\lambda}$. Let $\chi \in X_{W}$. Given a tabloid $A = \nu I \in T_{\lambda}$, we note that the one-dimensional character $\beta_{\nu}$ of the stabilizer $W_{A}$ from (5.1.2) depends only on $A$, and on $\chi$ when $\theta$ is fixed, so we introduce the more precise notation $\beta_{\nu} = \beta_{A,\chi}$.

**Theorem 9.1.1.** Given $\nu \in N$, $\lambda \in P_{d}$, $\chi \in X_{W}$, $\theta \in X_{S_{\lambda}}$, one has:

(i) the automorphism $\hat{\nu}$ of the partially ordered set $T_{d;W}$ maps the set $T_{\lambda;\chi,\theta}$ of all $(\chi, \theta)$-orbits onto the set $T_{\lambda;\nu\chi,\theta}$ of all $(\nu\chi, \theta)$-orbits;

(ii) if $(1^d) \in D$, the hidden automorphism $\alpha \in \text{Aut}_{0}^{h;W'}(T_{D;W})$ of the partially ordered set $T_{D;W}$ maps the set $T_{\lambda;\chi,\theta}$ of all $(\chi, \theta)$-orbits in $T_{D;W}$ onto the set $T_{\lambda;\alpha\chi,\theta}$ of all $(\alpha\chi, \theta)$-orbits in $T_{D;W}$.

**Proof:** Obviously part (ii) is a consequence of part (i).

(i) Let $a \in T_{\lambda;\chi,\theta}$, and let $A \in a$, $A = \nu I$. For any $\nu \in N$ we have $\nu A = \nu \nu I$, $W_{\nu A} = \nu W_{A}\nu^{-1}$, and if $\sigma \in W$, then

$$\beta_{\nu A,\nu\chi}(\nu\sigma\nu^{-1}) = (\nu\chi)(\nu\sigma\nu^{-1})\theta((\nu\nu^{-1}\nu\sigma\nu^{-1}\nu\nu)) = \chi(\sigma)\theta(\nu^{-1}\sigma\nu) = \beta_{A,\chi}(\sigma).$$

In particular, $\beta_{A,\chi} = 1$ on $W_{A}$ if and only if $\beta_{\nu A,\nu\chi} = 1$ on $W_{\nu A}$. Therefore if $a \in T_{\lambda;\chi,\theta}$, then $\hat{\nu}(a) \in T_{\lambda;\nu\chi,\theta}$, and if $a \in T_{\lambda;\nu\chi,\theta}$, then $\hat{\nu}^{-1}(a) = \nu^{-1}(a) \in T_{\lambda;\chi,\theta}$, and we are done.

By substituting $\theta = 1_{S_{\lambda}}$ in (9.1.1) we obtain
Corollary 9.1.2. For any $\nu \in N$, any $\lambda \in S_{\lambda}$, and any $\chi \in X_W$ one has:

(i) the automorphism $\hat{\nu} \in Aut_0(T_d;W)$ maps the set $T_{\lambda;\chi}$ of all $\chi$-orbits onto the set $T_{\lambda;\nu\chi}$ of all $\nu\chi$-orbits;

(ii) if $(1^d) \in D$, the hidden automorphism $\alpha \in Aut_0^{h;W'}(T_d;W)$ maps the set $T_{\lambda;\chi}$ of all $\chi$-orbits in $T_{D;W}$ onto the set $T_{\lambda;\alpha\chi}$ of all $\alpha\chi$-orbits in $T_{D;W}$.

Corollary 9.1.3. For any $\nu \in N$, $\lambda \in P_d$, $\chi \in X_W$, and $\theta \in X_{S_{\lambda}}$, one has:

(i) $n_{\nu;\chi,\theta} = n_{\lambda;\chi,\theta}$ and $n_{\nu;\chi} = n_{\lambda;\chi}$;

(ii) if $(1^d) \in D$, then for any hidden automorphism $\alpha \in Aut_0^{h;W'}(T_d;W)$ one has $n_{\nu;\alpha\chi,\theta} = n_{\lambda;\chi,\theta}$ and $n_{\nu;\alpha\chi} = n_{\lambda;\chi}$.

Taking into account (9.1.3), (i), (5.2.4), (i), (iv), and [8, Ch. I, Sec. 7, 7.3], we establish

Corollary 9.1.4. (i) For any $\nu \in N$, and any $\chi \in X_W$ the induced monomial representations $Ind_{W}^{S_d}(\chi)$ and $Ind_{W}^{S_d}(\nu\chi)$ of the symmetric group $S_d$, are equivalent;

(ii) if $(1^d) \in D$, then for any hidden automorphism $\alpha \in Aut_0^{h;W'}(T_d;W)$ the induced monomial representations $Ind_{W}^{S_d}(\chi)$ and $Ind_{W}^{S_d}(\alpha\chi)$ of the symmetric group $S_d$, are equivalent.

9.2. Let $a, b \in T_{\lambda;W}$, $\lambda \in P_d$, and let $\chi \in X_W$, $\theta \in X_{S_{\lambda}}$. It is said that the pair of characters $(\chi, \theta)$ separates $a$ from $b$ if $a \in T_{\lambda;\chi,\theta}$ and $b \notin T_{\lambda;\chi,\theta}$. The character $\chi \in X_W$ separates $a$ from $b$ if $a \in T_{\lambda;\chi}$ and $b \notin T_{\lambda;\chi}$. We say that $a$ and $b$ are indistinguishable via pairs of characters if: (a) $a$ and $b$ are contained in one and the same $G''$-orbit, and

(b) for any pair of characters $(\chi, \theta)$ that separates $a$ from $b$ there exists a permutation $\nu \in N'$ such that $\nu(\chi, \theta)$ separates $b$ from $a$, and for any pair of characters $(\chi, \theta)$ that separates $b$ from $a$ there exists a permutation $\nu \in N'$ such that $\nu(\chi, \theta)$ separates $a$ from $b$.

It is said that $a$ and $b$ are indistinguishable via characters if: (a) $a$ and $b$ are contained in one and the same $G''$-orbit, and

(b) for any character $\chi \in X_W$ that separates $a$ from $b$ there exists a permutation $\nu \in N'$ such that $\nu(\chi)$ separates $b$ from $a$, and for any character $\chi \in X_W$ that separates $b$ from $a$ there exists a permutation $\nu \in N'$ such that $\nu(\chi)$ separates $a$ from $b$.

Otherwise, $a$ and $b$ are said to be distinguishable via pairs of characters, respectively, via characters.

By setting $\theta = 1_{S_{\lambda}}$ we obtain that if $a$ and $b$ are indistinguishable via pairs of characters, then $a$ and $b$ are indistinguishable via characters.

Theorem 9.2.1. The members of a chiral pair are indistinguishable via pairs of characters.

Proof: Let $a' \in T_{\lambda;W'}$ be a chiral pair, that is, $\psi^{-1}(a') = \{a, a_1\}$, $a, a_1 \in T_{\lambda;W}, a \not= a_1$.

In compliance with Lunn-Senior’s thesis 1.5.1, (2b), $a$ and $a_1$ are contained in one and the same $G''$-orbit. Corollary 8.2.4 yields that the chiral involution $\hat{\tau} \in Aut_0^{h;W'}(T_d;W)$ permutes $a$ and $a_1$. Now, suppose that the pair of characters $(\chi, \theta)$ separates $a$ from $a_1$, so $a \in T_{\lambda;\chi,\theta}$ and $a_1 \not= T_{\lambda;\chi,\theta}$. Then in compliance with Theorem 9.1.1, (i), $\hat{\tau}(T_{\lambda;\chi,\theta}) = T_{\lambda;\tau\chi,\theta}$. Therefore $a_1 \in T_{\lambda;\tau\chi,\theta}$ and $a \not= T_{\lambda;\tau\chi,\theta}$, so the pair $((\tau\chi, \theta))$ separates $a_1$ from $a$. Thus, $a$ and $a_1$ are not distinguishable via pairs of characters.

Corollary 9.2.2. The members of a chiral pair are indistinguishable via characters.
10. Examples of groups of chiral automorphisms

10.1. In this Subsection our constant reference is 6.4. We remind that the group $G$ of univalent substitution isomerism of ethene $C_2H_4$ is the Klein four group $G = \{(1), (12)(34), (13)(24), (14)(23)\}$ in $S_4$. There are no chiral pairs among the derivatives of ethene, so $G = G'$, and hence the group $\text{Aut}_0^h(T_4;G)$ of chiral automorphisms coincides with the group $\text{Aut}_0(T_4;G)$.

Here is the complete diagram:

$$T_{4;G}:$$

$$(4) \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad

The horizontal double arrow means that the two diamers are identical as structural isomers. The star $*$ below a structural formula indicates that all possible arrows from it to any structural formula from the next row are drawn.

Plainly, any automorphism $\alpha$ from $\text{Aut}_0(T_4;G)$ leaves invariant the elements $a_{(4)}$ and $a_{(3,1)}$, and if, for instance, $\alpha(a_{(2^2)}) = b_{(2^2)}$, then $\alpha(a_{(2,1^2)}) = b_{(2,1^2)}$. Similarly, if for example, $\alpha(a_{(2^2)}) = a_{(2^2)}$, then $\alpha(a_{(2,1^2)}) = a_{(2,1^2)}$, etc. On the six letters $a_{(1^4)}$, $b_{(1^4)}$, $c_{(1^4)}$, $e_{(1^4)}$, $f_{(1^4)}$, $h_{(1^4)}$, there are no restrictions on $\alpha$. Thus, we have proved

**Theorem 10.1.1.** One has

$$\text{Aut}_0(T_4;G) \simeq S_3 \times S_6,$$

where the permutations of $S_3$ simultaneously move the elements $a$, $b$, $c$ with indices $(2^2)$ and $(2,1^2)$, and $S_6$ consists of all permutations of the six elements with indices $(1^4)$.

We have $N = N' = S_4$, so in accord to Corollary 8.2.3 there are $|N/G| = 6$ hidden symmetries in $\text{Aut}_0(T_4;G)$, and we obtain

**Proposition 10.1.2.** The group $\text{Aut}_0^h(T_4;G)$ of hidden symmetries of ethene consists of the unit permutation, and

$$(12) = (b_{(2^2)} c_{(2^2)}) (b_{(2,1^2)} c_{(2,1^2)})(a_{(1^4)} b_{(1^4)})(c_{(1^4)} e_{(1^4)})(f_{(1^4)} h_{(1^4)}),$$

$$(23) = (a_{(2^2)} c_{(2^2)}) (a_{(2,1^2)} c_{(2,1^2)})(a_{(1^4)} e_{(1^4)})(b_{(1^4)} f_{(1^4)})(c_{(1^4)} h_{(1^4)}),$$

$$(13) = (a_{(2^2)} b_{(2^2)}) (a_{(2,1^2)} b_{(2,1^2)})(a_{(1^4)} h_{(1^4)})(b_{(1^4)} c_{(1^4)})(e_{(1^4)} f_{(1^4)}),$$

$$(123) = (a_{(2^2)} b_{(2^2)} c_{(2^2)}) (a_{(2,1^2)} b_{(2,1^2)} c_{(2,1^2)})(a_{(1^4)} c_{(1^4)} f_{(1^4)})(b_{(1^4)} h_{(1^4)} e_{(1^4)}),$$

$$(124) = (a_{(2^2)} c_{(2^2)} b_{(2^2)}) (a_{(2,1^2)} c_{(2,1^2)} b_{(2,1^2)})(a_{(1^4)} f_{(1^4)} c_{(1^4)})(b_{(1^4)} e_{(1^4)} h_{(1^4)}).$$

This yields
Corollary 10.1.3. The diamers of ethene in the pairs \{a_{(2^2)}, b_{(2^2)}\}, \{a_{(2,1^2)}, b_{(2,1^2)}\}, \{a_{(1^4)}, h_{(1^4)}\}, \{b_{(1^4)}, c_{(1^4)}\}, \{e_{(1^4)}, f_{(1^4)}\} are indistinguishable via substitution reactions.

Proof: Proposition 10.1.2 implies that the permutation 

\[(13) = (a_{(2^2)}, b_{(2^2)})(a_{(2,1^2)}, b_{(2,1^2)})(a_{(1^4)}, h_{(1^4)})(b_{(1^4)}, c_{(1^4)})(e_{(1^4)}, f_{(1^4)})\]

is an element of the group \(\text{Aut}^T_0(T_4;G) \leq \text{Aut}^T_0(T_4;G)\), and, moreover, in agreement with the consideration in [7, VI] and in 6.4, the diamers in the above pairs are structurally identical.

The Abelian group \(X_G\) of one-dimensional characters of the group \(G\) consists of the unit character, and the characters \(\chi_1, \chi_2, \text{ and } \chi_3\), defined in 6.4. The normalizer \(N = S_4\) acts on \(X_G\) and the unit character is one of the orbits of this action. The other orbit is

\[\{\chi_1, \chi_2, \chi_3\},\]

because \((123)\chi_1 = \chi_2,\text{ and } (123)\chi_2 = \chi_3\).

On the other hand, the Abelian group \(X_{S_{(2^2)}}\) of one-dimensional characters of the group \(S_{(2^2)} = \langle (12), (34) \rangle\) has four elements: the unit character \(\theta_0\), and the characters \(\theta_1, \theta_2,\text{ and } \theta_3\), defined by the equalities

\[
\begin{align*}
\theta_1((12)) &= 1, \quad \theta_1((34)) = -1, \\
\theta_2((12)) &= -1, \quad \theta_2((34)) = 1, \\
\theta_3((12)) &= -1, \quad \theta_3((34)) = -1.
\end{align*}
\]

The propositions below, together with (10.1.3), confirms the conclusions in [7, VI], and in 6.4.

Proposition 10.1.4. The members of the diamicer pairs \{a_{(2^2)}, b_{(2^2)}\}, \{a_{(2,1^2)}, b_{(2,1^2)}\}, \{a_{(1^4)}, h_{(1^4)}\}, \{b_{(1^4)}, c_{(1^4)}\}, \{e_{(1^4)}, f_{(1^4)}\} cannot be distinguished via pairs of characters.

Proof: In compliance with 5.1 and 6.4, we obtain

\[
\begin{align*}
&a_{(2^2)} \notin T_{(2^2);\chi_{1},\theta_0}, \quad b_{(2^2)} \notin T_{(2^2);\chi_{1},\theta_0}, \quad a_{(2^2)} \in T_{(2^2);\chi_{2},\theta_0}, \quad b_{(2^2)} \notin T_{(2^2);\chi_{2},\theta_0}, \\
&a_{(2^2)} \notin T_{(2^2);\chi_{3},\theta_0}, \quad b_{(2^2)} \in T_{(2^2);\chi_{3},\theta_0}, \\
&a_{(2^2)} \in T_{(2^2);\chi_{1},\theta_1}, \quad b_{(2^2)} \in T_{(2^2);\chi_{1},\theta_1}, \quad a_{(2^2)} \notin T_{(2^2);\chi_{2},\theta_1}, \quad b_{(2^2)} \in T_{(2^2);\chi_{2},\theta_1}, \\
&a_{(2^2)} \in T_{(2^2);\chi_{3},\theta_1}, \quad b_{(2^2)} \notin T_{(2^2);\chi_{3},\theta_1}, \\
&a_{(2^2)} \in T_{(2^2);\chi_{1},\theta_2}, \quad b_{(2^2)} \in T_{(2^2);\chi_{1},\theta_2}, \quad a_{(2^2)} \notin T_{(2^2);\chi_{2},\theta_2}, \quad b_{(2^2)} \in T_{(2^2);\chi_{2},\theta_2}, \\
&a_{(2^2)} \in T_{(2^2);\chi_{3},\theta_2}, \quad b_{(2^2)} \notin T_{(2^2);\chi_{3},\theta_2}, \\
&a_{(2^2)} \notin T_{(2^2);\chi_{1},\theta_3}, \quad b_{(2^2)} \notin T_{(2^2);\chi_{1},\theta_3}, \quad a_{(2^2)} \in T_{(2^2);\chi_{2},\theta_3}, \quad b_{(2^2)} \notin T_{(2^2);\chi_{2},\theta_3}, \\
&a_{(2^2)} \notin T_{(2^2);\chi_{3},\theta_3}, \quad b_{(2^2)} \in T_{(2^2);\chi_{3},\theta_3}, \\
&\text{so we get the statement about the } (2^2)-\text{pair. The statements about the } (2,1^2)-\text{ and } (1^4)-\text{pairs are obvious because the stabilizers of any representatives of these } G\text{-orbits are trivial.} 
\end{align*}
\]
Corollary 10.1.5. The members of the diameric pairs \(\{a(2^2), b(2^2)\}, \{a(2,1^2), b(2,1^2)\}, \{a(1^4), h(1^4)\}, \{b(1^4), c(1^4)\}, \{e(1^4), f(1^4)\}\) cannot be distinguished via characters.

10.2. The group \(G\) of benzene \(C_6H_6\) is defined up to conjugation in [7, IV] (see also [2]) and has order 12. We know from the experiment that there are no chiral pairs among the products of benzene and this conclusion is confirmed by the Lunn-Senior’s model with the fact that there are no groups \(G'\) of order 24 that contain \(G\) (see [7, V]). Therefore \(G = G'\) and \(Aut'_0(T_{D,G}) = Aut_0(T_{D,G})\) for any \(D \subset P_6\). The classical Körner relations among the di- and tri-substitution homogeneous derivatives (see 7, I) yield immediately

Theorem 10.2.1. If \(D = \{(4, 2), (3^2)\}\), then the group \(Aut'_0(T_{D,G})\) is the unit group.

Corollary 10.2.2. The di-substituted (para, ortho, and meta), and tri-substituted (asymmetric, vicinal, and symmetric) derivatives of benzene are distinguishable via the Körner genetic relations.

Remark 10.2.3. In [5], it is shown that the same is true for any organic compound whose molecule can be divided into a skeleton and six univalent substituents, and such that it has one mono-substitution and at least three di-substitution homogeneous derivatives, and, moreover, has a group \(G\) of univalent substitution isomerism of order 12.

10.3. The groups \(G\) and \(G'\) of univalent substitution isomerism and stereoisomerism, respectively, of cyclopropane \(C_3H_6\) are found up to conjugation in [7, V], and in [4], and have orders 6 and 12, respectively. Moreover, the group \(G\) is dihedral. We set

\[
D = \{(6), (5,1), (4,2), (4,1^2), (3^2)\}.
\]

The possible substitution reactions among the products with empirical formula in \(D\) are represented in the tables below (see [5, Section 5] up to notation).

**Zooms of \(T_{D,G}\):**

\[
\begin{array}{cccc}
(6) & a(6) & \downarrow \\
(5,1) & a(5,1) & \\
(4,2) & a(4,2) & b(4,2) & c(4,2) & e(4,2)
\end{array}
\]

\[
\begin{array}{cccc}
(4,2) & a(4,2) & b(4,2) & c(4,2)
\end{array}
\]

\[
\begin{array}{cccc}
(3^2) & b(3^2) & c(3^2) & a(3^2)
\end{array}
\]

\[
\begin{array}{cccc}
(4,2) & e(4,2)
\end{array}
\]

\[
\begin{array}{cccc}
(3^2) & a(3^2) & b(3^2) & c(3^2)
\end{array}
\]

\[
\begin{array}{cccc}
(4,2) & a(4,2) & b(4,2) & c(4,2) & e(4,2)
\end{array}
\]

\[
\begin{array}{cccc}
(4,1^2) & a(4,1^2) & b(4,1^2) & c(4,1^2) & e(4,1^2)
\end{array}
\]
The $G'$-orbits are

\[
\begin{align*}
&a_{(4,2)} \cup b_{(4,2)}, \quad c_{(4,2)}, \quad e_{(4,2)}, \\
&a_{(3^2)} \cup b_{(3^2)}, \quad c_{(3^2)}, \quad e_{(3^2)}, \\
&a_{(4,1^2)} \cup b_{(4,1^2)}, \quad c_{(4,1^2)}, \quad e_{(4,1^2)} \cup f_{(4,1^2)}.
\end{align*}
\]

In particular, the pairs \{a_{(4,2)}, b_{(4,2)}\}, \{a_{(3^2)}, b_{(3^2)}\}, \{a_{(4,1^2)}, b_{(4,1^2)}\}, \{e_{(4,1^2)}, f_{(4,1^2)}\}, are chiral.

**Theorem 10.3.5.** (i) One has

\[
\text{Aut}_0(T_{D;G}) \simeq S_3 \times S_2,
\]

where the permutations of $S_3$ simultaneously move the elements $a$, $b$, $c$ with indices $(4, 2)$, $(3^2)$, and $(4, 1^2)$, and $S_2$ consists of all permutations of $e_{(4,1^2)}$, $f_{(4,1^2)}$;

(ii) one has

\[
\text{Aut}'_0(T_{D;G}) \simeq S_2 \times S_2,
\]

where the permutations of the first direct component $S_2$ simultaneously move the elements $a$, $b$ with indices $(4, 2)$, $(3^2)$, and $(4, 1^2)$, and the second direct component $S_2$ consists of all permutations of $e_{(4,1^2)}, f_{(4,1^2)}$.

**Proof:** Let $\alpha \in \text{Aut}_0(T_{D;G})$. In accordance with (10.3.1), $\alpha(a_{(6)}) = a_{(6)}$, $\alpha(a_{(5,1)}) = a_{(5,1)}$, and the diagrams (10.3.2) and (10.3.3) yield $\alpha(e_{(3^2)}) = e_{(3^2)}$ and $\alpha(e_{(4,2)}) = e_{(4,2)}$. The last equality together with (10.3.4) implies that the sets \{e_{(4,1^2)}, f_{(4,1^2)}\}, and \{a_{(4,1^2)}, b_{(4,1^2)}, c_{(4,1^2)}\} are $\alpha$-stable. Now, comparing (10.3.2) with (10.3.4), we get (i). Part (ii) can be obtained from (i) by taking into account that a chiral automorphism $\alpha \in \text{Aut}_0(T_{D;G})$ maps a chiral pair onto a chiral pair.

**Corollary 10.3.6.** The products that correspond to the different sets of structural formulae below are distinguishable via substitution reactions among the elements of $T_{D;G}$:

\[
\begin{align*}
\{a_{(4,2)}, b_{(4,2)}\}, \quad \{c_{(4,2)}\}, \quad \{e_{(4,2)}\}, \\
\{a_{(3^2)}, b_{(3^2)}\}, \quad \{c_{(3^2)}\}, \quad \{e_{(3^2)}\}, \\
\{a_{(4,1^2)}, b_{(4,1^2)}\} \{c_{(4,1^2)}\}, \quad \{e_{(4,1^2)}, f_{(4,1^2)}\}.
\end{align*}
\]

The products that correspond to the members of a particular set are indistinguishable via substitution reactions.

**Proof:** For the first statement, it is enough to note that all sets are $\text{Aut}_0'(T_{D;G})$-stable. Since all pairs are chiral, we get the second statement by using Theorem 8.2.6.

Theorem 2.1 and Section 5 from [5], and [4, 7.3.1] yield immediately

**Remark 10.3.7.** All statements in this Subsection are true for any organic compound whose molecule can be divided into a skeleton and six univalent substituents, and such that it has one mono-substitution and at least three di-substitution homogeneous derivatives, and, moreover, has a group $G \leq S_6$ of univalent substitution isomerism of order 6, that is dihedral.

**Remark 10.3.8.** The more precise definition of distinguishability of two compounds that includes chirality, Corollary 10.3.6, and Remark 10.3.7, specify the conclusions in [5, Section 5].
In [7, VII], the group $G''$ of structural isomerism of cyclopropane is described. In particular, the order of $G''$ is 48, and we have $G \leq G' \leq G''$. The $G''$-orbits in $T_D$ are

\[ a_{(6)}, \]
\[ a_{(5,1)}, \]
\[ a_{(4,2)} \cup b_{(4,2)} \cup c_{(4,2)}, \]
\[ a_{(3^2)} \cup b_{(3^2)}, \]
\[ a_{(4,1^2)} \cup b_{(4,1^2)} \cup e_{(4,1^2)} \cup f_{(4,1^2)}, \]

Therefore we obtain the next proposition which completes the description of the isomers of cyclopropane, considered in present Subsection.

**Proposition 10.3.9.** The products of cyclopropane that correspond to the structural formulae within any one of the sets
\[
\{a_{(6)}\},
\{a_{(5,1)}\},
\{a_{(4,2)}, b_{(4,2)}, c_{(4,2)}\},
\{a_{(3^2)}\},
\{a_{(4,1^2)}, b_{(4,1^2)}, e_{(4,1^2)}, f_{(4,1^2)}\},
\{c_{(4,1^2)}\}
\]

are structurally identical, and the products that correspond to members of different sets and have the same empirical formula, are structural isomers.

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