

# Criteria for a Structure to be Mesoionic

Georgii N. Sizov<sup>a,b</sup>, Eugene V. Babaev<sup>b,c,\*</sup>

<sup>a</sup>*Faculty of Materials Science, Lomonosov Moscow State University,  
Leninskie Gory 1, building 73, 119991 Moscow, Russia;*

<sup>b</sup>*Faculty of Chemistry, Lomonosov Moscow State University, 1, GSP-1,  
1-3 Leninskiye Gory, 119991 Moscow, Russia;*

<sup>c</sup>*Higher School of Economics, National Research University, 7 Vavilova  
Str., 117312 Moscow, Russia*

george.n.sizov@gmail.com, babaev@org.chem.msu.ru

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## Abstract

In the article, at the mathematical level of rigor, it is shown that the pair of concepts "covalence — mesoionicity" correlates in the same way as the pair "kekuleness — non-kekuleness". A criterion for a structure to be mesoionic (mesoionicity criterion) is formulated and proved, which makes it possible to enumerate all mono-charged mesoionic structures (mesomeric betaines) on a given graph. The mesoionicity criterion and the Kasteleyn theorem (on counting the number of perfect matchings in a graph) were used as the basis for a computer program that classifies dipolar resonance structures. The work of the program is demonstrated on the lists of obtained mesoionic structures. A general approach to mesoionicity is discussed.

## 1 Introduction

Currently, a large number of molecules are known to have structure that cannot be satisfactorily expressed using a single structural formula con-

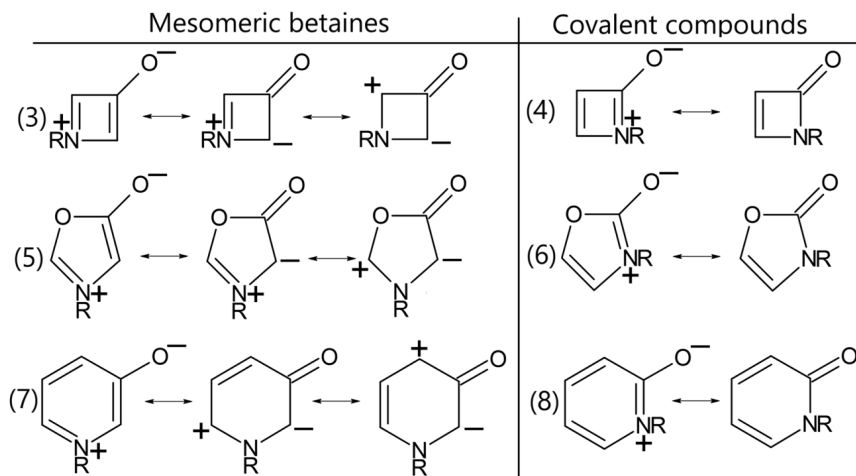
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\*Corresponding author.



theory presented will also be true for acyclic dipolar conjugated structures. Further in the text, the terms mesoionic compound and mesomeric betaine are synonymous.

Mesoionic compounds are not only widely used in organic synthesis, but also have a wide range of other applications. Thus, mesoionic compounds in the liquid state can be "distilled" analogs of ionic liquids, being super-polar media [5,6]. They also find application in catalysis [7] and are used as non-linear optical materials [8].



**Figure 2.** Comparison of mesomeric betaines (3), (5), (7) and heterocyclic compounds (4), (6), (8) having a covalent representation.

Katritzky and Balaban proposed [9] to divide mesoionic structures into two odd alternant fragments, one of which bears a delocalized positive charge, and another – a negative charge. Ramsden noted that the different mutual orientations of these odd chains can form the basis of a classification of alternant mesoionic compounds [10], which divides them into only five classes (using the formalism of connectivity matrices).

Our early work was devoted to the problems of chemical topology [11,12], application of graph theory to heterocyclic structures and reactions [13–15], and experimental aspects of heterocyclic synthesis [16,17].

In this article, we propose a novel approach to listing all (and not just

alternant) mesoionic structures. The theorems we have proved can be easily implemented in the form of a computer program, which makes it easy to enumerate all mesoionic structures with a given number of atoms.

## 2 Results and discussion

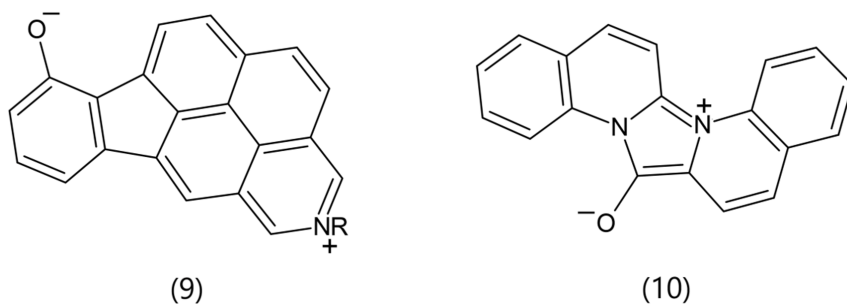
While constructing a general theory, we tried to answer the following questions:

(a) Let the structure be defined by the resonance dipolar formula. How to determine that the structure is covalent? In other words, is it possible to find a resonance structure equivalent to the original one, in which the positive and negative charges are compensated?

(b) Let a molecular graph be given, that is, a graph that can be realized as a structural  $\sigma$ -skeleton of an organic molecule. Is it possible (and if possible, then how) to place on it the signs of  $\pi$ -charges “+” and “-” along with double bonds so that the resulting structure is mesoionic?

The theorem that allows answering these questions is called the mesoionicity criterion.

To demonstrate that the problem is not evident, we invite the reader to determine, whether non-alternant structures (9) and (10) (Fig. 3) have a covalent representation.



**Figure 3.** Do these structures have a covalent representation?

A preliminary answer to problems (a) and (b) was given by Ramsden [17]. It has been pointed out that if a heterocyclic molecule with

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heteroatoms having two  $\pi$ -electrons ( $2\pi$ -heteroatom) contains (1) a non-Kekule hydrocarbon fragment or (2) two independent odd alternant fragments, then the molecule does not have a covalent representation. This statement requires detailed consideration, clarification, and formalization, which will be provided in subsequent sections. The entire previous theory of the structure of mesoionic compounds predominantly described only alternant structures. In our paper, we will discuss the most general arbitrary case.

The structure of this article is the following. Section 3 discusses a class of dipolar structures that is important for the formulation and application of the criterion –  $\pi$ -perfect structures, and also introduces a convenient WXYZ-notation. Section 4 formulates the mesoionicity criterion and demonstrates examples of its application. Section 5 is devoted to a rigorous proof of the mesoionicity criterion. Section 6 describes the connection between the results obtained and the well-known Kasteleyn theorem in statistical physics; also, Section 6 demonstrates a computer algorithm that implements the mesoionicity criterion. In Section 7, this computer algorithm was used to obtain a library of all mesoionic  $\pi$ -perfect structures containing a small number of non-hydrogen atoms (up to 7 atoms inclusive). Section 8 is devoted to a discussion of mesoionic compounds containing heteroatoms that participate in  $\pi$ -conjugation. Section 9 deals with the problem of poly-charged structures. In Section 10, we formulate a scientific program to use our results to build a complete list of all mesoionic compounds. A number of chemical limitations of the theory can be found in section 11. Conclusions are given in Section 12.

### 3 $\pi$ -Perfect structures

Careful consideration of a large array of mesoionic structures [3, 4] led us to the conclusion that the existence of a covalent resonance is determined not by the entire molecular structure, but only by a certain fragment of it. Indeed, it is obvious, for example, that hydrogen atoms in conjugated systems do not play any role in solving problems (a) and (b) from the pre-

vious section. The same can be said about atoms that do not participate in  $\pi$ -conjugation, since it is difficult to place a  $\pi$ -charge on such atoms using resonance formulas.

We propose to call the dipolar fragments that determine the mesoionicity to be  $\pi$ -*perfect*. The choice of the term  $\pi$ -perfect is due to the fact that the condition for the existence of such structures is expressed in the language of perfect matchings of graphs [18], as will be shown below.

An organic resonance structure is called  $\pi$ -perfect if each of its non-hydrogen atoms participates in the formation of one multiple bond and/or has a  $\pi$ -charge of any sign.  $\pi$ -Perfect structures usually contain only the following fragments (not necessarily all of them):

(i) Any number of pairs of atoms linked by a multiple bond (such as, for example,  $C = C$ ,  $C = N$ ,  $N = N$ , and their analogues) and attached to each other in an arbitrary manner.

(ii) The group  $C = X^+$  attached to the structure in an arbitrary way. Such groups can be, for example, the immonium cation  $R_2N^+ = CR_2$  (and its analogs) or the pyridinium cation (and its analogs).

(iii) Group  $C = Z^-$  attached to the structure in an arbitrary way. Such groups can be, for example, the anion  $R_2C = BR_2^-$  (and its analogs) or the anion of boron-substituted benzene (and its analogs).

(iv) Atoms and groups  $Y^-$  bearing a negative  $\pi$ -charge. The  $Y^-$  atom can be, for example, terminal atoms of oxygen, nitrogen, carbon, their analogues according to the periodic table, or divalent vicinal groups formed by the same atoms.

(v) Atoms and groups  $A^+$  bearing a positive  $\pi$ -charge. Such groups can be, for example, carbocation centers.

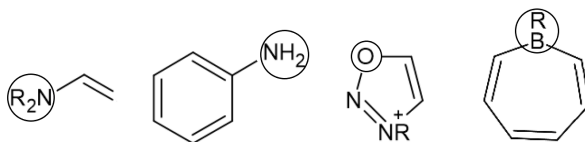
Aza-, phospho-, arsa-, or any other substitutions of carbon atoms in  $\pi$ -perfect structures do not affect the existence of a covalent representation of the dipolar structure, so structures with such substitutions will also be called  $\pi$ -perfect.

Examples of  $\pi$ -perfect structures are shown in Figs. 4. We note that these structures are not zwitter-ionic, which means that the concept of mesoionicity makes no sense for them.

(i): C=C	(i), (ii): C=C, C=X <sup>+</sup>	(i), (iii): C=C, C=Z <sup>-</sup>	(i), (iv): C=C, Y <sup>-</sup>	(i), (v): C=C, A <sup>+</sup>

**Figure 4.** Examples of  $\pi$ -perfect structures. The top line shows the conditions from the text that these structures satisfy. Note that any substitution of carbon atoms for other atoms does not affect the presence of the  $\pi$ -perfection property.

It is important to note that  $\pi$ -perfect structures can NOT contain heteroatoms that contribute two  $\pi$ -electrons or zero  $\pi$ -electrons, that is, atoms that do not participate in the formation of multiple bonds and do not have a  $\pi$ -charge in this dipolar resonance structure. (Below in Fig. 6, this criterion for the absence of the property of  $\pi$ -perfectness will be denoted by the sign (vi)). Let us agree that  $2\pi$ - and  $0\pi$ -heteroatoms in all further figures will be circled (Fig. 5).

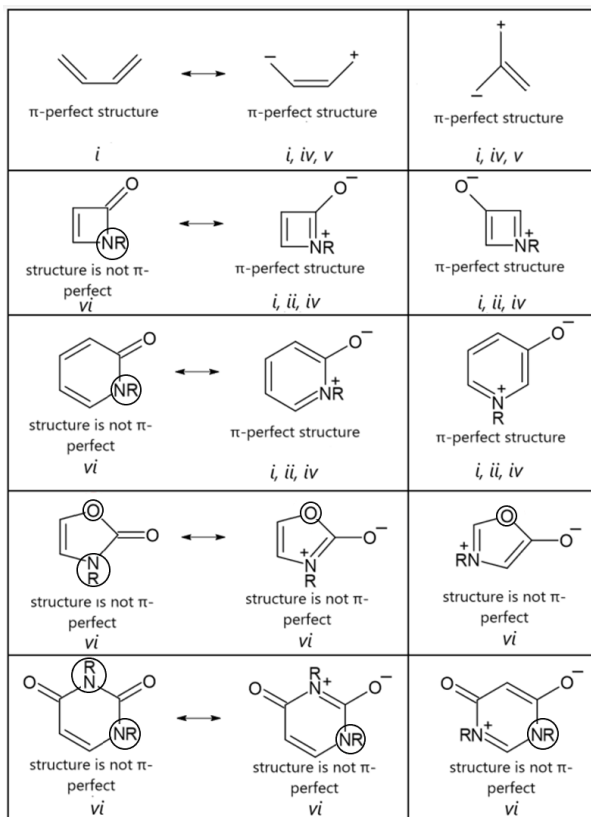


**Figure 5.** Examples of structures that are not  $\pi$ -perfect

An illustration of how the concept of  $\pi$ -perfection can correlate with the concept of mesoionicity is shown in Fig. 6. Note that often for the same molecule, one resonance structure is  $\pi$ -perfect, while the other is not. This is especially true for non-mesoionic structures with an odd number of atoms participating in the formation of a  $\pi$ -system: in such systems, the covalent resonance structure is often not  $\pi$ -perfect. In some molecules,  $\pi$ -perfect resonance structures may not exist at all, as for example, in the

five-membered cycles in Fig. 2, where all the resonance structures of the molecule (5) are not  $\pi$ -perfect, while the leftmost resonance of the molecule (7) is  $\pi$ -perfect, while the other two are not.

Further in the text of this section, all structures under consideration are  $\pi$ -perfect, as well as monocharged dipolar, that is, such structures contain exactly one negative and exactly one positive  $\pi$ -charge.



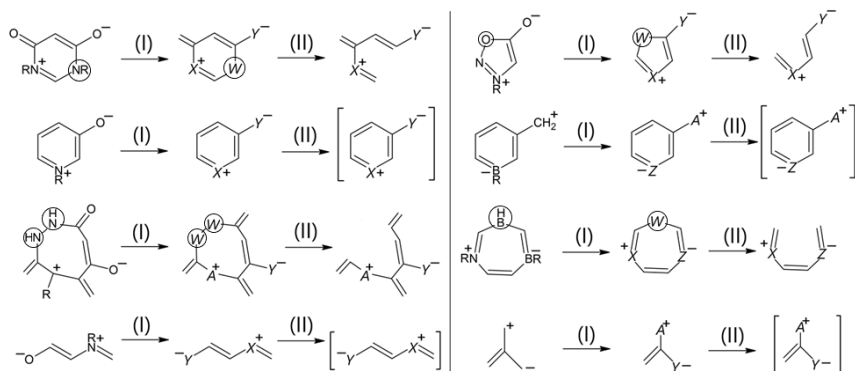
**Figure 6.** Comparison of mesoionic and covalent structures indicating that they have the property of  $\pi$ -perfection.

For further discussion, we need an advanced notation (WAXYZ-notation). Let us agree that in molecules it is possible to formally replace the  $NR^+$  group and its analogs ( $PR^+$ ,  $O^+$ ,  $S^+$ , etc.) by  $X^+$ . We replace the four-coordination boron and its analogues with  $Z^-$ . Atoms carrying a negative



$\pi$ -charge will be denoted, as before, by the symbol  $Y^-$ . Carbocationic centers (iv) will be denoted by the symbol  $A^+$ . Finally, the symbol W will denote neutral  $2\pi$ - and  $0\pi$ -heteroatoms that do not participate in the formation of a multiple bond. Thus, any studied structural formula can be redrawn using the WXYZ-notation (Fig. 7). Naturally, it is assumed that in the structure under consideration there are no non-hydrogen atoms that are not included in the  $\pi$ -conjugation chain. It is also necessary that all aza-, phospho- and other substitutions in dipolar structures must be replaced by carbon atoms.

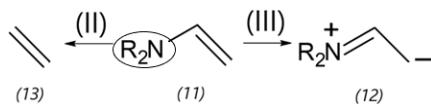
We will adhere to the following notation in the figures: (I) is the operation of transition from the structural formula to the formula in WXYZ-notation, (II) is the removal of the W heteroatom from a non- $\pi$ -perfect structure, (III) is the separation of positive and negative charges into different atoms, as will be described below.



**Figure 7.** (I) Using WXYZ-notation. (II) Selection of a  $\pi$ -perfect fragment in some graph. In square brackets it is indicated that under the action of operation (II) the structure does not change

Once again, we note that not all resonance structures of the same molecule containing a  $\pi$ -electronic structure are  $\pi$ -perfect. However, they all contain a  $\pi$ -perfect subgraph, or may be equivalent to a  $\pi$ -perfect resonance formula. For example, enamine (11) (Fig. 8) does not fall under the definition given above, but it can be converted into a  $\pi$ -perfect structure by charge delocalization (operation (III), structure (12)) or by formal

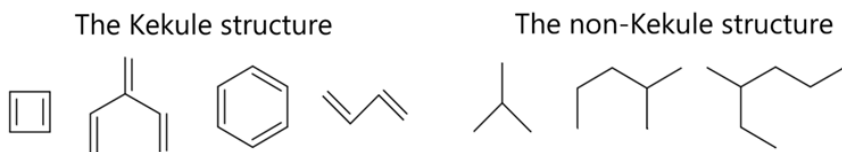
removal of the nitrogen atom (operation (II) ), structure (13)).



**Figure 8.** Two ways to isolate the  $\pi$ -perfect fragment: removal of the  $2\pi$ -heteroatom (II) or delocalization (III)

Therefore, there are two ways to search for a  $\pi$ -perfect fragment: delocalization and removal of  $2\pi$ -heteroatoms. Let us present a specific algorithm related to the removal of vertices. First of all, you need to redraw the given molecule, taking into account the WXYZ-notation. Next, remove all atoms of type W from the structure. The remaining subgraph will be the maximum  $\pi$ -perfect fragment in the molecule under study. Fig. 7 shows how to use this algorithm to extract  $\pi$ -perfect subgraphs in some structures.

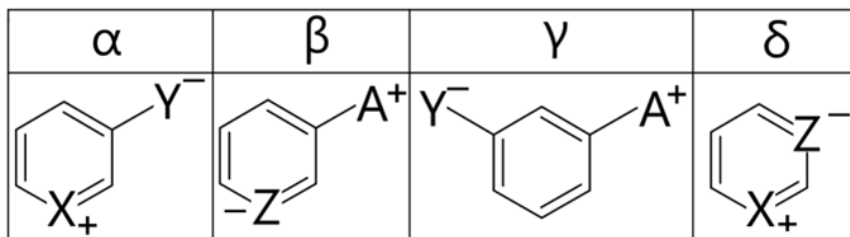
To proceed further, we need to remind the reader of a few terms from graph theory. A graph has a perfect matching [19] if there is a set of pairwise non-adjacent edges covering all the vertices of the graph. A molecular structure is called Kekule structure if it has a perfect matching, or in the language of chemistry, is covered by a system of double bonds. Otherwise, we can speak of a non-Kekule structure (Fig. 9).



**Figure 9.** Examples of Kekule and non-Kekule structures

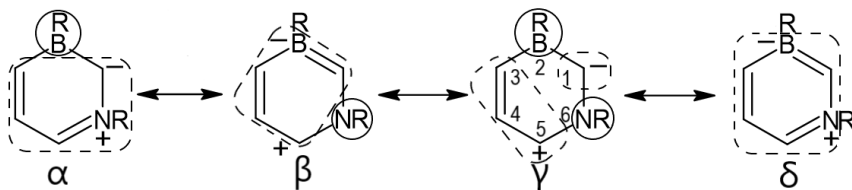
Let us divide all  $\pi$ -perfect zwitter-ionic structures into four classes (Fig. 10). Structures of the  $\alpha$  type have an odd number of non-hydrogen atoms and contain  $C = X^+$  and  $Y^-$  fragments. Structures of the  $\beta$  type have an odd number of non-hydrogen atoms and contain  $C = Z^-$  and  $A^+$  fragments. Structures of the  $\gamma$  type have an even number of non-hydrogen atoms and contain fragments  $A^+$  and  $Y^-$ . Structures of the  $\delta$  type have

an even number of non-hydrogen atoms and contain  $C = X^+$  and  $C = Z^-$  fragments.



**Figure 10.** Four types of dipolar  $\pi$ -perfect structures.

Note that different resonance structures of the same molecule (not necessarily  $\pi$ -perfect) often contain  $\pi$ -perfect substructures of different types (Fig. 11). Note that sometimes a  $\pi$ -perfect subgraph is not connected ( $\gamma$  in Fig. 11 contains two non-Kekule fragments: 1 and 3-5). In such cases, the entire theory presented is still applicable.



**Figure 11.** Various resonance structures of 1,3-azaborine containing  $\pi$ -perfect structures of various types. The  $\pi$ -perfect subgraphs are pointed by dashed lines for  $\alpha, \beta, \delta$ . For  $\gamma$  type  $\pi$ -perfect fragment contains disconnected sets of atoms 1 and 3,4,5. W-type heteroatoms are marked with a circle.

Note that in  $\pi$ -perfect  $\delta$ -type structures, every non-hydrogen atom participates in the formation of a double bond, or, as mathematicians say [18], the graph of a  $\pi$ -perfect  $\delta$ -type molecule has a perfect matching (is Kekule structure). In  $\pi$ -perfect structures of the  $\alpha$ -type, every non-hydrogen atom, with the exception of the  $Y^-$  atom, forms a double bond, which means that the entire structure without the  $Y^-$  atom has a perfect matching. Similar conditions can be formulated for structures of the  $\beta$  and  $\gamma$  types.

The conditions of the previous paragraph will be called necessary conditions for the existence of a  $\pi$ -perfect fragment. They can be generalized as the following obvious theorem:

**Theorem 1.** (*condition for the existence of a  $\pi$ -perfect structure*) *Let  $G$  be a  $\pi$ -perfect structure in WXYZ-notation. Then the removal of all  $A^+$  and  $Y^-$  type atoms from the  $G$  structure leads to a Kekule structure.*

These conditions are important if we want to draw a  $\pi$ -perfect fragment on a given arbitrary graph. The necessary condition for the existence of  $\pi$ -perfect structures will be used in a computer algorithm in the problem of enumeration of all mesoionic structures on a given graph in the following sections.

## 4 Mesoionicity criterion

In this section, the main theorems of the article will be formulated, and examples of their use for specific mesoionic structures will also be shown. The next section will be devoted to a rigorous justification.

Let  $G$  be a graph in WXYZ-notation. If now in this graph we replace all multiple bonds with single ones, and the WXYZ atoms with simple vertices (carbon atoms), then we get a new  $S_G$  graph.

A graph containing only carbon atoms and single bonds will be called simple. The graph  $S_G$  is obviously simple. So, we have the following consequence of graphs:

$M$  is structural formula  $\Rightarrow G$  is graph  $M$  in WXYZ-notation  $\Rightarrow S_G$  is a simple graph  $M$

Let us introduce the following notation: if  $S_G$  is a simple graph, and  $V$  is its vertex, then  $S_G - V$  is a graph in which the vertex  $V$  and all adjacent edges have been removed.

We can now rigorously formulate four theorems answering question (a) of Section 2 for structures containing  $\pi$ -perfect fragments of various types.

**Theorem 2 $\alpha$ .** *Let  $M$  be a molecular dipolar structure with a  $\pi$ -perfect fragment  $G$  of type  $\alpha$  ( $G$  contains atom types  $X^+$  and  $Y^-$ ), and  $S_G$  the simple graph corresponding to this fragment with a marked vertex  $V^*$  in place of the vertex  $X^+$  of the graph  $G$ . The structure  $M$  is mesoionic if and only if the graph  $S_G - V^*$  does not have a perfect matching.*

**Theorem 2 $\beta$ .** *Let  $M$  be a molecular dipolar structure having a  $\pi$ -perfect fragment  $G$  of type  $\beta$  ( $G$  contains atom types  $A^+$  and  $Z^-$ ), and  $S_G$  the simple graph corresponding to this fragment with a marked vertex  $V^*$  in place of the vertex  $Z^-$  of the graph  $G$ . The structure  $M$  is mesoionic if and only if the graph  $S_G - V^*$  does not have a perfect matching.*

**Theorem 2 $\gamma$ .** *Let  $M$  be a molecular dipolar structure with a  $\pi$ -perfect fragment  $G$  of type  $\gamma$  ( $G$  contains atom types  $A^+$  and  $Y^-$ ), and let  $S_G$  be the simple graph corresponding to this fragment. The structure  $M$  is mesoionic if and only if the graph  $S_G$  does not have a perfect matching.*

**Theorem 2 $\delta$ .** *Let  $M$  be a molecular dipolar structure with a  $\pi$ -perfect fragment  $G$  of type  $\delta$  ( $G$  contains atom types  $X^+$  and  $Z^-$ ), and  $S_G$  the simple graph corresponding to this fragment with marked vertex  $V_1^*$  in place of the vertex  $X^+$  and vertex  $V_2^*$  in place of the vertex  $Z^-$  of the graph  $G$ . The structure  $M$  is mesoionic then and only if the graph  $S_G - V_1^* - V_2^*$  does not have a perfect matching.*

The above theorems can be generalized by the following simple fact:

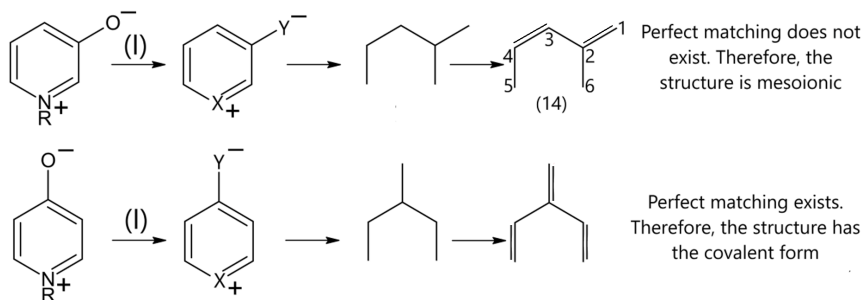
**Theorem 2** (mesoionicity criterion). *Let  $M$  be a molecular dipolar structure in WXYZ-notation.  $S$  is a simple graph corresponding to the molecular structure  $M$  from which all  $W$ ,  $X^+$  and  $Z^-$  type atoms (if any) have been removed. The structure  $M$  is mesoionic if and only if the graph  $S$  is non-Kekule.*

If the structure contains a small number of atoms, then the mesoionicity can be determined manually by drawing all the resonance structures. For more complex structures, the use of the mesoionicity criterion is preferable. So, you need to act according to the following algorithm:

1. The given structure  $M$  needs to be redrawn in WXYZ-notation.

2. Remove from the structure all atoms of type  $W$ ,  $Z^-$  and  $X^+$ .
3. Replace all remaining non-hydrogen atoms with carbon atoms and remove all multiple bonds.
4. On the resulting simple graph  $S$ , try to arrange a system of non-cumulated double bonds, in the formation of which each non-hydrogen atom participates. If this succeeds, then the original structure  $M$  has a covalent representation. If this cannot be done, then the initial structure is mesoionic.

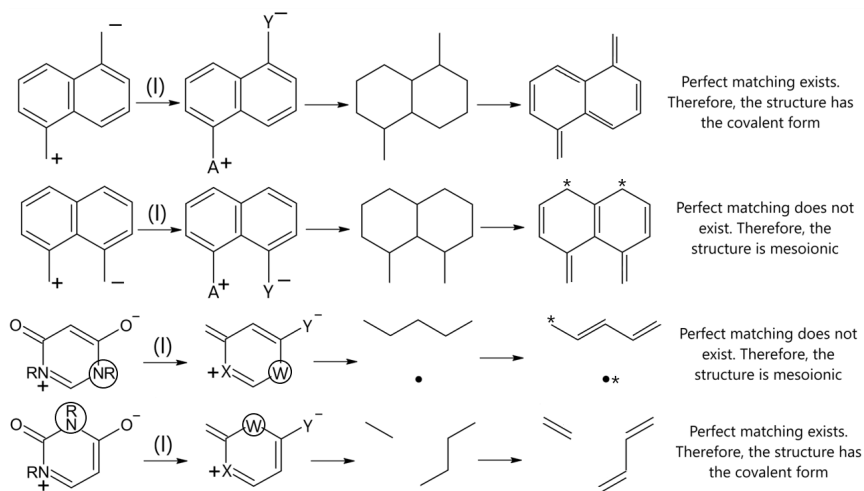
Let us consider examples of using the mesoionicity criterion. Fig. 12 shows a pair of dipolar structures – mesoionic 1-methyl-3-hydroxypyridinium olate and 1-methyl-4-hydroxypyridinium olate having a covalent representation. The simple graph  $S$  for 3-hydroxypyridinium does not have a perfect matching. This can be easily explained in the following way. Edge 1-2 is terminal, so if a matching exists, then it necessarily covers it. But in this case, there is only one way to cover vertex 3 with a double bond – edge 3-4. However, after this there is no way to draw a multiple bond between vertices 5 and 6. Therefore, the structure is mesoionic. In the case of 4-hydroxypyridine, when the  $X^+$  atom is removed in WXYZ-notation, we can easily draw a perfect matching, which indicates the covalence of this molecule.



**Figure 12.** An illustration of the applicability of the mesoionicity criterion to the dipolar structures of 3- and 4-hydroxypyridinium olates

More examples can be found in Figure 13. Note that despite the need to introduce the concept of  $\pi$ -perfectness in the general theory, we can

easily apply the mesoionicity criterion without referring to it. However, this  $\pi$ -perfectness will be important for theorem proving and computer enumeration of all mesoionic structures on a given graph.



**Figure 13.** An illustration of the applicability of the mesoionicity criterion for various dipolar structures.

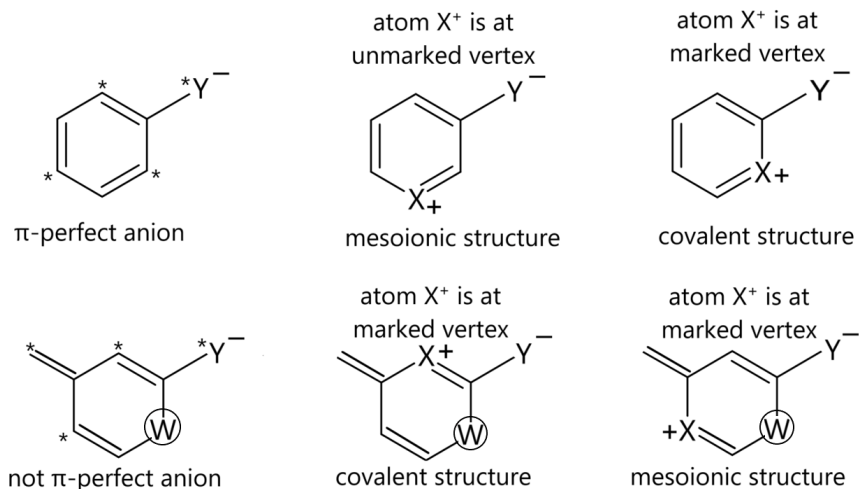
**Table 1.** A brief description of all mentioned types of atom removals

What type of atom/atoms is being removed?	For what purpose?
W atoms in structures that are not $\pi$ -perfect	To isolate a $\pi$ -perfect fragment
Atoms of types $A^+$ , $Y^-$ , $W$	To apply the necessary condition for the existence of a $\pi$ -perfect structure
Atoms of types $X^+$ , $Z^-$ , $W$	To apply the mesoionicity criterion

## 5 Proof of the mesoionicity criterion

Initially, we will prove Theorem  $2\alpha$ , the mesoionicity criterion for  $\pi$ -perfect structures of the  $\alpha$ -type, that is for structures with an odd number of non-hydrogen atoms containing only heteroatoms of the  $Y^-$  and  $X^+$  types. Note that  $\pi$ -perfect odd anions of this type were previously used by Ramsden [1] to answer questions (a) and (b) in the following way. Let  $G$  be a  $\pi$ -perfect alternant odd anion. Then, firstly, some of its atoms can be

marked with the symbol "\*" (star) so that any marked atom can be covalently bonded only with an unmarked one, and each unmarked one with a marked one (the property of alternance [1]). Second, the formal replacement of one carbon atom by  $X^+$  leads to a dipolar structure  $G_1$ , which is isoelectronic to the original structure  $G$ . Now let the  $Y^-$  atom be marked. If the  $X^+$  atom is located at a vertex that is not marked, then the  $G_1$  structure will necessarily be mesoionic, otherwise it is impossible to give an unambiguous answer (Fig. 15). This approach to the definition of mesoionicity is suitable for a very narrow class of conjugated alternant structures. Also, this method does not work for structures that are not  $\pi$ -perfect. Our approach to the consideration of the mesoionicity criterion is more general and is applicable to all structures, and not only to alternating ones.



**Figure 14.** An illustration of Ramsden's [1] approach to problems (a) and (b). Ramsden's approach to the alternant structures does not allow to consider the second non- $\pi$ -perfect anion due to the W-type atom. The answer to the question why these structures are mesoionic or covalent can be found in Fig. 2 and Fig. 13. See description in text.

Let us proceed to the proof of the mesoionicity criterion. This will require some preparatory definitions and lemmas.

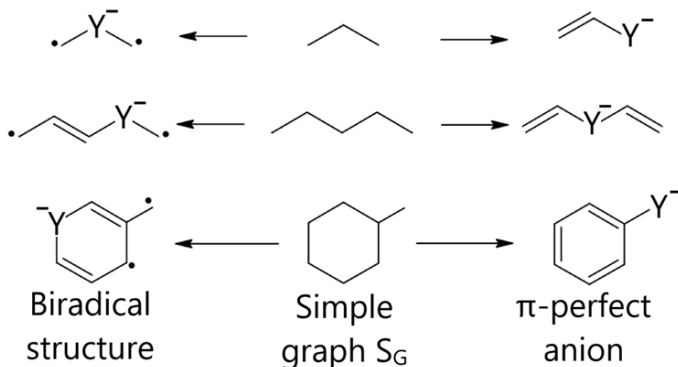
Assume that  $S_G$  is an odd simple graph. On this graph, you can introduce



the structure of a  $\pi$ -perfect odd anion in WXYZ-notation, that is, to place a negative charge  $Y^-$  on one of the atoms and cover the rest of the graph with a perfect matching. In other words, consider the first arrow in the following diagram:

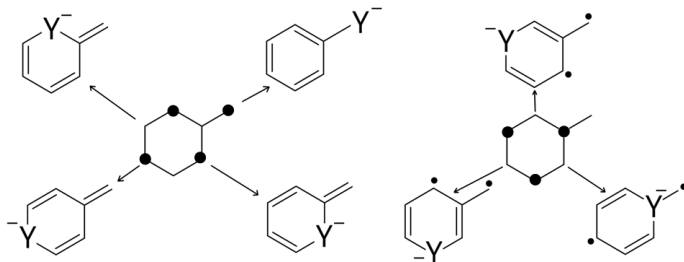
$S_G$  is simple graph  $M \Rightarrow G$  is graph  $M$  in WXYZ-notation  $\Rightarrow M$  is structural formula

If we take a simple graph  $S_G$  as a starting point for constructing a  $\pi$ -perfect anion, we can see the following. Placing  $\pi$ -electrons and a  $Y^-$  atom on a simple graph can lead to either a  $\pi$ -perfect or a biradical anion (Fig. 16). This fact, within the framework of the theory already developed above, is an illustration of the necessary condition for the existence of a  $\pi$ -perfect structure, since a  $\pi$ -perfect structure  $G$  exists only if the graph  $G - Y^-$  is Kekule.



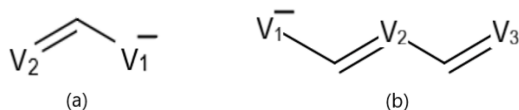
**Figure 15.** Placing  $\pi$ -electrons and  $Y^-$  on a simple graph results in either a  $\pi$ -perfect or biradical anion

Note that the possibility of passing from a simple graph to a  $\pi$ -perfect structure  $G$  (and not to a biradical) depends solely on the position of the  $Y^-$  atom. We say that an atom  $V$  in a simple graph  $S_G$  is allowed if there exists a  $\pi$ -perfect structure  $G$  in which a negative  $\pi$ -charge is concentrated on the atom  $V$ . Fig. 17 shows allowed and restricted positions for a given simple graph.



**Figure 16.** The scheme on the left – all possible ways to go from a given simple graph to a  $\pi$ -perfect anion, on the right – to a biradical structure. Atoms that are allowed for a negative charge are marked by circle solid in the left, those that are not allowed are marked in the right.

If, in two resonance structures defined on the same simple graph, negative  $\pi$ -charges can be localized on the allowed atoms  $V_1$  and  $V_2$  separated by a third atom, as shown in Figure 18a, then we shall say that the allowed atoms  $V_1$  and  $V_2$  are conjugated. Further, we can say that if the  $V_1$  atom is conjugated with the  $V_2$  atom, and the  $V_2$  atom is conjugated with the  $V_3$  atom, then the  $V_1$  atom is also conjugated with  $V_3$  (Fig. 18b). As a result, long chains of conjugated atoms can be considered.



**Figure 17.** (a)  $V_1$  and  $V_2$  atoms are conjugated, (b)  $V_1$ ,  $V_2$ ,  $V_3$  atoms are conjugated

**Lemma 1** (the connectivity of conjugated atoms). *Let  $V_1$  and  $V_2$  be allowed positions for a negative charge in an odd connected  $\pi$ -perfect structure, then  $V_1$  and  $V_2$  are conjugated.*

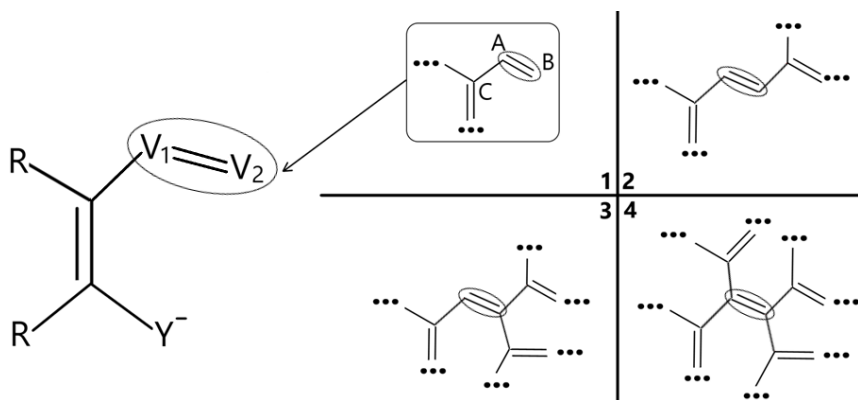
*Proof of the Lemma.* We will carry out the proof by induction of the number of atoms in the structure.

For a structure with 1 atom, the lemma is obviously true.

Let now we have a structure with  $2k+1$  atoms and the property being proved is true for it. Let us now prove that the structure with  $2k+3$  atoms will also obey the required property.

In a generic simple graph  $S_G$  with  $2k+3$  atoms, select an edge  $E$  consisting of atoms  $V_1$  and  $V_2$  and the remaining subgraph  $S'_G$  with  $2k+1$  atoms. In Fig. 19 one can see different ways of attaching  $E$  to  $S'_G$ . Cases 1 – 4 in Fig. 19 differ in the number of covalent bonds by which the edge  $E$  is connected to the subgraph  $S'_G$ . Note that additions of  $E$  are also possible not to vicinal atoms  $S''_G$ , but to terminal ones, therefore, generally speaking, the number of different ways of joining  $E$  and  $S'_G$  is quite large. However, in each particular case, the proof of the inductive step is very simple. We present the argument only for case 1 in Fig. 19. The remaining combinations are left to the reader as an easy exercise.

So, we need to prove that if the atoms  $V_1$  and/or  $V_2$  are allowed, then they will be conjugated with other allowed atoms. In case 1, the atom  $V_1$  cannot be allowed: if a negative charge is localized on it, then  $V_2$  cannot be covered with a double bond. For atom  $V_2$ , there are two options. First, the atom  $V_2$  may not be allowed, and then there is nothing to prove, since all allowed atoms are in  $S'_G$ , where the conditions of the lemma are satisfied. Second, the  $V_2$  atom can be allowed. In this case,  $V_2$  is conjugated with  $C$  (fig.19.1), which in this case is allowed, and hence the requirements of the lemma are satisfied. ■



**Figure 18.** Illustration for the proof of the lemma

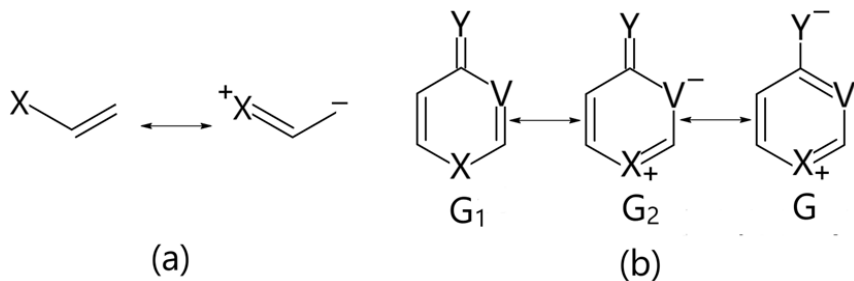
Now we can proceed to the proof of the main theorem.

**Theorem 2 $\alpha$ .** *Let  $M$  be a molecular dipolar structure with an odd  $\pi$ -perfect fragment  $G$  of type  $\alpha$ , and let  $S_G$  be the simple graph corresponding to this fragment with a marked vertex  $V^*$  in place of the vertex  $X^+$  of the graph  $G$ . The structure  $M$  is mesoionic if and only if the graph  $S_G-V^*$  does not have a perfect matching.*

*Proof of the theorem 2.* Recall that in the WXYZ-notation, any odd  $\pi$ -perfect structure of type  $\alpha$  is composed of an atom  $Y^-$ , a group  $C = X^+$ , and also any number of non-cumulated  $C = C$  double bonds connected to each other in an arbitrary way. Let's go directly from the molecular structure  $M$  to the  $\pi$ -perfect fragment  $G$  in WXYZ-notation.

Let  $M$  be non-mesoionic, then we can draw a covalent resonance structure by moving the negative charge from the  $Y^-$  atom to the  $X^+$  atom ( $X$  and  $Y$  are conjugated), as this was exactly shown in Figure 2. Note that in odd  $\pi$ -perfect structures of type  $\alpha$ , for the mesoionicity property only resonance structures turn out to be conjugated, as shown in Fig. 20a. Such conjugations do not change the number of double bonds in the structure, which means that in the covalent resonance structure, all atoms except  $X$  will be bound by double bonds. This exactly corresponds to the proven Kekule property of  $S_G-V^*$ .

Let  $S_G-V^*$  be Kekule structure (explanatory figure – 20b), that is, it has a perfect matching. Let's depict it on a simple graph  $S_G$  by drawing a covalent resonance structure  $G_1$ . Now it remains to prove that this resonance structure is equivalent to the original structure  $G$ . To do this, using operation (III), we delocalize the positive and negative charges on the  $X$  atom and the  $V$  carbon atom adjacent to it, as shown in Fig. 20b. As a result, we obtain a dipolar  $\pi$ -perfect resonance structure  $G_2$ . In this structure, the  $V$  atom is allowed for a negative charge, just like the  $Y$  atom. Then, according to the proved lemma, the  $V$  and  $Y$  atoms are conjugated, therefore, there is a set of resonance structures that shift the negative charge from  $V$  to  $Y$ . Structure  $G_2$  is equivalent to both the original  $G$  and the covalent  $G_1$ . Hence  $G$  is non-mesoionic.

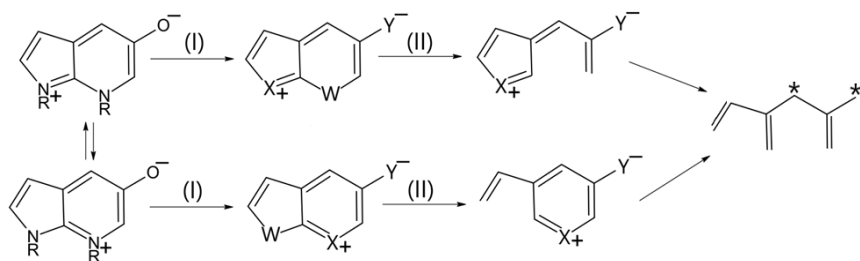


**Figure 19.** Resonance structures mentioned in the text

Essentially, there are two things to prove. First, the presence of W-type heteroatoms does not affect the mesoionicity of a  $\pi$ -perfect fragment of a given type  $\alpha$ . The point is that the presence of two or more W-type heteroatoms in a  $\pi$ -perfect fragment of the  $\alpha$  type can lead to equivalence of resonance structures with different  $\pi$ -perfect fragments (Fig. 21). However, this does not change the essence of the theorem being proved, since the removal of both heteroatoms of type W and the current atom  $X^+$  leads to the same simple graph  $S_G$ .

Second, some resonance structures may have a different type of  $\pi$ -perfect fragment ( $\beta$ ,  $\gamma$ ,  $\delta$  types). Structures of type  $\alpha$  can be easily transformed into structures of type  $\gamma$  (as shown in Fig. 11). In this case, it is obvious that the mesoionicity of a structure of one type is equivalent to the mesoionicity of a structure of another type. ■

The proof of Theorems  $2\beta - 2\delta$  is trivial, because of the possibility of passing from a  $\pi$ -perfect fragment of type  $\alpha$  to the others, as was indicated in Section 3 (Fig. 11). For these theorems, it suffices to pass to a perfect fragment of type  $\alpha$  and refer to Theorem 2.

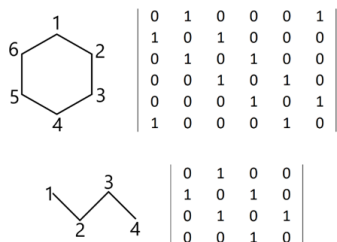


**Figure 20.** An example of different ways to choose a  $\pi$ -perfect fragment in a molecule. Despite this, all procedures for removing atoms lead to the analysis of the Kekule property of the same graph.

## 6 Kasteleyn's theorem and mesoionicity

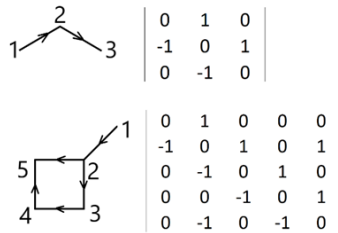
The criteria formulated and proven above can be easily implemented in the form of a computer program, if we see its connection with the Kasteleyn theory. The problem of calculating the number of perfect matchings was solved by Fischer, Kasteleyn and Temperley [19, 20]. They proposed an algorithm that is now known as the FKT algorithm. In this section, we will briefly outline how this algorithm can be easily applied to design all mesoionic molecules on a given graph.

Let  $G$  be a molecular graph with  $N$  vertices. We number its vertices with numbers from 1 to  $N$  arbitrarily. Then the undirected adjacency matrix is the square matrix  $N \times N$   $A_{ij}$ ;  $A_{ii} = 0$  for all  $i$ , and  $A_{ij} = 1$  if vertices  $i$  and  $j$  are connected by an edge, otherwise  $A_{ij} = 0$ . Examples of such matrices are shown in Fig. 22.



**Figure 21.** Examples of undirected adjacency matrices

The next mathematical object is the orientation on the graph. Orientation on the graph – the choice of direction on each edge. A directed graph can be assigned a directed adjacency matrix. This is an antisymmetric matrix  $N \times N$   $B_{ij}$ ;  $B_{ii} = 0$  for all  $i$ ,  $B_{ij} = 1$  if edge  $ij$  is oriented from  $i$  to  $j$ , and  $B_{ij} = -1$  if edge  $ij$  is directed from  $j$  to  $i$ . In all other cases  $B_{ij} = 0$ . Examples of directed graphs and adjacency matrices are shown in Figure 23. We will henceforth denote the directed matrix of a directed graph  $G$  as  $B(G)$ .



**Figure 22.** Examples of oriented graphs and oriented adjacency matrices

**Theorem 3** (Kasteleyn [19]). *Let  $G$  be a planar graph and  $M$  the number of perfect matchings on this graph. Then there is an orientation such that  $\det B = M^2$*

An example of using the theorem is shown in Figure 24. We will omit all the details associated with Pfaffians and Hafnians, which are usually inherent in this theory, since they are not essential in what follows.

$$\det \begin{vmatrix} 0 & 1 & 0 & 1 \\ -1 & 0 & 1 & 0 \\ 0 & -1 & 0 & 1 \\ -1 & 0 & -1 & 0 \end{vmatrix} = 4 = 2^2$$

**Figure 23.** An example of using Kasteleyn's theorem

Using the Kasteleyn theorem, one can reformulate the mesoionicity criterion (Theorem 2).

**Theorem 4** (algebraic representation of the mesoionicity criterion for odd structures). *Let  $G$  be a dipolar structure in WXYZ-notation.  $G_1$  is the structure  $G$  from which atoms of types  $A^+$ ,  $Y^-$ ,  $W$  have been removed.  $G_2$  is the structure  $G$  from which atoms of types  $Z^-$ ,  $X^+$ ,  $W$  have been removed. Then*

1. *The graph  $G_1$  has at least one edge orientation such that  $\det A(G_1) \neq 0$ . (a necessary condition for the existence of a  $\pi$ -perfect anion).*
2. *The structure  $G_2$  is mesoionic if and only if, for all orientations of the graph  $G_2$  it is true that  $\det A(G_2) = 0$*

The use of these theorems opens wide possibilities for computer enumeration of all possible mesoionic compounds on a given simple graph. We have written several programs for verifying the obtained assertions.

First of all, we are interested in the complete list of all  $\pi$ -perfect structures of types  $\alpha$  and  $\gamma$ .

The program algorithm was as follows:

Algorithm 1.

1. Input of an undirected adjacency matrix for a given simple graph  $S_G$
2. Generation of an directed adjacency matrix for the graph  $G$ . The required orientation is selected manually. The orientation of the graph can, generally speaking, not be set manually by writing a standard procedure in many programming languages – a FOR loop that goes through all possible orientations.

Determining the parity of the number of vertices of a graph  $G$ :

- 3.1. If the number of vertices is odd ( $\alpha$ -type), then the search and output of all mesoionic positions using Theorem 2 $\alpha$  by enumeration of all possible pairs of vertices for  $X^+$  and  $Y^-$  atoms.
- 3.2. If the number of vertices is odd ( $\gamma$ -type), then the search and output of all mesoionic positions using Theorem 2 $\gamma$  by enumeration of all possible pairs of vertices for atoms  $A^+$  and  $Y^-$ .

The program that executes this algorithm has been systematically tested on simple graphs containing from 5 to 7 atoms. In all cases, the result of the program's operation coincides with that of the "manual" check. A list



of all mesoionic structures on these graphs can be found in Section 7.

## 7 Library of all $\pi$ -perfect mesoionic structures for small graphs

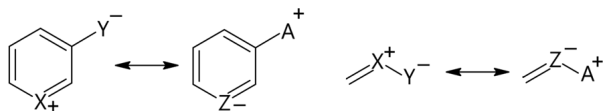
In this section, we invite the reader to get acquainted with the table of all  $\pi$ -perfect mesoionic graphs of types  $\alpha$ - $\delta$ , containing no more than 7 atoms. Tables 2,3,4 are filled with structures of types  $\alpha$ ,  $\gamma$ ,  $\delta$ , as follows. Next to each graph are numbers corresponding to the positions of the positively charged  $X^+$  group and the negatively charged  $Y^-$  group. The reader must place these atoms on the vertices of the corresponding numbers and place the system of conjugated double bonds on a subgraph containing all vertices except  $Y^-$  (example in Fig. 25). The third column of the table corresponds to the number of prototypes of mesoionic structures on a given graph (the number of nonequivalent prototypes is indicated in brackets, taking into account the symmetry of the graph).

		The number of $\pi$ -perfect structures without symmetry (with symmetry)
	$X^+ : 1, 2, 3$ <hr/> $Y^- : 4, 5$	<div style="border: 1px solid black; border-radius: 10px; padding: 5px; display: inline-block;">6 (3)</div>
 $X^+ : 1$ $Y^-$ $Y^- : 4 \text{ or } 5$	 $X^+ : 2$ $Y^-$ $Y^- : 4 \text{ or } 5$	 $X^+ : 3$ $Y^-$ $Y^- : 4 \text{ or } 5$

**Figure 24.** How to use the table with all mesoionic  $\pi$ -perfect structures

Note that structures of type  $\alpha$  and  $\beta$  are dual (Fig. 26). Therefore, the

table of all  $\pi$ -perfect structures of type  $\beta$  completely coincides with Table 2 up to the replacement of the atom  $Y^-$  by  $A^+$  and  $X^+$  by  $Z^-$ .



**Figure 25.** Examples expressing the duality of dipolar  $\pi$ -perfect structures of  $\alpha$  and  $\beta$  types

**Figure 26.** Table 2. List of all  $\pi$ -perfect structures of  $\alpha$ -type. (See Fig. 25 for how to use the table)

Structures containing three atoms					
	X+: 2 Y-: 1, 3	2 (1)			
Structures containing five atoms					
	X+: 2, 4 Y-: 1, 3, 5	6 (3)		X+: 1, 2, 3 Y-: 4, 5	6 (3)
	X+: 2 Y-: 1, 3, 4, 5	4 (3)		X+: 2, 4 Y-: 1, 3, 5	6 (3)
	X+: 2, 4 Y-: 1, 3, 5	6 (4)		X+: Y-:	0 (0)
Structures containing seven atoms					
	X+: 2, 4, 6 Y-: 1, 3, 5, 7	12 (6)		X+: 1, 2, 3, 4, 5 Y-: 6, 7	10 (5)
	X+: 2, 4, 5, 6 Y-: 1, 3, 7	12 (12)		X+: 1, 2, 3, 4, 7 Y-: 5, 6	10 (5)
	X+: Y-:	0 (0)		X+: 2, 4, 6 Y-: 1, 3, 5, 7	12 (6)
	X+: 4, 6 Y-: 1, 2, 3, 5, 7	10 (8)		X+: 5, 6, 7 Y-: 1, 2, 3, 4	12 (9)
	X+: 4, 6 Y-: 1, 2, 3, 5, 7	10 (8)		X+: 5, 6, 7 Y-: 1, 2, 3, 4	12 (9)
	X+: 1, 2, 3, 4, 5 Y-: 6, 7	10 (4)		X+: 2, 3, 5 Y-: 1, 4, 6, 7	12 (12)

**Figure 27.** Table 2 (continued). The end of the list of all  $\pi$ -perfect structures of  $\alpha$ -type. (See Fig. 25 for how to use the table).

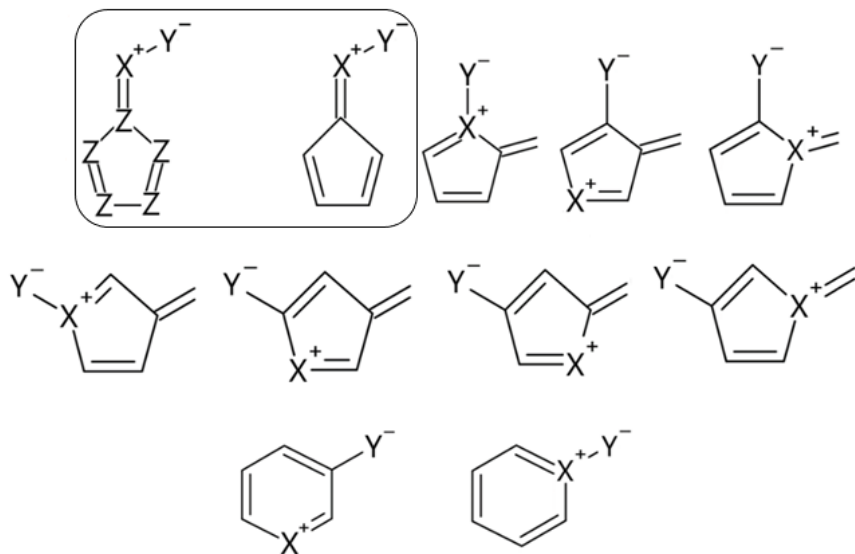
	X+:1, 2, 3, 4, 7	10 (5)		X+:4, 6	10 (5)
	Y-:5, 6			Y-:1, 2, 3, 5, 7	
	X+:2, 3, 5	12 (7)		X+:2, 4, 6	12 (9)
	Y-:1, 4, 6, 7			Y-:1, 3, 5, 7	
	X+:1, 2, 3, 4, 5	10 (4)		X+:2, 4, 6	12 (12)
	Y-:6, 7			Y-:1, 3, 5, 7	
	X+:2, 4, 5, 6	12 (8)		X+:2, 3, 4, 6	12 (7)
	Y-:1, 3, 7			Y-:1, 5, 7	
	X+:2	6 (4)		X+:2, 4, 6	12 (8)
	Y-:1, 3, 4, 5, 6, 7			Y-:1, 3, 5, 7	
	X+:2, 3, 4, 5	12 (6)		X+:2, 4, 6	12 (9)
	Y-:1, 6, 7			Y-:1, 3, 5, 7	
	X+:	0 (0)		X+:	
	Y-:			Y-:	

**Figure 28.** Table 3. List of all  $\pi$ -perfect structures of  $\gamma$ -type. (See Fig. 25 for how to use the table)

Structures containing four atoms					
	A+:	0 (0)		A+:1,3,4	6(1)
	Y-:			Y-:1,3,4	
	A+:	0 (0)			
	Y-:				
Structures containing six atoms					
	A+:	0 (0)		A+:1, 3, 5, 6	12 (7)
	Y-:			Y-: 1, 3, 5, 6	
	A+:	0(0)		A+: 1, 3	4 (2)
	Y-:			Y-: 4, 6	
	A+:	0(0)		A+:	0(0)
	Y-:			Y-:	
	A+:	0(0)		A+:	0(0)
	Y-:			Y-:	
	A+:	0(0)		A+:	0(0)
	Y-:			Y-:	
	A+:	0(0)		A+:	
	Y-:			Y-:	
	A+:	0(0)		A+:	
	Y-:			Y-:	

**Figure 29.** Table 4. List of all  $\pi$ -perfect structures of  $\delta$ -type. Pairs  $(X^+, Z^-)$  mean the positions of atoms  $X^+$  and  $Z^-$  that give mesoionic prototypes

Structures containing four atoms					
	$(X^+, Z^-): (3,1), (3,2), (4,2)$	3		$(X^+, Z^-):$ impossible	0
	$(X^+, Z^-): (1,3)$	1			
Structures containing six atoms					
	$(X^+, Z^-): (3,1), (5,1), (3,2), (4,2), (5,2), (6,2), (1,3), (2,3), (5,3)$	9		$(X^+, Z^-):$ impossible	0
	$(X^+, Z^-): (3,1), (4,1), (5,1), (3,2), (4,2), (5,2), (6,2), (1,3), (2,3), (2,3), (2,6)$	10		$(X^+, Z^-):$ impossible	0
	$(X^+, Z^-): (1,3), (3,1), (2,3)$	3		$(X^+, Z^-): (3,1), (5,1), (3,2), (4,2), (5,2), (6,2), (1,3), (2,3), (5,3), (2,4), (5,4), (1,5), (2,5), (3,5), (4,5), (2,6)$	16
	$(X^+, Z^-): (3,1), (3,2), (4,2), (5,2), (1,3), (2,3), (2,4), (5,4), (2,5), (4,5)$	10		$(X^+, Z^-): (3,1), (5,1), (3,2), (4,2), (5,2), (6,2), (1,3), (2,3), (5,3)$	9
	$(X^+, Z^-): (3,1), (5,1), (3,2), (4,2), (5,2), (1,3), (2,3), (5,3), (2,4), (6,4), (1,5), (2,5), (3,5)$	13		$(X^+, Z^-): (3,2), (4,2), (2,3), (5,3), (2,4), (5,4), (5,4), (6,4)$	7
	$(X^+, Z^-): (1,3)$	1			



**Figure 30.** List of all  $\pi$ -perfect structures in WXYZ notation containing seven non-hydrogen atoms and including a five- or six-membered ring. Substitution of carbon atoms by any suitable heteroatom is possible (example in box).

## 8 Mesoionic compounds containing W-heteroatoms. Five-membered rings with one substituent.

The theory of the previous sections was based mainly on the consideration of  $\pi$ -perfect structures. However, a significant number of known mesoionic compounds cannot be considered as  $\pi$ -perfect structures. In particular, the widely studied sydnons and munchnons in WXYZ-notation have one  $2\pi$ -heteroatom W. In this section, we will discuss algorithms that make it possible to apply the theory developed above to structures containing W-heteroatoms. A library of all (not only  $\pi$ -perfect) mesoionic structures of  $\alpha$  and  $\gamma$  types for a five-membered cycle with one substituent will also be built. Essentially, we are again talking about tasks (a) and (b) from section 2:

Task (a): let a dipolar resonance structure be given (with any number of W atoms). It is necessary to determine whether it is mesoionic.

Task (b): list all mesoionic structures (also with any number of W atoms) on a given simple graph. We can also talk about two different approaches to solving these problems:

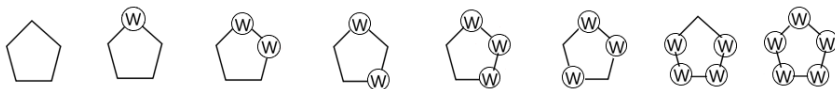
Approach 1: Find a pen-and-paper way to solve the problem using the mesoionicity criteria from Section 4

Approach 2: Implement computer algorithm based on the Kasteleyn theory and mesoionicity criteria from section 6.

Both approaches, as shown in Section 6, are synonymous.

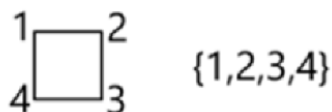
Let us discuss here how we can approach the solution of problem (b) using both approaches.

First, note that in mesoionic structures, all atoms involved in the formation of  $\pi$ -orbitals either belong to a  $\pi$ -perfect fragment or are W-type atoms. It is reasonable to divide all mesoionic structures according to the number and location of W-type atoms. For example, Fig. 31 shows all possible ways to arrange an arbitrary number of W atoms in a pentagonal structure.



**Figure 31.** All ways to arrange an arbitrary number of W atoms in a pentagonal structure.

Next, you need to be able to find all possible ways to fill a given graph with W atoms. This procedure is equivalent to the standard combinatorial procedure for writing out all possible enumerations [18] for a given set. An enumeration is an ordered set of elements of a given set without repetition. For example, enumerations for the set of digits 1, 2, 3, 4 are shown in Fig. 33.



Enumeration		w atoms type position		mesonic prototype	examples of non-mesoionic prototype
$\emptyset$					
{1}	{2}				
{4}	{3}				
{1,2}	{2,3}				
{1,4}	{3,4}				
{1,3}	{2,4}				
{2,3,4}	{1,3,4}				
{1,2,3}	{1,2,4}				
{1234}					

**Figure 32.** Enumerations of a four-element set and the corresponding ways to arrange atoms of type W on a four-membered cycle.

The reader may notice that the structures and enumerations in Fig. 33 are grouped according to the symmetry of the W-containing structures. A significant drawback of the presented approach is its inability to distinguish symmetrically equivalent structures. This must be done manually or involve third-party algorithms.

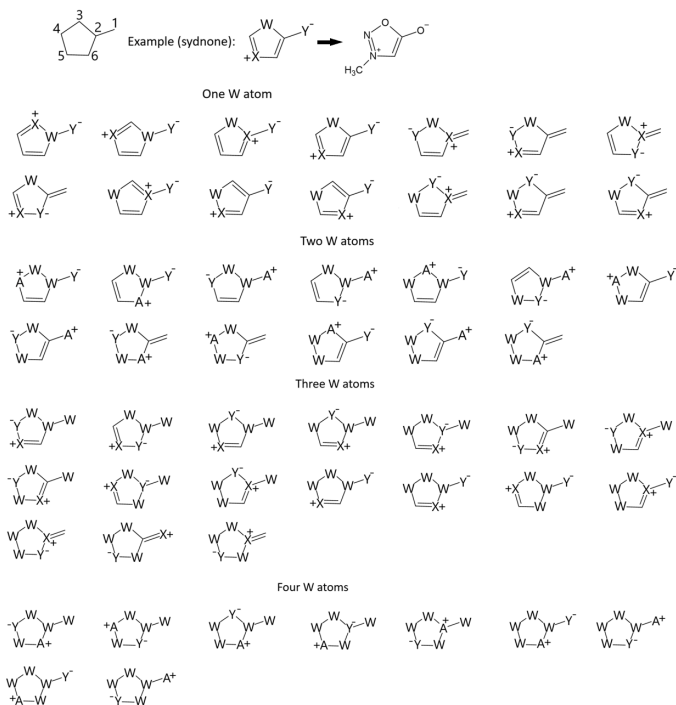
Thus, we have a simple graph with numbered vertices, then we can enumerate all possible positions for W atoms. After that, Algorithm 1 can be easily applied to the remaining subgraphs, which are  $\pi$ -perfect, to search for all mesoionic structures. Thus, we get



## Algorithm 2

1. The vertices of a given simple graph are numbered.
2. Write out all enumerations of graph atoms containing any number of atoms
3. For each enumeration, a  $\pi$ -perfect fragment is found.
4. Algorithm 1 is applied to  $\pi$ -perfect fragments.

The complete set of all mesoionic structures of  $\alpha$  and  $\beta$  types (in WXYZ-notation) on a five-membered ring with one substituent, obtained using Algorithm 2, is presented below. Among the structures, let us pay special attention to the already known syndons and munchnons. Therefore, we can state that our approach is verified by the fact that it reproduces already widely known structures.

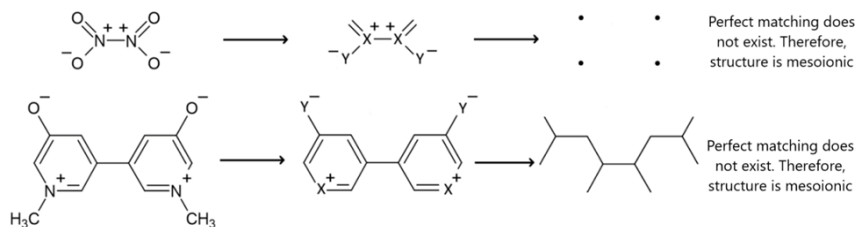


**Figure 33.** Library of all mesoionic structures on a five-membered cycle with one substituent.

## 9 Poly-charged mesoionic structures

There are poly-charged mesoionic compounds. The simplest example is the  $N_2O_4$  molecule (Fig. 35). More complex examples can be imagined (see also second structure on Fig. 35).

In this case, we can formulate similar theorems regarding their mesoionicity. We will further consider structures that do not have atoms of type  $A^+$  in the WXYZ-notation (the consideration of the case with atoms of type  $A^+$  is similar). First of all, we note that if a bis-dipolar resonance structure has a covalent representation, then we can say that its subfragment, which does not contain atoms of the  $X$  type, is Kekule. atoms of type  $X$  will necessarily be non-Kekule (Fig. 36).



**Figure 34.** Examples of bis-mesoionic structures and application of the mesoionicity criterion to them.

Note that in the poly-charged case, it is also possible to specify an algorithm that will enumerate all possible mesoionic compounds.

Algorithm 3.

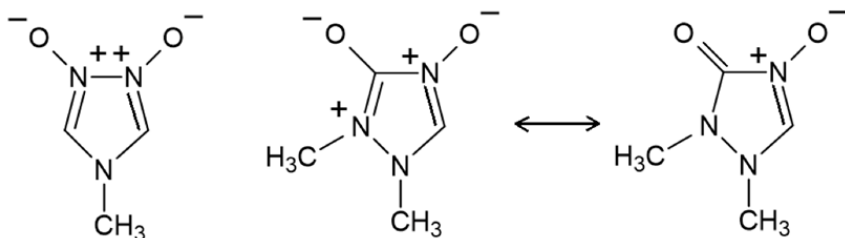
1. The vertices of the given graph are numbered.
2. All pairs of mismatched enumerations of vertices  $(P_1, P_2)$  are written out, the first enumeration  $P_1$  in the pair corresponds to  $Y^-$  atoms bearing a negative  $\pi$ -charge, the second  $P_2$  to atoms with a positive  $\pi$ -charge  $X^+$ .
3. For each pair of permutations, the necessary condition for the existence of the structure is checked:  $G - P_1$  must have a perfect matching
4. For each pair of permutations, the criterion of mesoionicity is checked:  $G - P_2$  has a perfect matching if and only if  $G$  is covalent.

However, this algorithm has two significant drawbacks.

First, as in the case of Algorithm 2, Algorithm 3 distinguishes between

structures that differ only in the permutation of different atoms of the group  $P_1$  and different atoms of the group  $P_2$ . Thus, the result of the algorithm will be a set of equivalent structures that will need to be manually sorted out.

Secondly, a situation is possible when the initially bis-charged mesoionic dipolar resonance structure is equivalent to a resonance structure with only one charge separation. Thus, the algorithm will produce poly-charged structures not only with the required number of charges of each sign, but also with a smaller number of charges.



**Figure 35.** An illustration of the pseudo-bis-mesoionicity problem. The structure on the left has two pairs of uncompensated charges. The structure on the right has only one pair, despite being able to draw the resonance formula with two pairs.

Consideration of the computer implementation of this section of mesoionicity is still under the progress of solving by us.

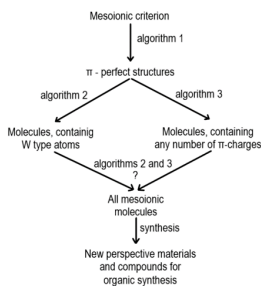
## 10 General case

So, at this stage, we potentially have all the technical means to consider the issue of enumerating any mesoionic compounds: Algorithm 1 for handling  $\pi$ -perfect structures, Algorithm 2 for enumerating all mono-charged mesoionic structures containing W-heteroatoms, and Algorithm 3 for poly-charged mesoionic structures. Algorithms 2 and 3, as already mentioned, have a drawback associated with not taking into account the symmetry of the structures, which significantly complicates manual processing of the

result for molecules containing a large number of atoms. Despite this, these algorithms have demonstrated the infallibility of their work, based on the theorems proved earlier in the text. Thus, we can conclude that in this work we have found an extremely efficient mathematical formalism for describing mesoionicity that can be easily translated into computer language. However, a number of technical implementation problems still need to be solved and may be the subject of future publications. Let us try to formulate a further program of actions (Fig. 37) for applying our results in questions of systematization and classification of mesoionic structures:

1. Solve the problem associated with not taking into account the symmetry of structures in algorithms 1 and 2.
2. Algorithms 1, 2 and 3 must be combined to enumerate all mesoionic structures on given graphs.
3. Analysis of the obtained lists of all mesoionic compounds in order to construct a new classification without missing classes.
4. Synthesis of new compounds obtained for organic synthesis and materials science.

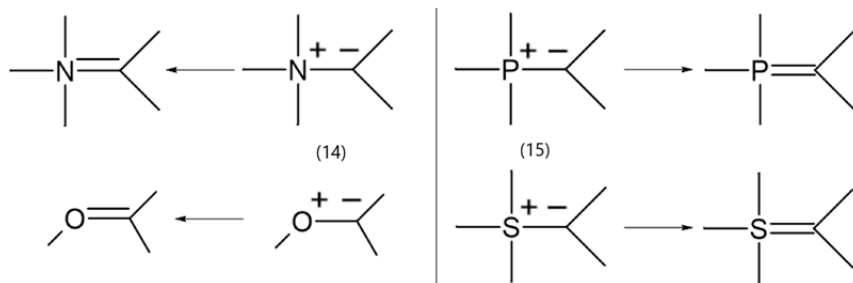
As a conclusion of this section, we note that, without exaggeration, there are many different mesoionic compounds (which is demonstrated, for instance, by the lists of structures in Fig. 30 and tables 2-4). However, only a very small part of them has been synthesized and studied, and we hope that our work will make it possible to simplify the preparation of new promising mesoionic molecules.



**Figure 36.** Potential applications of the mesoionicity criterion.

## 11 Feature of the elements of the second period

Fig. 38 shows pairs of dipolar resonance structures. In each pair, one of the structures contains a heteroatom of the second period of the periodic system, and the other – of the third. Despite the formal possibility of drawing a covalent resonance for both types of structures, molecules containing elements of the second period are not covalent. For example, in the molecule (14) there cannot be a neutral five-coordinate nitrogen (four  $\sigma$ -bonds and one  $\pi$ -bond), since at the external level it has only four atomic orbitals. On the contrary, in the phosphorus atom of structure (15), such a configuration is possible because it has a  $3d$ -sublevel. The same feature can be observed for elements of other groups of the periodic system. Consideration of these examples is important because they are exceptions to our mesoionicity rules, despite the fact that all the theorems formally remain true.



**Figure 37.** Mesoionic structures are shown on the left, covalent structures on the right.

## 12 Conclusions

1. An important concept of a  $\pi$ -perfect structure is introduced. It is shown this concept can be used in order to consider all mesoionic structures. The WXYZ-notation has been introduced, which simplifies the language for studying mesoionic structures.
2. The mesoionicity criteria for molecules in the WXYZ-notation are

formulated and proved, which makes it possible to classify all mesoionic molecules. The obtained criteria indicate that the pair of concepts mesoionicity – covalence correlates in the same way as the pair of non-Kekule – Kekule properties.

3. The connection between the criterion of mesoionicity and the matrix theory of Kasteleyn about counting the number of matchings on an arbitrary graph is shown. A matrix theory of mesoionicity has been developed. On its basis, an algorithm that classifies mesoionic molecules was invented. The algorithm allows to write a computer program that enumerates all monocharged mesoionic molecules. A library of all  $\pi$ -perfect mesoionic molecules containing no more than seven non-hydrogen atoms and a library of all monocharged structures for a five-membered graph with one substituent have been constructed.

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## Appendix

Also in this section we provide Python computer program that allows to list all mesoionic compounds of all types and containing any number of W atoms on given graph. The work of this program based on algorithms 1-4

```

from itertools import combinations
import numpy as np
import math

=====Selection by one element of the minor=====
def OneMinor(A, n, atomn):
    B=A.copy()
    B[atomn, :]=0
    B[:, atomn]=0
    B[atomn, atomn]=1
    return B

=====Isolation of the minor=====
def Minor(A, n, wnumbers):
    for i in wnumbers:
        A=OneMinor(A, n, i)
    return A

=====Mesoionic_Alpha=====
def Mesoionic_alpha(Dcur, WXYZ, i, n):
    D1cur=Dcur.copy()
    WXYZ1=WXYZ.copy()
    neg=0
    pos=0
    if ((n-i)%2!=0):
        for neg in range(n):
            for pos in range(n):
                if ((neg!=pos) and (WXYZ1[neg]!="W")
                    and (WXYZ1[pos]!="W")):
                    if (np.linalg.det(Minor(D1cur, n, [pos]))
                        ==0):
                        if (np.linalg.det(Minor(D1cur, n, [neg])
                            )!=0):
                            WXYZ1[neg]="Y"
                            WXYZ1[pos]="X"
                            for k in range(n):
                                print(k+1, end=" ")
                            print()
                            for k in range(n):

```



```

                print(WAXYZl[k], end=" ")
                print()
                print()
                WAXYZl=WAXYZ.copy()
#=====Mesoionic_Beta=====#
def Mesoionic_beta(Dcur, WAXYZ, i, n):
    D1cur=Dcur.copy()
    WAXYZl=WAXYZ.copy()
    neg=0
    pos=0
    if ((n-i)%2!=0):
        for neg in range(n):
            for pos in range(n):
                if ((neg!=pos) and (WAXYZl[neg]!="W")
                    and (WAXYZl[pos]!="W")):
                    if(np.linalg.det(Minor(D1cur, n, [pos]))
                       ==0):
                        if(np.linalg.det(Minor(D1cur, n, [neg])
                           !=0):
                            WAXYZl[neg]="Z"
                            WAXYZl[pos]="A"
                            for k in range(n):
                                print(k+1, end=" ")
                            print()
                            for k in range(n):
                                print(WAXYZl[k], end=" ")
                            print()
                            print()
                            WAXYZl=WAXYZ.copy()
#=====Mesoionic_Gamma=====#
def Mesoionic_gamma(Dcur, WAXYZ, i, n):
    D1cur=Dcur.copy()
    WAXYZl=WAXYZ.copy()
    neg=0
    pos=0
    if ((n-i)%2==0) and (np.linalg.det(D1cur)==0):
        for neg in range(n):
            for pos in range(n):
                if ((neg!=pos)
                    and (np.linalg.det(Minor(D1cur, n, [pos, neg]))
                       !=0)):
                    if ((WAXYZl[neg]!="W") and (WAXYZl[pos]!="W"
                        )):
                        WAXYZl[neg]="Y"
                        WAXYZl[pos]="A"
                        for k in range(n):
                            print(k+1, end=" ")
                        print()
                        for k in range(n):
                            print(WAXYZl[k], end=" ")
                        print()
                        print()

```

---

```

                WXYZl=WXYZ.copy()
#=====Mesoionic_Delta=====#
def Mesoionic_delta(Dcur, WXYZ, i, n):
    D1cur=Dcur.copy()
    WXYZl=WXYZ.copy()
    neg=0
    pos=0
    if ((n-i)%2==0) and (np.linalg.det(D1cur)!=0):
        for neg in range(n):
            for pos in range(n):
                if ((neg!=pos)
                    and (np.linalg.det(Minor(D1cur, n, [pos, neg]))
                        ==0)):
                    if ((WXYZl[neg]!="W") and (WXYZl[pos]!="W
                        ")):
                        WXYZl[neg]="Z"
                        WXYZl[pos]="X"
                        for k in range(n):
                            print(k+1, end=" ")
                        print()
                        for k in range(n):
                            print(WXYZl[k], end=" ")
                        print()
                        print()
                        print()
                        WXYZl=WXYZ.copy()
#=====main function=====#
print("Enter_the_number_of_vertices_in_the_column")
n=int(input())
print("Input_Undirected_Graph_Adjacency_Matrix")
A = [] #undirected adjacency matrix
for i in range(n):
    A.append([int(j) for j in input().split()])
D = np.array(A)
D[np.triu_indices_from(D)] *= -1
WXYZ = list(range(n))#the type of each atom in WXYZ-notation
for i in range(n):
    WXYZ[i] = "C"
tmp = range(n)
allatoms = [int(n) for n in tmp]
for i in range(n): #cycle by the number of atoms W
    print("structures_containing_", i, "W_atoms")
    for j in combinations(allatoms, i): #permutation loop
        wnumbers = list(j)
        for k in range(i):
            WXYZ[wnumbers[k]] = "W"
        #padding the string WXYZ with a W atom
        Dcur=OneMinor(D, n, wnumbers)
        #copy of matrix D for current work
        print("alpha-type")
        print()
        Mesoionic_alpha(Dcur, WXYZ, i, n)
        print("beta-type")
        print()

```

---

```
Mesoionic_beta(Dcur, WXYZ, i, n)
print("gamma-type")
print()
Mesoionic_gamma(Dcur, WXYZ, i, n)
print("delta-type")
print()
Mesoionic_delta(Dcur, WXYZ, i, n)
for k in range(n):
    WXYZ[int(k)] = "C"
print("=====")
print("end")
```