The New Approach of Expansion Baldwin-Aibassov’s Rules for Ring-Closing Reaction for d- and f-elements Periodic Table of Elements

Aibassov Yerkin, Yemelyanova Valentina, Shakieva Tatyana, Bulenbaev Maxat and Blagikh Evgeniy
Research Institute of New Chemical Technologies and Materials, Kazakh National University Al-Farabi, Almaty 005012, Kazakhstan

Abstract: The authors have studied the effect of a magnetic field on Baldwin’s rules. The authors have proposed a new mechanism that takes into account the effect of the angle and energy endo- or exo-cyclization. The authors propose to extend the rule Bouldwin not only for sp³-, sp²- and sp-orbits, but and for d¹ - d¹⁰ and f¹ - f¹⁴ elements of I-VIII of the Periodic table.

Key words: Magnetic field, mechanism of the Baldwin’s rule, endo- or exo-cyclization.

I. Introduction

Recently, much attention is paid to finding new approaches to extend and modify Bouldina rules for the endo- or exo-cyclization in Bioorganic and Medicinal Chemistry. In this article the authors consider an important aspect of the influence of magnetic field on Baldwin’s rule [1-11].

The goal to explore studied the effect of a magnetic field on Baldwin’s rules; and to determine the relationship Baldwin-Aibassov’s rules for ring-closing reaction for d- and f-elements Periodic Table of Elements.

2. Theory

In 1976, J.E. Baldwin formulated a set of rules/guidelines governing the ease of intramolecular ring-closing reaction. Baldwin used these rules to gain valuable insight into the role of stereoelectronic effects in organic reaction and predict the feasibility of these reactions in synthetic sequences. A few years later in 1983, J. D. Dunitz and co-workers demonstrated that there are favored trajectories for the approach of one reactant molecule toward another. The authors must note, however, that there is substantial limitation on these rules; a large number of examples are known for which they do not apply.

Baldwin discovered that orbital overlap requirements for the formation of bonds favour only certain combinations of ring size and the exo/endo/dig/trig/tet parameters. Interactive 3D models of several of these transition states can be seen here (javascript required).

There are sometimes exceptions to Baldwin’s rules. For example, cations often disobey Baldwin’s rules, as do reactions in which a third-row atom is included in the ring.

Table 2 shows the Baldwin dis/favoured ring closures.

The rules apply when the nucleophile can attack the bond in question in an ideal angle. These angles are 180° (Walden inversion) for exo-tet reactions, 109° (Bürgi-Dunitz angle) for exo-trig reaction and 120° for endo-dig reactions. Angles for nucleophilic attack on alkynes were reviewed and redefined recently. The “acute angle” of attack postulated by Baldwin was replaced with a trajectory similar to the Bürgi–Dunitz angle [4-11].
The New Approach of Expansion Baldwin-Aibassov’s Rules for Ring-closing Reaction for d- and f-elements Periodic Table of Elements

Table 1  Shows of the most important ring closures: (F = favored, D = disfavored).

<table>
<thead>
<tr>
<th>Ring size</th>
<th>Exo-dig</th>
<th>Exo-trig</th>
<th>Exo-tet</th>
<th>Endo-dig</th>
<th>Endo-trig</th>
<th>Endo-tet</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>D</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>D</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>D</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>D</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>D</td>
<td>D</td>
</tr>
<tr>
<td>6</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>D</td>
</tr>
<tr>
<td>7</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Some examples of exo- and endo-cyclization:

![Examples of cyclization](image)

Table 2  Baldwin dis/favoured ring closures.

<table>
<thead>
<tr>
<th>type</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>tet</td>
<td>✓</td>
<td>×</td>
<td>✓</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>trig</td>
<td>✓</td>
<td>×</td>
<td>✓</td>
<td>×</td>
<td>✓</td>
</tr>
<tr>
<td>dig</td>
<td>×</td>
<td>✓</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>
The New Approach of Expansion Baldwin-Aibassov’s Rules for Ring-closing Reaction for d- and f-elements Periodic Table of Elements

Table 3  Characteristic of some heteroazols.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Configuration</th>
<th>Electronic couple E</th>
<th>Nature of the cycle</th>
<th>Enantiomers</th>
<th>Pyrrole</th>
<th>Phosphole</th>
<th>Arsole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Planar</td>
<td>Part 6πn-system</td>
<td>Aromatic</td>
<td>No</td>
<td>Pyramid</td>
<td>Pyramid</td>
<td></td>
</tr>
</tbody>
</table>

3. Results and Discussion

Can you use a rule Bouldina for d- and f-elements in the periodic system of elements?

For example, consider the synthesis of biologically active organic compounds of Group V phosphorus, arsenic, antimony and bismuth. Heteroarenes C₅H₅E (E = N, P, As, Sb, Bi) were synthesized by reacting:

\[ \text{HC} = \text{C-CH₂-CH} + \text{n-Bu₂SnH₂} \rightarrow \text{C₅H₅Sn(n-Bu)}₂ + \text{ECl₃} \rightarrow \text{C₅H₅E-Cl} + \text{DBU} \rightarrow \text{C₅H₅E} \quad (1) \]

where, E = N, P, As, Sb, Bi.

Heteroarenes Stability decreases in the order: N > P > As > Sb > Bi; arsabenzo stable stiba- and vismabenzoly, which quickly polymerize.

In phospholene and arsoli stabilization trigonal-bipirimidalnogo condition occurs due to coupling. The data presented in Table 3, indicate a decrease in participation E = C interaction with increasing atomic number E.

Thus, the table shows that the decline in the contribution of π-bond interactions in E-C is also observed during the transition from phosphorus to arsenic.

Cyclopentadienyl complexes of actinides prepared by reacting:

\[ \text{AnCl₄} + 4 \text{KCP} \rightarrow \text{C₅An} + 4\text{KCl} \quad (2) \]

where An = Th, U, Np.

The authors suggested a simple and affordable methods for the synthesis of large series of new compounds, which will be used generally for Baldwin-Aibassov rule for ring-closing reaction for d- and f-elements Periodic Table of Elements. These methods may be used when searching for new biologically active compounds.

4. Conclusions

Thus, the authors propose to extend and modify the rule for Baldwin exo- and endo-cyclization to d- and f-elements of the periodic table as well as the triple, double and single bonds, to mono- and poly-heterocyclic rings etc. heteroatomic.

The authors have proposed to take into account the rules Bouldina the formation of octahedra, flat, bipyramidal, tetrahedral configurations, etc.

The authors propose to extend the rule Baldwin not only for sp³-, sp²- and sp- orbits, but and for d¹ - d¹⁰ and f¹ - f¹⁴ elements of I-VIII of the Periodic Table.

In the future, work will continue to use the modified rules Baldwin to form a (hetero) cycles with triple, double and single bonds, including for hetero atoms I-VIII of the Periodic Table.

This will expand the scope of use of the modified rules Baldwin important in the synthesis of biologically active substances.

References

The New Approach of Expansion Baldwin-Aibassov’s Rules for Ring-closing Reaction for d- and f-elements Periodic Table of Elements


