Short Communication

A NEW APPROACH TO EXPANSION OF BALDWIN-AIBASSOV'S RULES CONCERNING THE RING-CLOSING REACTION OF THE d- AND f-ELEMENTS OF THE PERIODIC TABLE OF ELEMENTS

Yerkin Aibassov[2], Valentina Yemelyanova[1], Maxat Bulenbayev[1],
Ruslan Nurlybaev[1], Bagdat Altaibayev[1]

[1] *Satbayev University*
22 Satbayev str., Almaty, Republic of Kazakhstan
E-mail: mbulenbaev@mail.ru
[2] *Columbia University, 3000 Broadway, New York, NY, 10027, USA*
E-mail: erkin53@mail.ru

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ABSTRACT

We have studied the magnetic field effect on Baldwin's rules. We suggest a new mechanism that takes into account the effect of the angle and the energy of endo- or exo-cyclization. We propose to extend the Bouldwin's rule not only to sp^3-, sp^2- and sp- orbits, but also to d^1 - d^{10} and $f^1 – f^{14}$ elements of I-VIII groups of the Periodic Table.
Keywords: *magnetic field, Baldwin's rule, endo- or exo-cyclization.*

INTRODUCTION

Recently, much attention is paid to finding new approaches to extend and modify Baldwin's rules for the exo and endo cyclization in bioorganic and medicinal chemistry. In this article, we consider an important aspect of the influence of the magnetic field on Baldwin's rule [1 - 11].

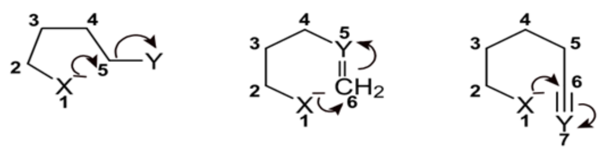
The aim of the work is to study the effect of a magnetic field on Baldwin's rules and to determine the relationship expressed through Baldwin-Aibassov's rules for ring-closing reaction for d- and f-elements of the Periodic Table of Elements.

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 stereo-electronic effects in organic reactions and to 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. We must note, however, that these rules have substantial limitations - a large number of examples are known for which they do not apply.

Table 1 illustrates the most important ring closures.

Some examples of exo- and endo-cyclization:



5-exo-tet 6-endo-trig 6-exo-dig

Baldwin discovered that the orbital overlap requirements for the formation of bonds favour only certain combinations of the 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, Table 2).

There are sometimes exceptions to Baldwin's rules. For example, cations often disobey Baldwin's rules, as do

Table 1. The most important ring closures (F = favored, D = disfavored).

Ring size	Exo-dig	Exo-trig	Exo-tet	Endo-dig	Endo-trig	Endo-tet
3	D	F	F	F	D	-
4	D	F	F	F	D	-
5	F	F	F	F	D	D
6	F	F	F	F	F	D
7	F	F	F	F	F	-

reactions in which a third-row atom is included in the ring.

The rules apply when the nucleophile can attack the bond in question at an ideal angle. These angles are 180° (Walden inversion) for *exo-tet* reactions, 109° (Bürgi–Dunitz angle) for *exo-trig* reactions and 120° for *endo-dig* reactions. The angles required for a nucleophilic attack on alkynes were reviewed and redefined recently. The "acute angle" of the attack postulated by Baldwin was replaced with a trajectory similar to the Bürgi–Dunitz angle [4 - 11].

EXPERIMENTAL

Cyclization of penta-1,4-diene by reaction with phosphorus, arsenic and antimony trichloride was carried out according to the standard procedure of Ashe [12].

RESULTS AND DISCUSSION

Can you use Baldwin's rule 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 C_5H_5E (E = N, P, As, Sb, Bi) are synthesized following the reaction:

$$HC{=}C\text{-}CH_2\text{-}C{=}CH + n\text{-}Bu_2SnH_2 \rightarrow C_5H_5Sn(n\text{-}Bu)_2 + ECl_3 \rightarrow C_5H_5E\text{-}Cl + DBU \rightarrow C_5H_5E, \quad (1)$$

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

Heteroarenes stability decreases in the order: N > P > As > Sb > Bi; arsabenzol is stable, while stiba- and vismabenzol polymerize quickly.

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

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

Cyclopentadienyl complexes of actinides are obtained in accordance with the reaction:

$$AnCl_4 + 4KCp \rightarrow Cp_4An + 4KCl, \quad (2)$$

where An = Th, U, Np.

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

Table 2. Baldwin dis/favoured ring closures.

	3		4		5		6		7	
type	*exo*	*endo*	*exo*	*endo*	*exo*	*endo*	*eexo*	*endo*	*eexo*	*endo*
tet	✓		✓		✓	✗	✓	✗	✓	✗
trig	✓	✗	✓	✗	✓	✗	✓	✓	✓	✓
dig	✗	✓	✗	✓	✓	✓	✓	✓	✓	✓

Table 3. Characteristics of some heteroazols.

Formula	Pyrrole	Phosphole	Arsole
Configuration E	Planar	Pyramid	Pyramid
Electronic couple E	Part 6πe-system	Lone	Lone
Nature of the cycle	Aromatic	Dien	Dien
Enantiomers	No	No	Yes

CONCLUSIONS

Thus, we propose to extend the Baldwin's rule to exo- and endo-cyclization of d- and f-elements of the Periodic Table as well as to the triple, double and single bonds, to mono- and poly-heterocyclic rings, etc.

We suggest taking into account the Baldwin's rule in case of formation of octahedra, as well as flat, bipyramidal, tetrahedral configurations, etc.

We propose to extend the Baldwin's rule not only to sp^3-, sp^2- and sp- orbits, but also to d^1 - d^{10} and f^1 – f^{14} elements of I-VIII groups of the Periodic Table.

The modified Baldwin-Aibassov rule expands the scope of application. It is important in the synthesis of biologically active substances.

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