# Universidade Federal de Goiás

# Instituto de Química

# Coordenação de Pós-Graduação em Química

# SELEÇÃO DO PROGRAMA DE PÓS-GRADUAÇÃO EM QUÍMICA – 2018/2

# EXAME DE SUFICIÊNCIA EM LÍNGUA INGLESA

**IDENTIFICAÇÃO DO CANDIDATO - Número de Inscrição: _______________**

**INSTRUÇÕES IMPORTANTES:**

- identifique TODAS as folhas com seu número de inscrição;
- leia o texto e responda cada questão somente no espaço indicado;
- respostas a lápis não serão consideradas;
- é permitido o uso de dicionário;
- a prova tem duração de 2 horas;
- os candidatos poderão ausentar-se em definitivo da sala de aplicação da prova somente após decorridas 1 (uma) hora e 30 (trinta) minutos do início da prova, sob pena de eliminação;
- os candidatos poderão ir ao banheiro somente após decorridas 1 (uma) hora e 15 (minutos) minutos do início da prova;
- os 3 (três) últimos candidatos deverão permanecer na sala até que o último candidato termine a prova;
- o uso de celular ou outro equipamento de comunicação não é permitido.

**LEIA O TEXTO A SEGUIR.**

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ARTICLES
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# A new fundamental type of conformational isomerism

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**Isomerism is a fundamental chemical concept, reflecting the fact that the arrangement of atoms in a molecular entity has a profound influence on its chemical and physical properties. Here we describe a previously unclassified fundamental form of conformational isomerism through four resolved stereoisomers of a *transoid* (BF)O(BF)-quinoxalinoporphyrin. These comprise two pairs of enantiomers that manifest structural relationships not describable within existing IUPAC nomenclature and terminology. They undergo thermal diastereomeric interconversion over a barrier of $104 \pm 2$ kJ $\text{mol}^{-1}$, which we term 'akamptisomerization'. Feasible interconversion processes between conceivable synthesis products and reaction intermediates were mapped out by density functional theory calculations, identifying bond-angle inversion (BAI) at a singly bonded atom as the reaction mechanism. We also introduce the necessary BAI stereodescriptors *parvo* and *amplo*. Based on an extended polytope formalism of molecular structure and stereoisomerization, BAI-driven akamptisomerization is shown to be the final fundamental type of conformational isomerization.**

Isomerism is a key concept in chemistry, and understanding the relationships that exist between different isomers—compounds made up of the same atoms, but arranged in different manners—is not only of fundamental interest but also holds vast structural and functional implications. Constitutional isomers, for example, present the same general formula, but their atoms are held together through different chemical bonds, making them distinct compounds. In contrast, stereoisomers feature the same connectivities but their atoms are arranged differently. They result from the dynamical nature of molecules, and can be further divided into subcategories: configurational isomers are inhibited from interconversion by large energy barriers (this is the case for *E*/*Z* isomers of alkenes) and are easy to isolate under ambient conditions, whereas conformational isomers interconvert over low barriers (such as a rotation around a single bond), which renders their isolation difficult. Figure 1 provides an overview of the key IUPAC terms[1] and current practice[2–10] involved in describing isomerism, emphasizing stereoisomerism and in particular conformational isomerism; for reference, a full list of relevant terms and their formal definitions is provided in Supplementary Section 1.

In some cases, specific circumstances can lead conformational isomers having unusually high interconversion barriers, rendering them isolable. The first of these instances to be discovered was the unexpected bond-rotation-based phenomenon called atropisomerism, reported in 1914[11,12] and described in 1922[13] and 1933[14]. In 1961, similar isolable conformational isomerization involving pyramidal inversion was discovered in phosphorus compounds[15], and then in isolable nitrogen compounds in 1968[16]. Are there other fundamental forms of conformational isomerization remaining unidentified? The polytope formalism[17–25] (introduced in detail in Supplementary Section 1b) was developed to understand stereoisomerization processes in molecules containing atoms with high coordination numbers (that is, chemically bonded to a large number of other atoms), leading to the identification of possible conformational isomers, but such a systematic analysis has yet to be applied to low-coordinate species and has not previously been used to describe internal rotation as a reaction pathway.

We show how the polytope formalism can be extended to include bond rotations and provide a comprehensive description of the fundamental stereoisomerism processes for each coordination number. Applying this to the lower-coordinate systems, we found an unrecognized fundamental type of conformational isomerism that, for example, could be produced by a bond-angle inversion (BAI) reaction mechanism about centres of the form $M_1{-}X{-}M_2$ (where the central atom X exhibits a bent geometry and $M_1$ and $M_2$ are any atoms) linked by only single bonds. Isolable compounds distinguished by only this feature have not previously been synthesized, although the process has been envisaged as occurring at linkages inside polymeric systems[26]. We make isolable compounds by encapsulating $B{-}O{-}B$ as (BF)O(BF), inside a porphyrin macrocycle.

No existing IUPAC terminologies[1] can describe the relationships between the compounds synthesized. We term these stereoisomers 'akamptisomers', and their process of interconversion 'akamptisomerization'. In Fig. 1, the listed standard IUPAC nomenclature has been extended to include this new process. Also, we introduce the new stereodescriptors *parvo* and *amplo* for naming the akamptisomers and related structures, including classification of transition-state structures and some as yet undiscovered structural possibilities.

## Results and discussion

### Generalized polytope formalism for conformational isomerism.

In Fig. 1, the relationships between existing definitions of isomerization (according to the IUPAC[1]) are depicted graphically using a

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Considerando apenas as informações contidas no texto INTRODUTÓRIO (iniciando com a letra I em caixa alta e terminando ao final do parágrafo antecessor à seção **Resultados e discussão**), responda, em português, as seguintes questões:

**01)** Quais são as duas grandes classes de isômeros?

**02)** Qual é a característica fundamental que diferencia as classes de isômeros?

**03)** Estereoisômeros conformacionais são facilmente isolados sob condições ambientais. Esta afirmação é verdadeira ou falsa? Valide sua resposta informando a razão da veracidade ou falsidade do fenômeno supracitado.

**04)** Quais são os dois fenômenos responsáveis pelo isolamento de isômeros conformacionais que foram, respectivamente, descobertos em 1914 e 1961?

**05)** O que são átomos com alto número de coordenação?

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**RESPOSTAS:**

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