Question Bank

Questions and answers on Molecules with different spatial arrangements due to rotation around single bonds. Example: Atropisomers in certain organometallic complexes.

Questions and Answers on Molecules with Different Spatial Arrangements Due to Rotation Around Single Bonds

Q1 What are atropisomers

A1 Atropisomers are a type of stereoisomer where the molecules have restricted rotation around a single bond, typically due to steric hindrance or other structural constraints. This restricted rotation leads to distinct spatial arrangements that are stable and can be isolated as separate entities.

Q2 How do atropisomers differ from other types of stereoisomers

A2 Unlike other stereoisomers (such as enantiomers or diastereomers) that arise from differences in the arrangement of atoms around a chiral center, atropisomers are specifically due to restricted rotation around single bonds. This restriction is often caused by bulky groups that prevent free rotation.

Q3 In what types of compounds are atropisomers commonly found

A3 Atropisomers are commonly found in biaryl compounds, where two aromatic rings are connected by a single bond. They can also occur in certain organometallic complexes where the metal coordination creates a similar barrier to rotation.

Q4 What factors influence the formation of atropisomers

A4 The formation of atropisomers is influenced by several factors, including

- Steric hindrance Bulky substituents around the single bond can prevent free rotation.

- Electronic effects Electronic interactions between substituents can stabilize certain conformations.

- Temperature Higher temperatures can sometimes allow for rotation that is restricted at lower temperatures.

Q5 How are atropisomers separated and identified

A5 Atropisomers can be separated using techniques such as

- Chromatography HPLC (High-Performance Liquid Chromatography) or other chromatographic methods can separate atropisomers based on differences in their interaction with the stationary phase.

- Spectroscopy NMR (Nuclear Magnetic Resonance) spectroscopy can be used to identify different atropisomers by their unique chemical environments.

Q6 Can atropisomers interconvert, and if so, how

A6 Yes, atropisomers can interconvert, but the rate of interconversion depends on the energy barrier to rotation. This barrier can be influenced by factors such as temperature and the presence of catalysts. In cases where the barrier is high, the atropisomers can be stable and isolated at room temperature.

Q7 Give an example of an organometallic complex that exhibits atropisomerism.

A7 An example of an organometallic complex that exhibits atropisomerism is a complex where two large ligands are coordinated to a central metal atom, creating steric hindrance that restricts rotation. Specific examples can include certain palladium or platinum complexes with bulky phosphine ligands.

Q8 Why is atropisomerism important in chemistry and pharmacology

A8 Atropisomerism is important because the different spatial arrangements can have distinct chemical and biological properties. In pharmacology, different atropisomers of a drug may have different levels of efficacy, toxicity, or metabolic stability, making it crucial to identify and separate them for proper drug development and use.

Q9 How does atropisomerism affect the properties of a molecule

A9 Atropisomerism can affect a molecule's properties in several ways, including

- Reactivity Different atropisomers may react differently with other molecules.

- Binding affinity in biological systems, one atropisomer may bind more strongly to a target protein or receptor than another.

- Physical properties Atropisomers can have different melting points, solubilities, and other physical properties due to their distinct spatial arrangements.

Conclusion

Atropisomers represent an interesting and important class of stereoisomers where restricted rotation around single bonds leads to distinct spatial arrangements. Understanding and identifying atropisomers is crucial in various fields of chemistry and pharmacology, where the specific arrangement of atoms can significantly impact the behavior and efficacy of molecules.

The distinction between pincer exergonic (green) and endergonic (red) complexes with chiral phosphine centers lies in their thermodynamic properties, specifically the energy changes associated with their formation and reactions.

Exergonic Pincer Complexes (Green)

- Thermodynamics: Exergonic processes are those where the overall change in free energy (ΔG) is negative. This indicates that the formation of the pincer complex is spontaneous and releases energy.

- Stability: Exergonic pincer complexes are generally more stable because their formation is energetically favorable.

- Applications: These complexes are often used in catalytic processes where a stable, energy-releasing transformation is required. Their stability makes them reliable for repetitive catalytic cycles.

- Chiral Phosphine Centers: The chirality of the phosphine centers in exergonic pincer complexes can lead to highly selective catalytic processes, as the chirality can influence the stereochemistry of the reactions they catalyze.

Endergonic Pincer Complexes (Red)

- Thermodynamics: Endergonic processes are those where the overall change in free energy (ΔG) is positive. This indicates that the formation of the pincer complex is non-spontaneous and requires an input of energy.

- Stability: Endergonic pincer complexes are less stable because their formation is energetically unfavorable. They require energy input, often making them transient or less common under standard conditions.

- Applications: These complexes might be used in situations where controlled reactivity is required, or where the release of energy in subsequent steps can drive the overall process. They can also be intermediates in multi-step synthetic processes.

- Chiral Phosphine Centers: The chirality of phosphine centers in endergonic pincer complexes can be crucial in driving selective transformations, especially in asymmetric synthesis. The energy input required for their formation can be utilized to control the reaction pathway and achieve desired stereochemical outcomes.

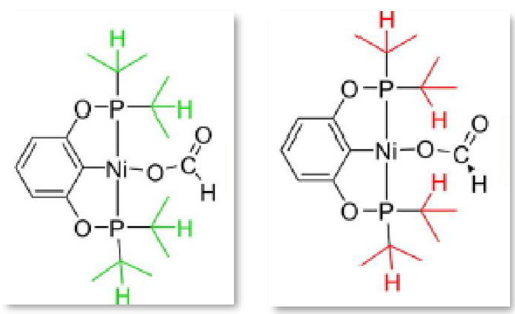


Figure 7. Pincer exergonic (green) and endergonic (red) complexes with chiral phosphine centers

Key Differences:

1. Energy Changes:

- Exergonic: Release energy ($\Delta G < 0$).

- Endergonic: Require energy input ($\Delta G > 0$).

2. Stability:

- Exergonic: Generally, more stable and energetically favorable.

- Endergonic: Less stable, energetically unfavorable, and often transient.

3. Formation and Use:

- Exergonic: Form spontaneously, used in stable, repetitive catalytic cycles.

- Endergonic: Require formation energy, used in controlled or multi-step processes.

4. Chirality and Selectivity:

- Exergonic: Chiral centers provide high selectivity in stable environments.
- Endergonic: Chiral centers drive specific, energy-requiring transformations for desired stereochemistry.

The key difference between pincer exergonic (green) and endergonic (red) complexes with chiral phosphine centers is the thermodynamic favorability and stability of their formation, which influences their practical applications and the control over reaction pathways in catalytic and synthetic processes.

Questions and Answers on Exergonic and Endergonic Pincer Complexes with Chiral Phosphine Centers

Exergonic Pincer Complexes (Green)

Q1: What defines an exergonic pincer complex?

A1: An exergonic pincer complex is defined by a negative change in free energy (ΔG) during its formation, indicating that the process is spontaneous and releases energy.

Q2: Why are exergonic pincer complexes generally more stable?

A2: Exergonic pincer complexes are more stable because their formation is energetically favorable, releasing energy and thus resulting in a lower overall energy state.

Q3: How does the chirality of phosphine centers affect exergonic pincer complexes?

A3: The chirality of phosphine centers in exergonic pincer complexes can enhance the selectivity of catalytic processes, allowing for precise control over the stereochemistry of the reactions they facilitate.

Q4: In what applications are exergonic pincer complexes commonly used?

A4: Exergonic pincer complexes are commonly used in catalytic processes where stability and the ability to undergo repetitive catalytic cycles are important, such as in hydrogenation, hydroformylation, and cross-coupling reactions.

Q5: Can you give an example of a reaction involving an exergonic pincer complex?

A5: An example would be the use of an exergonic pincer complex in a hydrogenation reaction, where the complex acts as a catalyst to reduce a substrate, releasing energy in the process and remaining stable for multiple cycles.

Endergonic Pincer Complexes (Red)

Q1: What characterizes an endergonic pincer complex?

A1: An endergonic pincer complex is characterized by a positive change in free energy (ΔG) during its formation, indicating that the process is non-spontaneous and requires an input of energy.

Q2: Why are endergonic pincer complexes less stable?

A2: Endergonic pincer complexes are less stable because their formation is energetically unfavorable, requiring energy input to maintain the complex, which makes them more transient and less common under standard conditions.

Q3: How does the chirality of phosphine centers influence endergonic pincer complexes?

A3: The chirality of phosphine centers in endergonic pincer complexes can drive specific, energy-requiring transformations, leading to desired stereochemical outcomes in reactions where control over the pathway is crucial.

Q4: In what situations are endergonic pincer complexes used?

A4: Endergonic pincer complexes are used in controlled or multi-step processes where an initial energy input is acceptable to drive a series of reactions, often leading to valuable or complex products.

Q5: Can you provide an example of a reaction involving an endergonic pincer complex?

A5: An example would be a multi-step synthesis where an endergonic pincer complex acts as an intermediate. The initial energy input to form the complex is followed by subsequent steps that release energy, making the overall process feasible.

Comparative Questions

Q1: What is the key thermodynamic difference between exergonic and endergonic pincer complexes?

A1: The key thermodynamic difference is that exergonic complexes have a negative ΔG, indicating spontaneous formation and energy release, while endergonic complexes have a positive ΔG, indicating non-spontaneous formation and the need for energy input.

Q2: How does the stability of exergonic and endergonic pincer complexes compare?

A2:Exergonic pincer complexes are generally more stable due to their energetically favorable formation, whereas endergonic pincer complexes are less stable because their formation requires energy input and is energetically unfavorable.

Q3: How does the role of chiral phosphine centers differ in exergonic versus endergonic pincer complexes?

A3:In exergonic pincer complexes, chiral phosphine centers enhance catalytic selectivity in stable environments. In endergonic pincer complexes, chiral phosphine centers help drive specific transformations, often requiring careful control of reaction conditions to achieve desired stereochemical outcomes.

Q4: Why might a chemist choose to use an endergonic pincer complex despite its instability?

A4: A chemist might choose to use an endergonic pincer complex for its ability to drive specific and valuable transformations, particularly in multi-step syntheses where controlled energy input can lead to the formation of complex or high-value products.

These questions and answers cover the fundamental differences, applications, and implications of using exergonic and endergonic pincer complexes with chiral phosphine centers in chemical reactions and catalysis.

What are Atropisomers in certain organometallic complexes?

Atropisomers in Certain Organometallic Complexes

Q1: What are atropisomers?

A1: Atropisomers are a type of stereoisomer resulting from restricted rotation around a single bond, usually due to steric hindrance or electronic effects. This restricted rotation leads to distinct, stable spatial arrangements of the atoms in the molecule.

Q2: How are atropisomers different from other types of isomers?

A2: Atropisomers differ from other types of isomers, such as enantiomers and diastereomers, because their isomerism arises from hindered rotation around single bonds rather than differences in the spatial arrangement around a central chiral atom. Enantiomers are non-superimposable mirror images, while diastereomers are not mirror images and differ in multiple stereocenters.

Q3: **In what types of compounds are atropisomers commonly found?**

A3: Atropisomers are commonly found in biaryl compounds, where two aromatic rings are connected by a single bond, and in certain organometallic complexes where the ligands or substituents create steric hindrance that restricts rotation.

Q4: Why do organometallic complexes often exhibit atropisomerism?

A4: Organometallic complexes often exhibit atropisomerism due to the presence of bulky ligands or substituents around the metal center, which create a significant barrier to free rotation around the single bonds connecting these groups. The metal coordination environment can also contribute to the stabilization of distinct atropisomers.

Q5: Can you provide an example of an organometallic complex that forms atropisomers?

A5: An example of an organometallic complex that forms atropisomers is a palladium complex with bulky phosphine ligands, such as Pd(PPh3)2Cl2, where the steric bulk of the triphenylphosphine ligands restricts rotation around the Pd-P bonds, leading to distinct atropisomeric forms.

Q6: How are atropisomers in organometallic complexes identified and separated?

A6: Atropisomers in organometallic complexes can be identified and separated using techniques such as:

- **Chromatography**: High-performance liquid chromatography (HPLC) or other chromatographic methods can separate atropisomers based on differences in their interaction with the stationary phase.

- Spectroscopy: Nuclear magnetic resonance (NMR) spectroscopy can be used to identify different atropisomers by their unique chemical environments.

- X-ray Crystallography: This technique can determine the precise 3D arrangement of atoms in a crystal, helping to distinguish between different atropisomers.

Q7: What factors influence the stability of atropisomers in organometallic complexes?

A7: The stability of atropisomers in organometallic complexes is influenced by:

- Steric Hindrance: Larger substituents or ligands increase the barrier to rotation, stabilizing distinct atropisomers.

- Electronic Effects: Electron-donating or withdrawing properties of the ligands can stabilize specific atropisomeric forms.

- Temperature: Higher temperatures can provide the energy needed to overcome rotational barriers, potentially leading to interconversion between atropisomers.

Q8: Why is atropisomerism important in the context of organometallic chemistry?

A8: Atropisomerism is important in organometallic chemistry because:

- Catalytic Activity: Different atropisomers can exhibit distinct catalytic properties, affecting the selectivity and efficiency of catalytic reactions.

- Pharmacological Properties**: In drug design, atropisomers can have different biological activities, toxicities, and metabolic stabilities, making it crucial to identify and separate them.

- Material Science: Atropisomeric organometallic complexes can have unique electronic, optical, and structural properties, useful in the development of advanced materials.

Q9: Can atropisomers interconvert, and what factors affect this interconversion?

A9: Yes, atropisomers can interconvert, but the rate of interconversion depends on the energy barrier to rotation. Factors affecting this include:

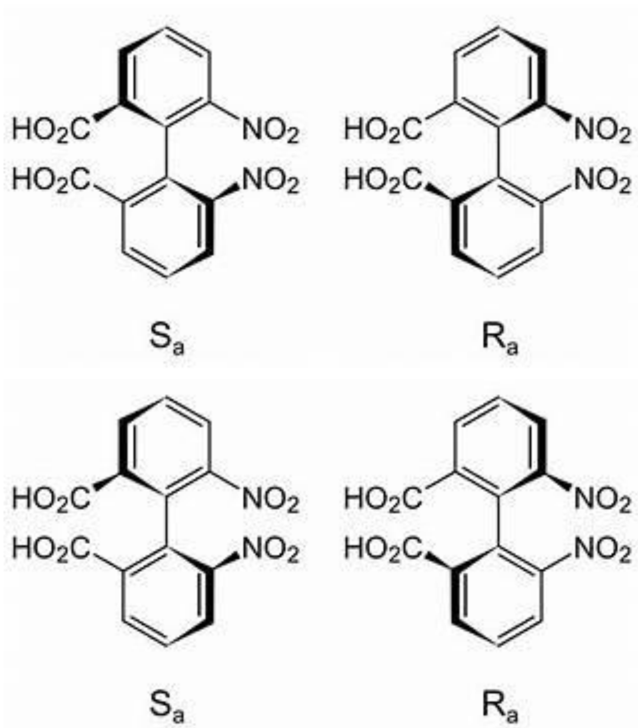
- Steric Bulk: Larger substituents increase the energy barrier, reducing the rate of interconversion.

- Temperature: Higher temperatures provide the thermal energy needed to overcome rotational barriers.

- Solvent Effects: The solvent can influence the energy landscape, either stabilizing or destabilizing certain atropisomers.

Conclusion

Atropisomers in organometallic complexes are distinct stereoisomers resulting from restricted rotation around single bonds, often due to steric and electronic factors. Their stability and interconversion are influenced by the size and electronic properties of the ligands, temperature, and solvent effects. Understanding atropisomerism is crucial for applications in catalysis, drug design, and materials science.



Explore

Atropisomers are a type of stereoisomers that arise due to hindered rotation about a single bond[1]. The term “atropisomer” is derived from the Greek words “a” meaning “not” and “tropos” meaning "turn"[23]. This hindered rotation is due to energy differences caused by steric strain or other factors, creating a barrier to rotation that is high enough to allow for isolation of individual conformers[1]. When the substituents are achiral, these conformers are enantiomers (atropoenantiomers), showing axial chirality; otherwise, they are diastereomers (atropodiastereomers)[1].

In the field of **chemistry**, atropisomers are significant for several reasons:

- They occur naturally and are important in the design of pharmaceuticals[1].

- They exhibit axial chirality (planar chirality). When the barrier to racemization is high, as illustrated by the BINAP ligands, the phenomenon becomes of practical value in asymmetric synthesis[1].
- Atropisomerism is connected to asymmetric synthesis, materials, and biological properties[4].
- The stability of individual atropisomers is conferred by the repulsive interactions that inhibit rotation[1].

In **pharmacology**, atropisomers have a prominent role:

- The ability of natural receptors to possess differential binding between atropisomers is an important factor when considering active and inactive atropisomeric drugs[5].
- Recently identified natural atropisomeric compounds with potential medicinal applications are presented[5].
- The atropisomeric natural products discussed include hibarimicinone, flavomannins, talaromannins, viriditoxin, rugulotrosin A, abyssomicin C, marinopyrroles, dixiamycins, streptorubin B, ustiloxins A-F, haouamine A, bisnicalaterines, and tedarene B, all of which show significant potential as leads in antibiotic, antiviral and anticancer studies[5].
- Considering the pharmacological benefits of preorganizing sigma bonds and limiting the number of accessible conformations of drug molecules, reports of synthetic bioactive molecules bearing configurationally stable axes of atropisomerism have been increasing significantly over the past decade[6].