

Steric Bulk-Dependent Photoresponse of Sulfonamide Azobenzene Ligand in Arene Ruthenium(II) Complexes

Publié le 4 mars 2024 - Helvetica Chimica Acta

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A series of sulfonamide azobenzenes bearing alkyl substituents of increasing steric bulk at the position ortho to the N=N bond and their corresponding chloro(hexamethylbenzene)ruthenium(II) complexes were synthesized. The latter bearing mono-substituted ligands exhibited an exocyclic azo bond under the E configuration, and underwent reversible E → Z photoisomerization upon irradiation with visible light, followed by thermal Z → E back isomerization upon resting in the dark at 20 °C. In contrast, the corresponding 2,6-dimethyl substituted azobenzene complex, while also exhibiting an exocyclic azo bond, was isolated as the Z- isomer and underwent uncommon solvent dependent irreversible photodissociation of azobenzene ligand upon visible light irradiation. Valuable insights into the photophysical and structural properties of these complexes were gained by combination of computational and X-ray diffraction studies.