Atropisomerism and Conformational Dynamics in Dioxa[6]helicene Enamine Constructs with Near-Infrared Absorption and Emission

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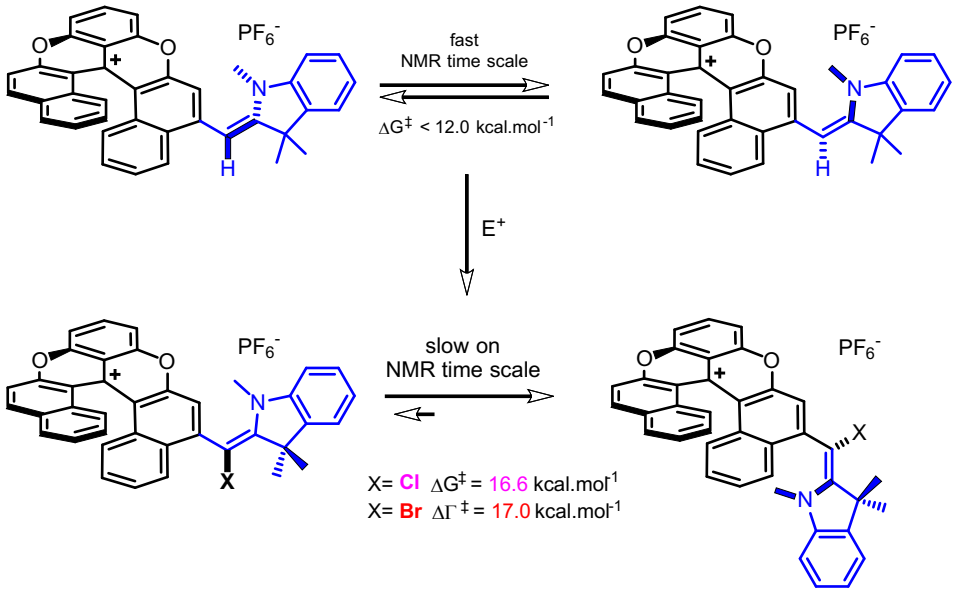
Helicenes are an important class of chiral *ortho*-fused polyaromatic derivatives characterized by an asymmetry originating from the steric repulsion between terminal substituents or rings.[1] In previous studies, direct oxidative cross-coupling between dioxa[6]helicene and methylindoline fragments was realized.[2] X-ray structural analysis revealed an out-of-plane twist of the cyclic enamine moiety, giving rise to two atropisomers in rapid conversion on the NMR time scale, even at –90 °C. Herein, alkene functionalization by electrophilic substitution is reported. As a consequence, barriers of epimerization increase up to 17 kcal.mol^{-1} (slow exchange NMR time scale). Detailed conformational investigations reveal unexpected geometrical changes.[3] In addition to the strong donor-acceptor character of hemicyanine core, halogens (F, Cl, Br) promote strong bathochromic shifts, extending absorption and emission further into the near infrared region (NIR), a domain of light particularly advantageous for biological applications.[4]



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