Effect of *meta*-methyl Substituents on Photochemical Properties of tetra-*ortho*-Chloro Azobenzenes

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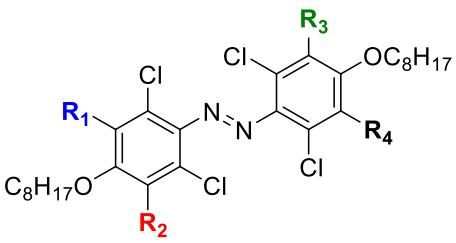
Keywords: Azobenzene; Structure-properties Relationship; Photoswitch; Photochromism

Azobenzene is a versatile photoisomerizable compound whose properties can be readily adjusted by various substituents. Many studies focused on effect of *ortho* and *para* substituent, owing to more pronounced effect of substituting on that position.[1] One of the most prominent effect is the bathochromic shift of azobenzenes by *ortho* substitution, particularly with halogen and methoxy.[2] On the other hand, *meta* substituent effect receive less attention due to its weaker effect on azobenzene properties. Therefore, we are interested to explore the effect of *meta*-mehyl substituents on photochemical properties of tetra-*ortho*-chloro azobenzenes bearing medium-length alkoxy chains on their para position.

Compound **1-6** were synthesized from with Pd-catalyzed late-stage halogenation[3] as a key step. All the compounds showed a redshift of nπ* band towards visible light region. The variation of number and position of *meta*-methyl groups subtly shift absorption bands in both *trans* and *cis* isomers. This variation in absorption bands affect the photostationary state (PSS) isomer ratio. Furthermore, we found that *meta*-methylation pattern also affects thermal stability of *cis* isomer. Generally, it can be said that the *cis* isomer becomes more stable with more *meta* methyl group. This effect is subtle except for fully-methylated compound **6**. This phenomenon can be applied to “fine-tune” the properties of various azobenzene-based systems in the future.



1 $R_1 = R_2 = R_3 = R_4 = H$

2 $R_1 = CH_3$, $R_2 = R_3 = R_4 = H$

3 $R_1 = R_3 = CH_3$, $R_2 = R_4 = H$

4 $R_1 = R_2 = CH_3$, $R_3 = R_4 = H$

5 $R_1 = R_2 = R_3 = CH_3$, $R_4 = H$

6 $R_1 = R_2 = R_3 = R_4 = CH_3$

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