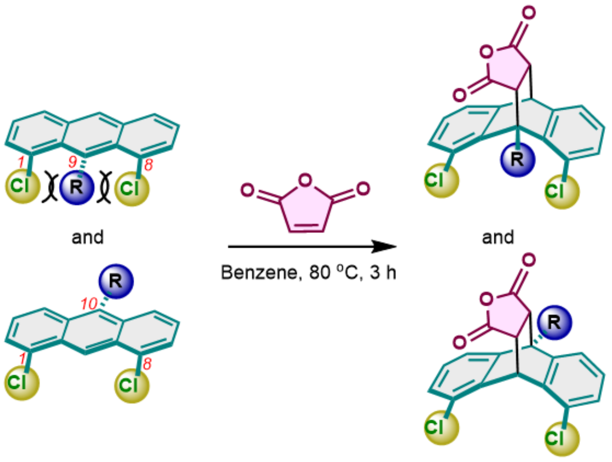
Non-Electronic Activation on Anthracene Ring by Steric Repulsion between Substituents

([1]*Graduate School of Engineering Science, Kochi University of Technology,* [2]*Research Center for Molecular Design, Kochi University of Technology*) ○Annisa Indah Reza,[1] Kento Iwai,[1,2] Nagatoshi Nishiwaki[1,2]

Keywords: Non-electronic activation; Steric repulsion; Ring distortion; Anthracene; Diels-Alder reaction

In our previous work, aromatic distortion of 1-methylquinolinium salts[1] and 1,8-dimethyl- and 1,8-diidonaphthalenes[2,3] was achieved using an intense steric repulsion between the *peri*-substituents. The reactivity was found to be higher as the substituent was bulkier. Herein, we extensively explored this non-electronic activation into another aromatic system using 1,8-dichloroantracene, where its 9- and 10-positions are separately substituted with methoxy and alkyl groups. The anthracene framework was distorted, especially in the vertical direction, compared to its 10-substituted counterparts, and the distortion was significant as the bulkiness of the substituent was larger. Thus, the distortion of the anthracene ring is due to the steric repulsion with chloro groups at the *peri*-positions. The Diels-Alder reactions with maleic anhydride were conducted to evaluate the distorted anthracenes' activation. Generally, the product yields became higher as the substituent was bulkier. Moreover, anthracene possessing an isopropyl group was more highly activated than derivative with a strongly electron-donating methoxy group, indicating the anthracene framework was activated non-electronically rather than influenced electronically.



R	Yield/%	Recovery/%
OMe	75	18
Me	79	15
Et	75	20
^{n}Pr	80	12
^{i}Pr	91	5

R	Yield/%	Recovery/%
OMe	53	36
Me	50	35
Et	63	20
^{n}Pr	58	30
^{i}Pr	75	12

1) *Bull. Chem. Soc. Jpn.* **2020**, *93*, 50–58. 2) *Molecules* **2023**, *28*, 5343. 3) *J. Org. Chem.* **2023**, *88*, 9409–9412.