Steric Repulsion between *peri*-Substituents Distorting Naphthalene Ring

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We have already demonstrated that steric repulsion between *peri*-substituents distorts the coplanarity in 1-methyl-3,6,8-trinitro-2-quinolone[1] and 1-methylquinolinium salts[2] frameworks, making them sensitive for functionalization merely relying on their non-electronic activation. This result intrigues us to extend the concept to a nonpolar aromatic carbon ring such as naphthalene. We studied the correlation between the substituents' bulkiness and the framework's distortion using brominated 1,8-dimethylnaphthalene. X-Ray crystallography revealed that 1,8-bis(bromomethyl)naphthalene **1** has a vertical strain (θ = 11.0°) which distorts the coplanarity of the naphthalene ring. On the other hand, the vertical distortion of 1,8-bis(dibromomethyl)naphthalene **2** was found to be smaller (θ = 8.3°) even though its *peri*-substituents became bulkier. Indeed, this framework was also horizontally distorted, as shown by the increasing distance between carbons at C1-C8 positions and the noticeable deviation angles in C1-C9-C10/C8-C9-C10 compared to the origin ring (119°). It was confirmed that the naphthalene ring was successfully distorted using steric repulsion between the *peri*-substituents.

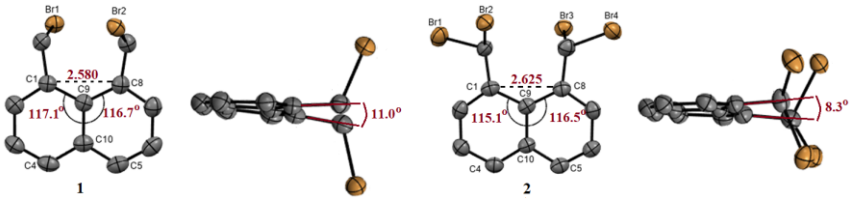
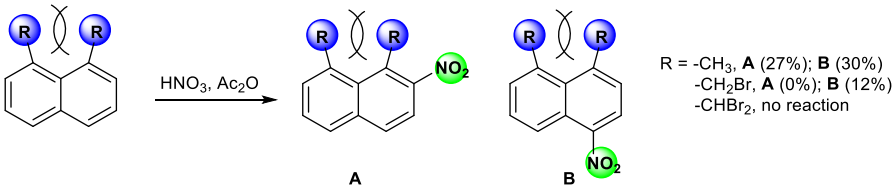


Figure 1. Horizontal and vertical strain evaluation

Since substrate **1** and **2** is highly distorted, it is also considered to be activated non-electronically. Therefore, a nitration reaction was employed to evaluate the reactivity to confirm this hypothesis. Unfortunately, the result is likely still influenced by the electronic effect. For instance, a *para*-nitration product (12%) was obtained using **1**, while **2** failed under the same condition, which might be due to the electron-withdrawing effect of bromo groups.



Scheme 1. Nitration reaction of distorted naphthalene

1) X. Chen, *Tetrahedron*. **2013**, *69*, 4624. 2) K. Iwai, *Bull. Chem. Soc. Jpn*. **2020**, *93*, 50.