Diphenyl Disulfide Derivatives Dominated by Halogen Bonds Superior to π-π Interactions

(1 *Institute of Industrial Science, The University of Tokyo*, 2 *Environmental Science Center, The University of Tokyo*) ○Hao Wu,[1] Hitomi Tabuchi,[1] Qi Zhou,[1] Isao Yoshikawa,[1] Hirohiko Houjou,[1,2] Tsuyoshi Minami[1]

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In the conventional discussion on an aggregation of aromatic molecules in the solid-state, halogen bonds could be just supplementary interactions in comparison to π-π stacking. In contrast, we observed both type I and more important type II halogen···halogen short contacts (*i.e.*, halogen bonds) (Fig. 1(a)) while no π-π interactions in the crystals of disulfaneyl diiodobenzene derivatives (Fig. 1(b)). By considering that π-π interactions can be found in 1,1'-disulfanediyl-2,2'-dimethylbenzene,[1] halogen bonds are superior to π-π interactions in those disulfaneyl diiodobenzene derivatives.

The molecular crystals of **1** and **3** (note: the state of **2** is liquid at room temperature) were characterized by single-crystal X-ray diffraction and Hirshfeld surface analysis (Fig. 1(c),(d)). The crystal space groups of **1** and **3** are $I4_1/a$ and *Ccc*2, respectively. The Hirshfeld surface shows a difference in the intensity of molecular interactions (strength order: red > white > blue). The red and white color regions of halogen bonds were observed while no π-π interactions appeared. As shown here, we demonstrated that halogen bonds are capable of driving crystallization superior to π-π interactions, and such findings can be introduced in the design of supramolecular materials.

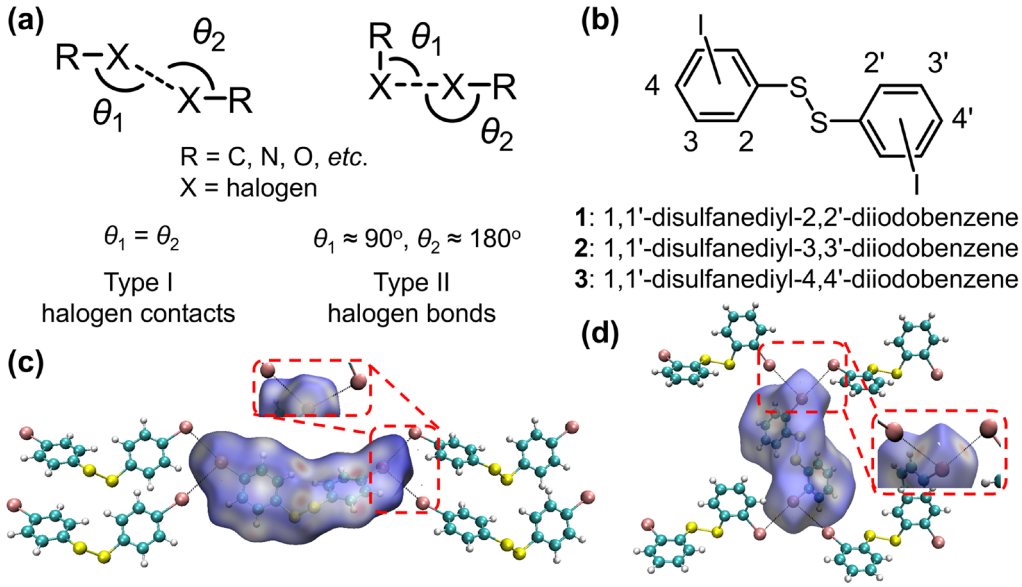

Fig. 1 (a) The structural scheme for halogen contacts (Type I) and halogen bonds (Type II). (b) The chemical structure of disulfanediyl diiodobenzene derivatives (**1**-**3**). The Hirshfeld surface analysis of crystal structures of (c) **3** and (d) **1**.

1) R. A. Stockman, et al., *Chem. Commun*. **2014**, *50*, 12630.