

Herringbone structures of 2,7-dihalogenated acridine tailored by halogen–halogen interactions



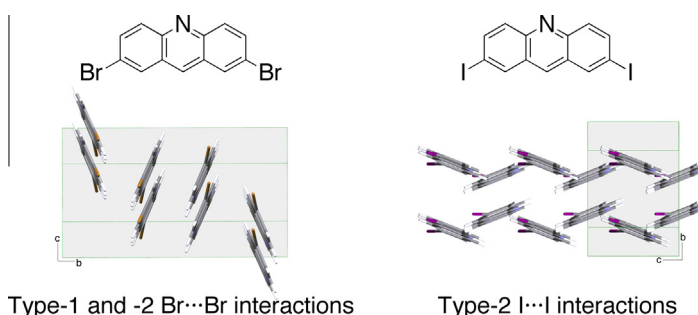
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HIGHLIGHTS

- 2,7-Dibromo- and 2,7-diiodoacridines (**2** and **3**) were synthesized.
- In the crystals, **2** and **3** were packed in a herringbone way.
- The Type-I and Type-II halogen–halogen interactions were shown in **2**.
- Only the Type-II interaction was shown in **3**.

GRAPHICAL ABSTRACT



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ABSTRACT

The crystal structures of the 2,7-dibromo- and 2,7-diiodoacridines (**2** and **3**) were determined by single-crystal X-ray diffraction analysis. Molecules of the brominated **2** were assembled through different types of halogen–halogen interactions (Type-I and Type-II). Conversely, molecules of the iodinated **3** were assembled only through Type-II interactions. Although both compounds were packed in a herringbone way, the intermolecular π - π stacking was observed only in the brominated **2**. In the solution and solid-state absorption spectra, a bathochromic shift in the absorption was observed, as the mass of the halogen atoms increased. Theoretical calculation indicated a substituent effect of the halogen on the π -orbital of the acridine moiety. In the solid state, the iodinated **3** exhibited a significant absorption in the orange-to-red wavelength region.

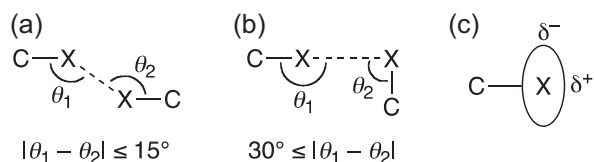
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Introduction

The assembly of π -conjugated compounds is of significant interest because the physical and electronic properties significantly depend on the intermolecular orientation of the compounds. Crystal engineering of π -conjugated compounds is especially important in the design of organic electronic materials such as OFET [1] or OLED [2]. Acridine is often used as a luminophore [3,4], electron-acceptor [5], and DNA-intercalator [6,7]. In

crystallography, acridine is well known to crystallize in seven polymorphic forms [8–14]. The complicated polymorphism of acridine is due to various intermolecular interactions, i.e., π - π , CH- π , and CH-N interactions. If the morphology of the acridine crystal can be controlled, acridine could find application as an organic functional material. The crystallization of acridine has been controlled by utilizing solvents [15] or through the deuterium isotope effect [16]. Halogen–halogen interactions are attractive forces that have been utilized in crystal engineering [17–24]. Although halogen–halogen interactions are a result of relatively weak van der Waals forces, they can play a significant role in defining the orientation of molecules [25]. Halogen–halogen interactions belong

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Scheme 1. Halogen-halogen interactions. (a) Type-I interactions, (b) Type-II interactions, and (c) polar flattening effect in halogenated organic compounds.

to two types based on their different geometries (Scheme 1) [26–28]. Type-I is the van der Waals type interaction to afford a symmetrical arrangement. Type-II is recognized as a Coulombic donor-acceptor interaction to afford a perpendicular arrangement. Allen concluded that halogens interact with nucleophiles in a “head-on” way and electrophiles in a “side-on” way (Scheme 1c) [29]. The donor-acceptor interaction between halogens in the Type-II way leads to an accurate molecular arrangement. The Type-II interaction is dominant when going from Cl to I because the heavier atom becomes more polarized.

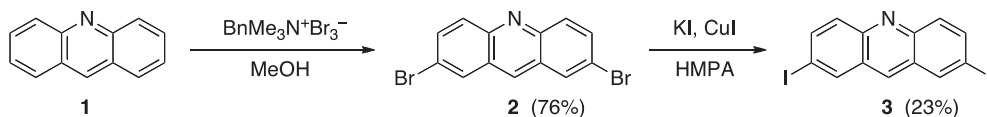
Despite the importance of both acridine and halogen-halogen interactions, there have been only two reports of crystallographic analysis of halogenated acridines without any other substituents; 9-chloroacridine [30] and 3,5,6,7,8-pentafluoroacridine [31]. Halogen-halogen interaction was seen only in 3,5,6,7,8-pentafluoroacridine. However, there are no reports of the structural analysis of acridines bearing heavier halogen atoms, which afford stronger interactions than fluorine. We have now synthesized and crystalized acridine derivatives bearing bromine or iodine, which are expected to form crystal structures that are controlled by halogen-halogen interactions.

Results and discussions

2,7-Dibromoacridine (**2**) was synthesized from acridine (**1**) according to the literature procedure [32] (Scheme 2). This synthetic method selectively gives **2** without any other multi-brominated products. 2,7-Diiodoacridine was synthesized by the iodination of **2** with KI and CuI [33]. In this study, crystallographic analysis of the compounds was initially performed.

Single-crystal X-ray diffraction analysis was used to determine the crystal structures of **2** and **3**. ORTEP diagrams are shown in Figs. 1 and 2. One molecule of **2** is present in an asymmetric unit. Compound **3** is positioned at the center of the mirror plane. The geometries of **1–3** were optimized by DFT calculation at the CAM-B3LYP/DGTZVP level. The structural parameters of both experimental and calculated structures of **1–3** are shown in Table 1. The theoretical calculation well reproduced the experimental structures within the deviation of DFT calculation. The acridine moieties are nearly planar with root-mean square deviations (RMSD) of 0.022 and 0.037 Å for **2** and **3**, respectively. The two bromine atoms of **2**, Br1 and Br2, are slightly separated from the least-square plane with the distances of 0.064 and 0.186 Å, respectively. The iodine atoms of **3** are also separated by a distance of 0.318 Å. These values indicate a more planar structure for **2** than for **3**.

In the crystal of **2**, a π dimer is formed through a stacking interaction with a distance of 3.3660(6) Å (Fig. 3a). The π dimers are arranged in a herringbone way with space group $P2_1/c$.



Scheme 2. Synthesis of 2,7-halogenated acridines.

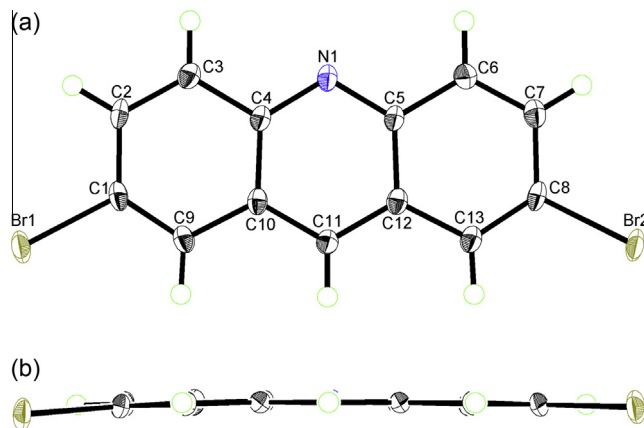


Fig. 1. ORTEP drawing of **2** with the 50% probability ellipsoid from (a) top and (b) side views.

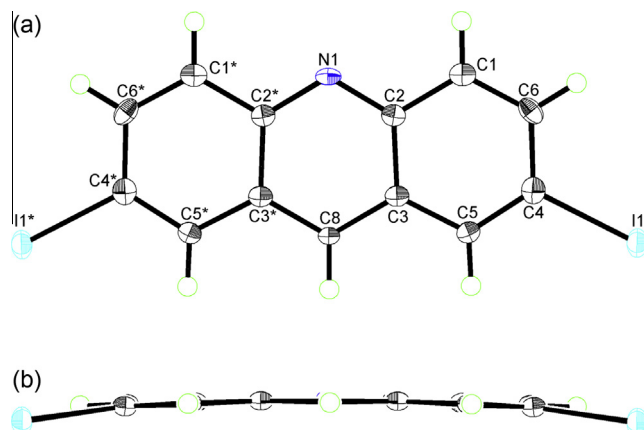


Fig. 2. ORTEP drawing of **3** with the 50% probability ellipsoid from (a) top and (b) side views.

Herringbone structures, which are generally observed in linear π -conjugated molecules, are important for high performance organic materials [34,35]. Noteworthy is that the bromine atoms make contact with each other in the crystal of **2** (Fig. 3b). This fact suggests that the assembly of the bromine atoms plays an important role in the construction of the packing structure.

In the crystal of **3**, molecules are arranged in a herringbone way (Fig. 4a) with the non-centrosymmetric space group $Cmc2_1$. In contrast to **2**, there is no π - π stacking in **3**. The iodine atoms contact each other in a similar way to **2** (Fig. 4b).

We investigated the closely located halogen atoms to shed light on the halogen-halogen interaction (Table 2). In the crystal **2**, one bromine atom contacts with two other bromine atoms with distances of 3.668 and 3.708(3) Å. These values are close to the sum of the van der Waals radii, 3.70 Å, suggesting halogen-halogen interactions. In the $\text{Br1} \cdots \text{Br2}^i$ contact, the carbon-halogen-halogen angles, θ_1 and θ_2 , are 141.0° and 127.6°, respectively. The θ_1 and θ_2 values indicate a Type-I interaction. On the other hand,

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