#### Journal of Molecular Structure 1093 (2015) 59-64

Contents lists available at ScienceDirect

### Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

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



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#### HIGHLIGHTS

- G R A P H I C A L A B S T R A C T
- 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 halogenhalogen interactions were shown in **2**.
- Only the Type-II interaction was shown in **3**.

#### ARTICLE INFO

Article history: Received 19 January 2015 Received in revised form 20 March 2015 Accepted 23 March 2015 Available online 31 March 2015

Keywords:AcridineHerringbone $\pi$ - $\pi$  stackingHalogen-halogen interactionAtoms-in-molecule

#### Introduction

The assembly of  $\pi$ -conjugated compounds is of significant interest because the physical and electronic properties significantly depend on the intermolecular orientation of the compounds. Crystal engineering of  $\pi$ -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

# Type-1 and -2 Br···Br f(x) = 0

#### ABSTRACT

The crystal structures of the 2,7-dibromo- and 2,7-diiodoacridines (**2** and **3**) were determined by singlecrystal 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  $\pi$ – $\pi$  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  $\pi$ -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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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.,  $\pi$ – $\pi$ , CH– $\pi$ , 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 crystallized 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 multibrominated 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 leastsquare 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  $\pi$  dimer is formed through a stacking interaction with a distance of 3.3660(6) Å (Fig. 3a). The  $\pi$  dimers are arranged in a herringbone way with space group  $P2_1/c$ .



**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  $\pi$ 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  $\pi$ - $\pi$  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 Br1…Br2<sup>i</sup> contact, the carbon–halogen– halogen angles,  $\theta_1$  and  $\theta_2$ , are 141.0° and 127.6°, respectively. The  $\theta_1$  and  $\theta_2$  values indicate a Type-I interaction. On the other hand,



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

#### Table 1

Selected bond lengths (Å), bond angles (°) torsion angles (°), and RMSDs in the acridine units (Å) of experimental and calculated structures of 1-3.

	Experimental	Calculated
	1	
C1–N1 (Å)	1.347	1.339
C2–N1 (Å)	1.348	1.339
C1-N1-C2 (°)	117.7	118.5
RMSD (Å)	0.034	0
	2	
C4–N1 (Å)	1.347(3)	1.338
C5–N1 (Å)	1.349(3)	1.338
Br1–C1 (Å)	1.898(2)	1.902
Br2-C8 (Å)	1.898(2)	1.902
C4-N1-C5 (°)	117.5(2)	118.4
RMSD (Å)	0.022	0
	3	
C2-N1 (Å)	1.344(7)	1.338
I1–C4 (Å)	2.086(4)	2.110
C2-N1-C2 <sup>i</sup> (°)	117.9(9)	118.4
RMSD (Å)	0.037	0

Symmetric operation, i: -x, +y, +z.

the Br1…Br2<sup>ii</sup> contact exhibited very different  $\theta_1$  and  $\theta_2$  values of 166.6° and 113.4°, which indicate a Type-II interaction. Thus, the packing of **2** is constructed through two different types of halogen–halogen interactions. In crystal **3**, one iodine atom also contacts with two other iodine atoms with the crystallographically identical distance of 4.063 Å, close to the I…I van der Waals distance 4.05 Å. The  $\theta_1$  value of the I…I<sup>iii</sup> contact, 156.5°, is much larger than the  $\theta_2$  value of 101.8°. Thus, the packing of **3** is constructed though only Type-II interactions. The fact that the intermolecular  $\pi$ – $\pi$  stacking was observed only in brominated **2** might result from the difference in their halogen–halogen interactions.

Theoretical calculations were performed to gain insight into the halogen–halogen interactions. An atoms-in-molecule (AIM) analysis [36] for the geometry of the contacted molecules of **3** gave the charge density  $\rho(\mathbf{r})$  and the Laplacian  $\Delta\rho(\mathbf{r})$  map (Fig. 5). A bond critical point (BCP) is observed in the center of the two iodine atoms. The existence of BCP is clearly indicative of the interatomic interaction. In the BCP, the  $\rho(\mathbf{r})$  value is  $+6.5 \times 10^{-3} \text{ e} \text{ a}^{-3}$ . In general, a negative value of the Laplacian  $\Delta\rho(\mathbf{r})$  at the BPC indicates that the atomic interaction is predominantly a closed-shell interaction, while a positive value of  $\Delta\rho(\mathbf{r})$  indicates that it is dominated by shared electron (covalent) interactions. The  $\Delta\rho(\mathbf{r})$  values at the BPC between the iodine atoms is the negative value of  $-4.0 \times 10^{-3} \text{ e} \text{ a}^{-5}$ , which is indicative of the closed-shell interaction. These results are consistent with the reported AIM analysis for the Cl...Cl interaction [37].

Thermal gravimetric analysis of **2** and **3** showed sharp, two-step mass losses (Fig. 6). Differential thermal analysis showed exothermic peaks when the mass loss started. These results suggested that most of compounds was sublimated against the intermolecular interactions. The onset temperatures were 210 and 276 °C for **2** and **3**, respectively. These values are higher than that of **1**, 179 °C [38]. Thus, the halogen–halogen interactions appear to contribute to the stabilization of the crystalline state, and the I–I interactions in **3** are probably stronger than the Br–Br interactions in **2**.

The UV–vis absorption spectra of **1–3** were measured in DMSO (Fig. 7). All the compounds showed an absorption in the 300–400 nm region. The absorption-maximum wavelength increases (357 nm for **1**, 368 nm for **2**, 374 nm for **3**) as the mass of the bounded atoms, H (**1**), Br (**2**), or I (**3**), increases. A time-dependent DFT calculation was performed to clarify the spectra (Fig. 8 and Table 3). The HOMOs and LUMOs are assigned to the  $\pi$  orbitals of the acridine moiety. The HOMO–LUMO gaps decrease in the



Fig. 3. Packing diagram of 2 from (a) *a*-axis and (b) *c*-axis.



Fig. 4. Packing diagram of 3 from (a) *a*-axis and (b) *b*-axis.

order of **1–3**. The lowest singlet excitation states ( $S_1$ ) for **1–3** were assigned to the  $\pi$ – $\pi$ \* transitions of the acridine units. The excitation energies for  $S_1$  decreased in the same order as the gaps. Thus, the substituent effect on the spectra is due to the orbital interaction of the acridine  $\pi$ -orbital with the halogen atoms.

In the reflectance spectra of the powdered samples of **1–3**, a red-shifted broad absorption was observed and compared to the solution spectra. The absorbance above 600 nm is in the order of **1–3**. The iodinated **3** exhibited a significant absorption in the

#### Table 2

Halogen–halogen distances (*d*), carbon–halogen–halogen angles ( $\theta_1$  and  $\theta_2$ ), and carbon–halogen–halogen–carbon torsion angles ( $\phi$ ) in **2** and **3**.

	d (Å)	$\theta_1$ (°)	$\theta_2$ (°)	φ (°)
Br1…Br2 <sup>i</sup>	3.668	141.0	127.6	106.5
Br1…Br2 <sup>ii</sup>	3.708	166.6	113.4	147.5
I1…I1 <sup>iii</sup>	4.063	156.5	101.8	155.9

Symmetric operation, i: -1 + x, 1/2-y, -1/2 + z, ii: -1 + x, +y, -1 + z, iii: 1/2-x, 1/2-y, 1/2 + z or -1/2 + x, 1/2-y, 1/2 + z.

orange-to-red region, 500–700 nm. The far-shifted absorption might be ascribed to the intermolecular interactions of the acridines.

The luminescence spectra of **1–3** are sharp, mirror images of the absorption spectra (Fig. 9). The maximum wavelengths (409 nm for **1**, 424 nm for **2**, 428 nm for **3**) are in the order of those in the absorption spectra.

#### Experimental

#### Materials and methods

All chemicals were reagent grade and used without further purification. All reactions were performed under nitrogen atmosphere. The NMR spectra were recorded on Bruker AVANCE400 (400 MHz) spectrometer. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. In the NMR measurements, tetramethylsilane was used as the internal standard (0 ppm). UV-vis absorption spectra were recorded on JASCO Ubest V-670. Solid-state reflectance spectra were measured by using an integrating sphere instrument equipping with the spectrometer. Gas chromatography-mass spectra were recorded on Shimazu QP-2100 by electron-ionization method. Elemental analysis was performed in Department of Chemistry, University of Tsukuba.

#### *Synthesis of 2,7-dibromoacridine (2)*

2,7-Dibromoacridine (**2**) was prepared according to the literature [32]. Pale yellow powder, yield 76%: <sup>1</sup>H NMR (400 MHz,



**Fig. 5.** Calculated  $\Delta \rho(\mathbf{r})$  maps in the C-I···I-C plane. The positive and negative values are represented in green and black colors, respectively. Only an I···I BCP is depicted, while the other BCPs ascribed to intermolecular bonding are omitted. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 6. Thermal gravimetric and differential thermal analyses of (a) 2 and (b) 3.

DMSO-*d*<sub>6</sub>):  $\delta$  9.19 (s, 1H), 8.57 (d, *J* = 2.2 Hz, 2H), 8.14 (d, *J* = 9.2 Hz, 2H), 8.04 (dd, *J* = 9.2, 2.2 Hz, 2H); MS (EI): *m*/*z* = 337 [M]<sup>+</sup>. Anal for C<sub>13</sub>H<sub>7</sub>NBr<sub>2</sub>, C; 46.33, H; 2.09, N; 4.16; found, C; 46.04, H; 2.04, N; 4.00.

#### Synthesis of 2,7-diiodoacridine (3)

A mixture of 2,7-dibromoacridine (**2**) (337 mg, 1.00 mmol), KI (5.01 g, 30.2 mmol), and CuI (1.90 g, 9.97 mmol) in HMPA (10 mL) was stirred at 155 °C for 72 h. After the reaction mixture was cooled to room temperature, 100 mL of water was added. Brown precipitate was collected and then Soxhlet extraction with toluene gave pale brown solid. Crystallization of crude solid from ethyl acetate gave yellow powder of **3** (101 mg, 23%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.99 (s, 1H), 8.68 (d, *J* = 2.0 Hz, 2H), 8.08 (dd, *J* = 9.2, 2.0 Hz, 2H), 7.92 (d, *J* = 9.2 Hz, 2H); MS (EI): *m/z* = 443 [M]<sup>+</sup>. Anal for C<sub>13</sub>H<sub>7</sub>NI<sub>2</sub>, C; 36.23, H; 1.64, N; 3.25; found, C; 36.05, H; 1.65, N; 3.13.

#### X-ray crystallographic analysis

Single crystals of **2** and **3** suitable for X-ray diffraction were obtained by recrystallization from the hot-DMSO solution. The



**Fig. 7.** UV-vis absorption spectra (lines) in DMSO  $(2.5 \times 10^{-5} \text{ M})$  and reflectance spectra of powder samples (dots) of **1** (black), **2** (red), and **3** (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 8. Kohn-Sham frontier orbitals of 1-3 at the CAM-B3LYP/DGTZVP level.

 Table 3
 Calculated singlet excited energies of 1–3 at the CAM-B3LYP/DGTZVP level.

		Transition (composition)	Excitation energy (nm) (oscillator strength)
1	S <sub>1</sub>	HOMO $\rightarrow$ LUMO (97%)	333 (0.0742)
2	S <sub>1</sub>	HOMO $\rightarrow$ LUMO (97%)	337 (0.0544)
3	S <sub>1</sub>	$HOMO \rightarrow LUMO (96\%)$	340 (0.0462)

X-ray diffraction intensities were collected on a CCD diffractometer at 120 K using Mo K $\alpha$  (graphite-monochromated,  $\lambda$  = 0.71073 Å) radiation. The data were integrated with SAINT (Bruker, 2007), and an empirical absorption correction was applied with SADABS (Bruker, 2007). The structure was solved by the direct method of SHELXS-97 and refined using the SHELXL-97 program [39]. All of the positional parameters and thermal parameters of non-hydrogen atoms were anisotropically refined on  $F^2$  by the full-matrix least-squares method. Hydrogen atoms were placed at the calculated positions (C-H = 0.95 Å) and refined riding on their corresponding carbon atoms with  $U_{iso}(H) = 1.2U_{eq}(C)$ . Structural refinement of **3** was completed as a perfect racemic twining (operation: -1000-1000-1). The crystallographic data are listed in Table 4. The detailed crystallographic information files (CIFs) have been deposited in the Cambridge Crystallographic Database Centre (CCDC). Deposits numbered CCDC-1043816 and 1043817 contain the supplementary crystallographic data for structures 2 and 3, respectively.



**Fig. 9.** Luminescence spectra of **1** (black), **2** (red), and **3** (blue) in DMSO ( $2.5 \times 10^{-5}$  M, excited at 380 nm). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 4			
Crystallographic data	of <b>2</b>	and 3.	

	2	3
Formula	C <sub>13</sub> H <sub>7</sub> NBr <sub>2</sub>	$C_{13}H_7NI_2$
Formula weight	337.02	431.00
Crystal size (mm <sup>3</sup> )	$0.20\times0.20\times0.03$	$0.20\times0.10\times0.05$
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	Cmc2 <sub>1</sub>
a (Å)	13.088(3)	27.058(4)
b (Å)	14.226(3)	7.0233(9)
c (Å)	5.9330(12)	6.0636(7)
α (°)	90	90
β (°)	97.624(2)	90
γ (°)	90	90
$V(Å^3)$	1094.9(4)	1152.3(2)
Ζ	4	4
$D_{\text{calcd}} (\text{g cm}^{-3})$	2.045	2.484
Collected/unique	6100/2457	3075/1257
R <sub>int</sub>	0.0622	0.0185
$\theta_{\max}$ (°)	27.571	27.545
F <sub>000</sub>	648	792
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	7.370	5.427
Limiting indices	$-16 \leqslant h \leqslant 15$	$-35 \leqslant h \leqslant 31$
	$-18 \leqslant k \leqslant 18$	$-9 \leqslant k \leqslant 5$
	$-7 \leqslant l \leqslant 6$	$-7 \leq l \leq 7$
Parameters/restraints	145/0	76/0
Goodness of fit $(F^2)$	1.065	1.020
$R_1 \ (I > 2\sigma(I))$	0.0342	0.0135
wR <sub>2</sub> (all date)	0.0938	0.0334

 $R_1 = \sum ||F_o| - |F_c| / \sum |F_o|, \ wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$ 

#### Thermal analyses

Thermal gravimetric and differential thermal analyses were performed at the same time on a Seiko Instruments Inc. EXSTAR7000: TG/DTA7300 in the Chemical Analysis Center at the University of Tsukuba. Samples were placed in aluminum pans and heated at a constant rate of 5 °C/min under argon atmosphere. Alumina powder was used as a reference.

#### Computational study

Quantum chemical calculations were performed using Gaussian 09 software [40]. The geometries for single molecules are optimized using the CAM-B3LYP functional [41] with DGTZVP basis set [42]. Time Dependent Density Functional Theory (TD-DFT) was used for the vertical excitation energies and oscillator strengths at the optimized geometries. Atoms-in-molecule (AIM)

analysis was performed using AIM2000 software [43] at the crystal structure obtained by X-ray diffraction analysis.

#### Conclusion

The crystal structures of the 2,7-dibromo- and 2,7-diiodoacridines (2 and 3) were determined by single-crystal X-ray diffraction analysis. Although both compounds were packed in a herringbone way, the intermolecular  $\pi$ - $\pi$  stacking was observed only in the brominated 2. Interestingly, alternative-layers of acridine and the halogen were constructed in both crystals. The halogen-halogen bonding was characterized by X-ray and AIM analyses. 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. Thermal analysis supported that the halogen-halogen interactions stabilize the crystal of acridine. In the absorption and luminescence spectra, a bathochromic shift was observed, as the mass of the halogen atoms increased. Theoretical calculation indicated a substituent effect of the halogen on the  $\pi$ -orbital of the acridine moiety. In the solid state, the iodinated 3 exhibited a significant absorption in the orange-to-red region. We will investigate the relationship between crystal structures and solid-state spectra. This study demonstrated that the halogen-halogen interactions afford the herringbone assembly of acridine, and the assembled structures are dependent on different types of interactions.

#### Acknowledgement

We are grateful to Prof. G.J. Richards (Ochanomizu University) for helpful discussion.

#### Appendix A. Supplementary data

These data can be obtained free of charge via www.ccdc.cam.ac. uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk]. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2015.03.042. These data include MOL files and InChiKeys of the most important compounds described in this article.

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