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Crystal engineering of brominated tectons: *N*-methyl-3,5-dibromopyridinium iodide gives particularly short C–Br···I halogen bonding†

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The crystal matrix of *N*-methyl-3,5-dibromopyridinium iodide is constituted of infinite helices where the cation and the anion alternate and are bound by the second shortest reported C–Br···I halogen bonding. The electron poor pyridinium scaffold is particularly effective in boosting the electron acceptor ability of bromine substituents.

The modular design of supermolecules and their directed assembly into higher aggregates are highly important steps in crystal engineering. Numerous examples using self-assembly techniques, host–guest chemistry, or template-assisted syntheses are described in the literature.[1] These concepts are nicely illustrated in recent works where intriguing architectures based on *hydrogen bonding* were constructed.[2]

We are involved in an on-going research project on self-assembly processes based on *halogen bonding*; that is the n → σ* electron donation from neutral or anionic lone-pair possessing atoms (Lewis bases, halogen bonding acceptors) to halogen atoms (Lewis acids, halogen bonding donors).[3] In most of our studies we have been using haloperfluorocarbon tectons[4] as the presence of fluorine, a strong electron withdrawing atom, boosts the ability of adjacent iodine, bromine, and chlorine atoms to work as Lewis acids.[5] Iodine derivatives are stronger halogen bonding donors than bromine analogues.[3a,b,6] For this reason, iodocarbon modules involved in self-assembly processes are much more numerous than and structurally different to bromocarbon modules. Indeed, the presence of adjacent electron withdrawing groups often becomes a prerequisite for bromocarbon involvement in self-assembly processes. For instance, diiodobenzenes give solid-co-crystals with dipyridyl derivatives, dibromobenzenes do not, but dibromotetrafluorobenzenes do self-assemble with dipyridyl derivatives. A small library of halogen bonded co-crystals could be obtained from these latter Lewis acids.[7]

As a part of our studies aimed at expanding the palette of bromocarbon derivatives that work as strong electron acceptors,[7,8] it is described here how the two bromine atoms of *N*-methyl-3,5-dibromopyridinium iodide **3b** are both halogen bonded to the iodide anion in the crystal. Both the iodide anion and the pyridinium cation work as bidentate modules. Infinite helical arrangements are formed where the electron donor and acceptor modules alternate (Fig. 1, see ESI† for a rotatable version of Fig. 1). The C–Br···I halogen bonding nearly equals the shortest reported in the crystallographic literature proving the electron poor pyridinium scaffold is particularly effective in boosting the electron accepting ability of bromine atoms, namely their ability to work as strong halogen bonding donors.

Pursuing the formation of infinite chains, we started our studies from a dibromopyridinium derivative. The 3,5 isomer was preferred over the others as it is the less hindered isomer and steric hindrance is known to disfavour halogen bonding formation.[3c,9] Emblematically, 4-iodopyridine gives very short

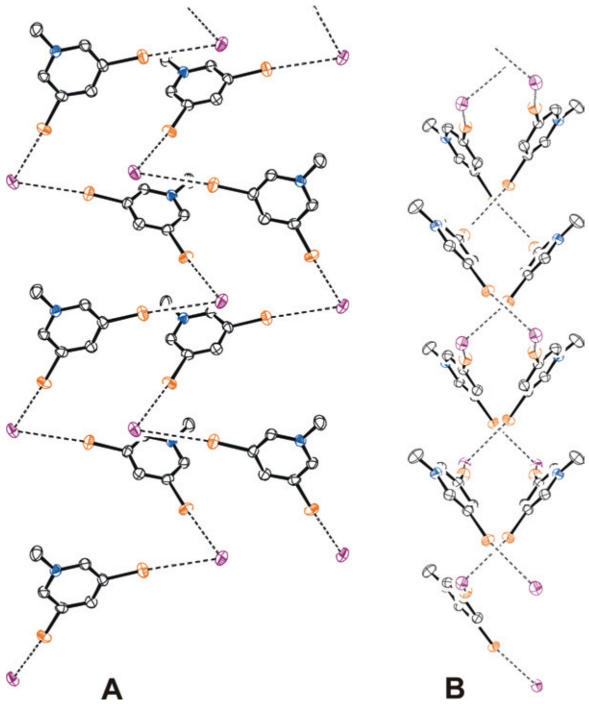

Fig. 1 Helices of **3b** viewed down the *a*-axis (A) and *c*-axis (B). Hydrogen atoms have been omitted for simplicity; dashed lines are halogen bondings. Colours are as follows: carbon, black; nitrogen, blue; bromine, orange, iodine, purple.

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† Electronic supplementary information (ESI) available: rotatable 3D versions of Fig. 1 and Fig. 3. See http://www.rsc.org/suppdata/nj/b4/b401421a/

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nitrogen–iodine contacts[10] while in 2,6-diiodopyridine no nitrogen–iodine interaction is present.[11]

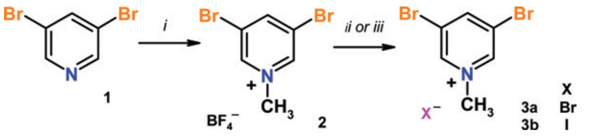
3,5-Dibromopyridine (**1**) was methylated with trimethlyoxonium tetrafluoroborate[12] in very high yield (Scheme 1). Anion methathesis was performed by dissolving the obtained fluoroborate **2** in acetonitrile and by adding tetrabutylammonium bromide or iodide. The pyridinium halides **3a**,**b** precipitated in very high yields and in pure forms.

3a,**b** are less soluble in most organic solvents than **2**, consistent with a stronger cation–anion association in pyridinium halides **3a**,**b** due to halogen bondings between the halide anions and bromine atoms of the pyridinium cation. Bromide and iodide anions are more polarizable and nucleophilic than the fluoroborate anion and they are thus expected to give rise to strong halogen bondings with the bromopyridinium cation.[6a,13] The melting points of halides **3** (**3a**, 286 °C; **3b**, 294 °C) are definitively higher than the melting point of tetrafluoroborate **2** (204 °C) and this also hints at a stronger cation–anion association due to the presence of stabilizing C–Br···Br and C–Br···I interactions. Previous studies have shown not only that the halogen bonding presence in a solid increases its melting point, but also that the stronger the halogen bonding, the greater the melting point increase.[7,14]

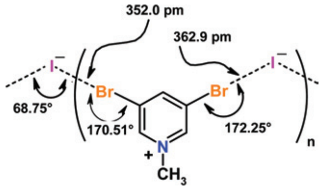
IR spectroscopy is a simple, sensitive, and highly diagnostic tool to detect the halogen bonding presence in a wide diversity of supramolecular architectures. The C–H stretching modes are very powerful probes for studying intermolecular interactions, halogen bondings included.[15] Among others, they have made fundamental contributions to the understanding of electron distributions in both molecules and polymers.[16] In our case, the aromatic ν_{CH} absorptions are red shifted moving from **2** to **3a** to **3b** (*e.g.* 3100 → 3100 → 3093 cm^{-1}, 3070 → 3067 → 3061 cm^{-1}, 3051 → 3050 → 3042 cm^{-1}, 3024 → 3022 → 3017 cm^{-1}). These changes can be correlated with a decreasing positive charge on the molecules and a decreasing acidic character of the pyridine protons moving from **2** to **3a** to **3b**. This is perfectly consistent with the expectation that the tetrafluoroborate anions in **2** give very weak, if any, halogen bondings and that the bromide anions in **3a** give C–Br···Br halogen bondings weaker than the C–Br···I halogen bondings present in **3b**. The n → σ* electron donation from the iodide anion being stronger than that of the bromide anion, the ν_{CH} red shifts are larger in **3b** than in **3a**.[7]

These indications of the halogen bonding presence between the anions and the cations in **3a**,**b** are confirmed by the single crystal X-ray analysis of **3b**. Iodide anions work as bidentate electron donors [Br1···I1···Br2$_{-x,-1/2-y,1/2-z}$ angle 68.75(1)°] and both bromine atoms of any pyridinium ring work as electron acceptors. Infinite helices result (Fig. 1) where iodide anions and pyridinium cations alternate, being connected by two different C–Br···I halogen bondings [C5–Br1···I1 352.0(1), C3–Br2$_{-x,-1/2-y,1/2-z}$···I1 362.9(1) pm] (Scheme 2). These non-covalent interactions are consistently longer than the covalent bromine–iodine bond (252.1(4) pm in uncoordinated IBr[17]) and definitively shorter than the sum of the van-der-Waals radii[18] of involved atoms (185 pm bromine, 198 pm iodide).

As required by the geometrical demands for an n → σ* electron donation from iodine to bromine, the C5–Br1···I1 and C3–Br2···I1$_{-x,1/2-y,1/2-z}$ groups are roughly linear, the C–Br···I angles being 170.51(6) and 172.25(7)°, respectively.



Scheme 1 (*i*) Me$_3$O$^+$BF$_4$$^-$, CH$_3NO_2$, 6 h, 0 °C to r.t.; (*ii*) Bu$_4$N$^+$Br$^-$, CH$_3$CN, 15 min, r.t.; (*iii*) Bu$_4$N$^+$I$^-$, CH$_3$CN, 10 min, r.t.



Scheme 2 C–Br···I$^-$ halogen bondings parameters in the **3b** helix.

A careful survey of the C–Br···I group in crystallographic literature revealed that the C5–Br1···I1 distance in **3b** nearly equals the shortest reported to date. Fig. 2 shows a scatterplot derived from the Cambridge Crystallographic Data Centre. It describes structures containing intermolecular short contacts between bromocarbons and iodine atoms.

The shortest C–Br···I interaction (351.5 pm) has been observed in the non-covalent trimer formed by a triiodide anion bridging two dibromotetrathiafulvalenium cations.[19] In general, a positively charged heterocycle is therefore a particularly effective scaffold to promote the electron accepting ability of appended bromine atoms. Two aspects are worth discussing. First, the tetrathiafulvalenium cation and pyridinium cation give rise to one and two halogen bondings, respectively. Second, the interaction given by the tetrathiafulvalenium acid is slightly shorter than the interactions given by the pyridinium cation. The former aspect may be the cause of the second. In other words, when two halogen bondings are formed the positive charge of the heterocyclic cation is more effectively counterbalanced than when one halogen bonding is formed. In the former case longer halogen bondings are formed than in the latter case.

In the three-dimensional structure of the halogen-bonded co-crystal **3b** two enantiomeric helices run parallel to each other and interdigitate as apparent in Fig. 3 (see ESI† for a rotatable version of Fig. 3). Each turn of the helix is built of two iodide anions and two pyridinium cations. The helix pitch is the *b* cell parameter [11.724(2) pm]. No π···π stacking occurs among overlapping pyridinium rings.

In conclusion, the palette of bromocarbon tectons for halogen bonding based crystal engineering has been expanded. Halogen atoms of halopyridine derivatives are known to be able to give rise to halogen bondings[8c,10,11,20] We reasoned that

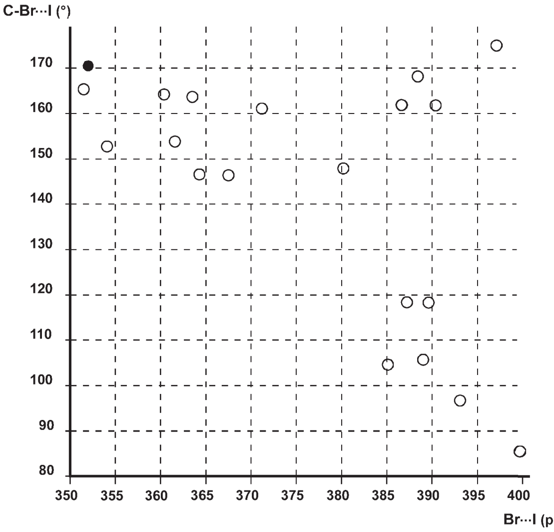


Fig. 2 Scatterplot derived from the CCDC (version 5.25, 298087 entries; only structures showing $R < 0.06$ are considered) reporting structures containing the intermolecular C–Br···I halogen bondings below 400 pm. The full circle refers to the C–Br···I contact present in **3b**. The preferential linear directionality of the interaction also emerges.

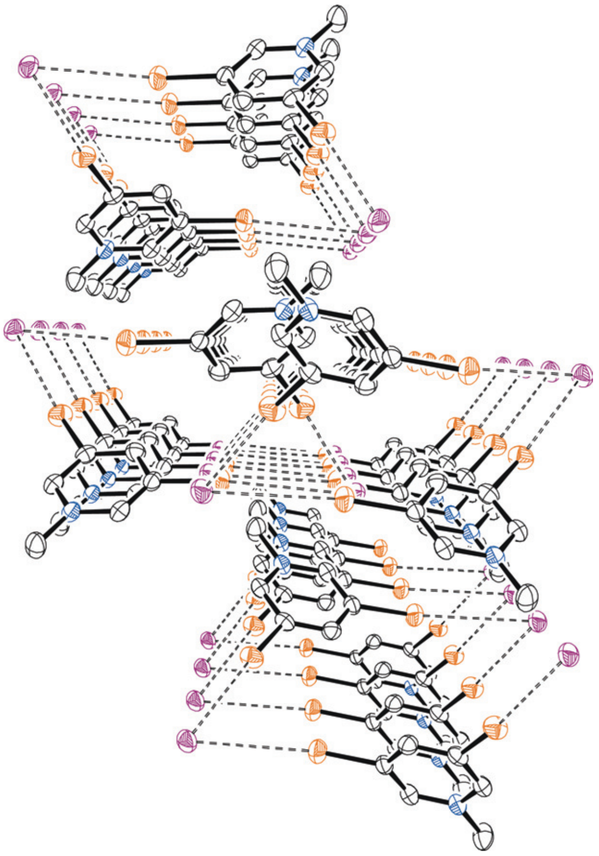


Fig. 3 Helices of **3b** viewed down the *b*-axis. Hydrogen atoms have been omitted for simplicity, dashed lines are halogen bondings. Colours are as follows: carbon, black; nitrogen, blue; bromine, orange, iodine, purple.

by decreasing the electron density on pyridine rings through nitrogen quaternarization, the electron accepting ability of halogen pendants would be promoted. Our crystal engineering was confirmed as the dibromopyridinium iodide **3b** gives rise to the second shortest C–Br···I non-covalent interaction of the crystallographic literature.

A supramolecular advantage of the dibromopyridinium tecton over the tetrathiafulvalenium tecton (showing the shortest C–Br···I interaction) is that several of the cation properties can be easier tuned in order to meet the pursued crystal engineering. For instance, the cation size can be easily varied by simply changing the alkylating agent used in the cationization reaction. In this way it can be easily assessed if the halogen bonding control over crystal structure is insensitive to cation size. Moreover, the electron density on the tetrathiafulvalene tecton can be changed only *via* the oxidation. In contrast, several approaches exist to tune the electron density on the pyridine tecton. Nitrogen alkylation generates a cation while metal coordination simply decreases the electron density, the extent of decrease varying with the metal.

Experimental

General: All solvents and reagents were purchased from Sigma-Aldrich Co. or Acros Organics in the highest purification grade and used without further purification.

N-Methyl-3,5-dibromopyridinium tetrafluoroborate (2)

Trimethyloxonium tetrafluoroborate (1.25 equiv., 4.32 mmol, 636 mg) is dissolved in nitromethane (30 mL) at 0 °C under an inert atmosphere and **1** (3.42 mmol, 810 mg) is added portion wise under vigorous stirring. Then the solution is allowed to warm to room temperature and stirred for a further six hours before the solvents are evaporated under reduced pressure. The crude mixture is crystallized from chloroform–methanol to yield pure **2** (92%). ^{1}H-NMR ([D$_6$]acetone, 300 MHz): $\delta = 4.63$ (s, 3H CH_3), 9.20 (t, $^4J_{HH} = 1.8$ Hz, 1H, *para*-C*H*), 9.43 (d, $^4J_{HH} = 1.8$ Hz, *ortho*-C*H*). ^{13}C–{^{1}H}–NMR ([D$_6$]acetone, 62.9 MHz): $\delta = 49.66$ (CH$_3$), 123.10 (*C*Br), 147.22 (*ortho*-*C*H), 150.65 (*para*-*C*H). IR (KBr): $\nu = 3167$, 3100, 3070, 3051, 3024, 2996, 2907, 1554, 1484, 1449, 1403, 1303, 1207, 864, 775, 654 cm^{-1}. Mp. (DSC analysis) 204 °C (onset temperature 199 °C); on melting decomposition occurs and 3,5-dibromopyridine sublimes as confirmed by IR and ^{1}H NMR of the condensed vapours.

N-Methyl-3,5-dibromopyridinium halides 3a,b

The tetrafluoroborate **2** (2.86 mmol, 970 mg) is dissolved in acetonitrile (50 mL) at room temperature and a solution of tetrabutylammonium bromide (2.86 mmol, 923 mg) or tetrabutylammonium iodide (2.86 mmol, 1.06 g) in the same solvent (30 mL). Slow evaporation at room temperature afforded, in crystalline and pure form, the bromide **3a** (88% white) or the iodide **3b** (92% yellowish). **3a**: ^{1}H-NMR (D$_2$O, 300 MHz): $\delta = 4.19$ (s, 3H, CH_3), 8.82 (s, 1H, *para*-C*H*), 8.96 (s, 2H, *ortho*-C*H*). IR (KBr): $\nu = 3162$, 3100, 3067, 3050, 3022, 2990, 2905, 1547, 1483, 1446, 1401, 1302, 1203, 863, 774, 653 cm^{-1}. Mp. (DSC analysis) 286 °C (onset temperature 280 °C); on melting decomposition occurs and 3,5-dibromopyridine sublimes as confirmed by IR and ^{1}H NMR of the condensed vapours. **3b**: ^{1}H-NMR (D$_2$O, 300 MHz): $\delta = 4.22$ (s, 3H, CH_3), 8.85 (s, 1H, *para*-C*H*), 8.98 (s, 2H, *ortho*-C*H*). IR (KBr): $\nu = 3150$, 3093, 3061, 3042, 3017, 2992, 2901, 1545, 1477, 1442, 1398, 1300, 1275, 1202, 863, 774, 652 cm^{-1}. Mp. 294 °C (onset temperature 286 °C); on melting decomposition occurs and 3,5-dibromopyridine sublimes as confirmed by IR and ^{1}H NMR of the condensed vapours.

Crystal data for $(C_6H_6Br_2N)^+I^-$ 3b

$M = 378.84$, orthorhombic, *Pbca*, $a = 11.571(2)$, $b = 11.724(2)$, $c = 14.461(2)$ Å, $U = 1961.8(5)$ Å^3, Mo-Kα radiation: $\lambda = 0.71073$ Å, $Z = 8$, $T = 293$ K, μ(Mo-Kα) $= 11.346$ mm^{-1}. 47 518 absorption corrected reflection (multi-scan, $T_{min} = 0.18495$, $T_{max} = 0.05103$). Bruker-SMART-APEX diffractometer 3114 unique ($R_{int} = 0.0301$), 2496 with $I_o > 2\sigma(I_o)$], $2\theta < 62.5°$. Structure solution by SIR92[21] and refinement on F^2 by SHELX97[22] program packages. Anisotropic displacement parameters for all heavy atoms; isotropic H atoms refined with restraints. At final convergence $R_1 = 0.0399$, $wR_2 = 0.0736$, [0.0270 and 0.0679, respectively for $I_o > 2\sigma(I_o)$], $S = 1.039$ for 128 parameters, 84 restraints using the following weighting scheme: $w = 1/[(\sigma^2(F_o^2) + (0.043P)^2 + 1.183P)]$, $P = (F_o^2 + 2F_c^2)/3$. Difference electronic density ranges between -0.98 and 1.51 eÅ^{-3}, the maximum and minimum residues being located at less than 0.8 Å from the Br2 atom. CCDC reference number 228986. See http://www.rsc.org/suppdata/nj/b4/b401421a/ for crystallographic data in .cif or other electronic format.

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