



Inorganic bromine in organic molecular crystals: Database survey and four case studies



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ABSTRACT

We present a Cambridge Structural Database and experimental study of multicomponent molecular crystals containing bromine. The CSD study covers supramolecular behaviour of bromide and tribromide anions as well as halogen bonded dibromine molecules in crystal structures of organic salts and cocrystals, and a study of the geometries and complexities in polybromide anion systems. In addition, we present four case studies of organic structures with bromide, tribromide and polybromide anions as well as the neutral dibromine molecule. These include the first observed crystal with diprotonated phenazine, a double salt of phenazinium bromide and tribromide, a cocrystal of 4-methoxypyridine with the neutral dibromine molecule as a halogen bond donor, as well as bis(4-methoxypyridine)bromonium polybromide. Structural features of the four case studies are in the most part consistent with the statistically prevalent behaviour indicated by the CSD study for given bromine species, although they do exhibit some unorthodox structural features and in that indicate possible supramolecular causes for aberrations from the statistically most abundant (and presumably most favourable) geometries.

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1. Introduction

Dihalogen molecules, X_2 (I_2 , Br_2) have long been known to act as Lewis acids, which determines both their reactivity as well as their supramolecular chemistry [1]. On the other hand, halogenide anions are Lewis bases, with their basicity and hardness diminishing with the size of the halogenide. Simultaneous presence of dihalogen molecules and halogenide ions can thus lead to their interconnection into polyhalogenide ions of various shapes and complexities [1,2].

Within the context of crystal engineering, the emphasis has mostly been on iodine – diiodine as a halogen bond donor, as well as design of polyiodides by combining diiodine, iodide and triiodide as building blocks and finding optimal cations to stabilise given polyiodide architectures. In comparison, bromine has been much less studied, both due to its reactivity [1,3] and somewhat weaker halogen bonding donating ability [4].

This bias toward iodine is well represented by the relative

occurrence of various bromine- and iodine-containing motifs in the Cambridge Structural Database (CSD) [5]. A survey of the CSD for all entries containing only organic molecules and bromine has shown that bromine-containing structures are rather common – more so than organic structures containing iodine (24610 datasets with bromine vs. 10455 with iodine, or 2.35:1 ratio). After the exclusion of datasets corresponding to organohalogen molecules, the majority of the remaining datasets corresponded to simple halogenide salts, which reflect the predominance of bromine over iodine containing structures – 4082 datasets containing bromide vs. 2893 containing iodide (1.41:1 ratio). However, when the number of entries containing the respective trihalogenide ions; the tribromide (120 datasets) in comparison with triiodide (777 datasets) becomes much less prominent (0.15:1 ratio). This trend continues with structures comprising molecular halogens with only 35 datasets containing Br_2 vs. 269 containing I_2 (0.13:1), although formation of halogen bonded complexes between dibromine and Lewis bases has been suspected by Bernal as early as 1940 [6] and experimentally observed by Hassel et al. in the 1950-ies [7]. Similarly, in spite of the first polybromide having been suspected since the discovery of extremely high solubility of bromine in alkali bromide solutions in the first half of the 19th century [8], most structures of poly- and oligobromides have only been reported recently [9,10], and overall

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remain extremely scarce.

Herein we present a database study of the supramolecular chemistry of bromide, dibromine and tribromides as well as the geometries of oligo- and polybromides in the crystalline state. We also present four case studies of novel organic bromine compounds; two phenazine ($\text{H}_2\text{phen Br}_2$ and $(\text{Hphen})_2 \text{Br Br}_3$) and two 4-methoxyppyridine derivatives ($p\text{-MeOPy Br}_2$ and $p\text{-MeOPy}_2 \text{Br}_6$) which demonstrate some of the more interesting features of supramolecular chemistry of inorganic bromine in organic crystals (Fig. 1).

2. Experimental section

2.1. Synthesis of compounds

$\text{H}_2\text{phen Br}_2$ has been obtained by dissolving 2.8 mmol (503 mg) of phenazine in hot ethanol (5.0 mL). The clear solution was added to 14.5 mL concentrated hydrobromic acid and cooled to room temperature. Acetone (20 mL) was added as a precipitant. Red single crystals suitable for X-ray analysis have been obtained after 3 days.

$(\text{Hphen})_2 \text{Br Br}_3$ has been obtained by dissolving 0.1 mmol (35.7 mg) of $\text{H}_2\text{phen Br}_2$ and 0.1 mmol (24.3 mg) of *N*-bromosuccinimide in a hot mixture of ethanol and acetonitrile (3.0 mL, vol. ratio 1:2). Orange single crystals suitable for X-ray analysis have been obtained after 5 days by slow evaporation.

$p\text{-MeOPy Br}_2$ and $p\text{-MeOPy}_2 \text{Br}_6$ have been obtained by dissolving 0.1 mmol (10.9 mg) of *p*-MeOPy and 0.1 mmol (24.3 mg) of *N*-bromosuccinimide in acetone. Yellow crystals of $p\text{-MeOPy Br}_2$ and brown crystals of $p\text{-MeOPy}_2 \text{Br}_6$ suitable for X-ray analysis appeared concomitantly after 2 days.

2.2. Structure determination

The crystal and molecular structures of obtained compounds were determined by single-crystal X-ray diffraction. Single-crystal diffraction experiments were performed at 295 K on an Oxford

Diffraction Xcalibur diffractometer with Sapphire3 CCD detector, using graphite-monochromated $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. The data sets were collected using the ω scan mode over the 2θ range up to 54° . Programs CrysAlis CCD and CrysAlis RED were employed for data collection, cell refinement, and data reduction [11]. All structures were solved by direct methods and refined using the SHELXS and SHELXL programs, respectively [12]. The structural refinement was performed on $|F|^2$ using all data. All alkyl and aryl hydrogen atoms were placed at calculated positions and treated as riding on their parent atoms. The N-bound hydrogen atom of $\text{H}_2\text{phen Br}_2$ was located from the electron difference map and refined isotropically. In the structure refinement of compound $(\text{Hphen})_2 \text{Br Br}_3$, the N-bound hydrogen atom was placed on a calculated position using riding model with isotropic displacement parameter 1.2 times the same parameter of the parent nitrogen atom. All calculations were performed using the WinGX crystallographic suite of programs [13]. The molecular structures of compounds are presented by ORTEP-3 [14], and their molecular packing projections were prepared by Mercury [15]. Supplementary crystallographic data for this paper can be obtained 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 336033; or deposit@ccdc.cam.ac.uk). CCDC 1475382–1475385 contain the supplementary crystallographic data for this paper.

2.3. CSD survey

The CSD data survey has been performed on the ver. 5.37 Update 2 (February 2016) CSD database using ConQuest version 1.18. When searching hydrogen- or halogen-bonded contacts, the contact angle was constrained to the range between 90° and 180° . For hydrogen-bonded contacts, the upper limit on the distance between the hydrogen bond donor and acceptor atoms was defined as the sum of their van der Waals radii $+0.5 \text{ \AA}$. The only exceptions were the $\text{C-H}\cdots\text{Br}_3$ and $\text{O-H}\cdots\text{Br}_3$ searches, where the distance restriction was eased by defining the contact as the sum of the van der Waals radii of carbon or oxygen and bromine atoms $+1.0 \text{ \AA}$. For halogen-bonded contacts, only the distance was restricted by defining the contact as the sum of the van der Waals radii of the donor and acceptor atom.

3. Results and discussion

3.1. Cambridge Structural Database survey

3.1.1. Bromide ion (Br^-)

The large number of CSD entries containing bromide ion allowed for a detailed study of the supramolecular chemistry of bromide in organic structures. In particular, we analysed the CSD data with respect to hydrogen bonds with the bromide acting as a hydrogen acceptor ($\text{N-H}\cdots\text{Br}$, $\text{O-H}\cdots\text{Br}$ and $\text{C-H}\cdots\text{Br}$). $\text{N-H}\cdots\text{Br}$ bonds were found to be present in 1341 data sets (32.9% of all entries containing bromide) which include both heterocyclic as well as amine nitrogen atoms.

In both cases the $\text{N-H}\cdots\text{Br}$ hydrogen bonds angles tend to be linear, although there is a somewhat wider dispersion of angles when the hydrogen bond donor is a terminal nitrogen atom, as opposed to when it is a member of a heterocyclic ring (Fig. 2). The bonds with heterocyclic nitrogen are also somewhat shorter (the maximal occurrence of $\text{N}_c\text{-H}\cdots\text{Br}$ length of 2.25 \AA , with the median $d(\text{N}\cdots\text{Br})$ of 3.31 \AA) than those with terminal nitrogen (the maximal occurrence of $\text{N}_a\text{-H}\cdots\text{Br}$ length of 2.35 \AA and median $d(\text{N}\cdots\text{Br})$ of 3.38 \AA ; Fig. 2).

$\text{O-H}\cdots\text{Br}$ bonds are present in 1216 datasets (29.8% of all

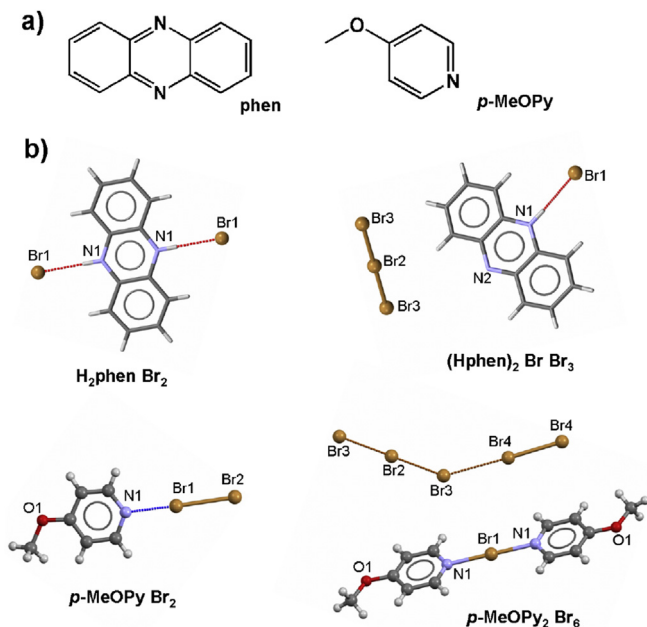


Fig. 1. a) Structures of reactants, phenazine (**phen**) and 4-methoxyppyridine (**p-MeOPy**) and b) molecular models obtained from single-crystal X-ray experiments.

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