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Crystallographic Charge Density Study of the Partial Covalent Nature of Strong N \cdots Br Halogen Bonds

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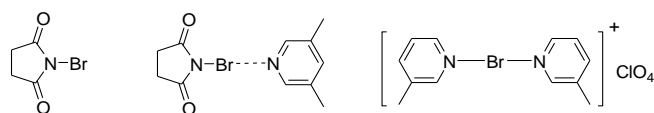
Dedicated to the memory of Professor Drago Grdenić (1919–2018), the founder of X-ray crystallography in Croatia

Abstract: Covalent nature of strong N–Br \cdots N halogen bond in a cocrystal (**2**) of *N*-bromosuccinimide (**NBS**) with 3,5-dimethylpyridine (**lut**) was determined from X-ray charge density and compared to a weak N–Br \cdots O halogen bond in pure crystalline **NBS** (**1**) and a covalent bond in bis(3-methylpyridine)bromonium cation (in its perchlorate salt, **3**). In **2** the donor N–Br bond is elongated by 0.0954 Å, while the Br \cdots acceptor distance of 2.3194(4) is by 1.08 Å shorter than the sum of van der Waals radii. Maximum electron density along the Br \cdots N halogen bond of 0.38 e Å⁻³ indicates a considerable covalent contribution to the total interaction. This value is intermediate to 0.067 e Å⁻³ for the Br \cdots O contact in **1**, and ca. 0.7 e Å⁻³ in both N–Br bonds of the bromonium cation in **3**. A computation of the NBO charges of contact atoms and the $\sigma^*(\text{N1}–\text{Br})$ population of **NBS** as a function of distance between **NBS** and **lut** has shown that charge transfer becomes significant at Br \cdots N distance below ca. 3 Å.

Halogen bond (XB), an attractive supramolecular interaction between a halogen atom acting as a Lewis acid and a Lewis base,^[1] has over the recent decades risen as one of the main intermolecular interactions in supramolecular chemistry^[2] and crystal engineering,^[3] and has also been found to play a significant role in several biological systems.^[4] In spite of its ubiquitous use in supramolecular chemistry today, the nature of halogen bond still remains a somewhat contentious question. The earliest description of halogen bond as a charge-transfer by Mulliken^[5] has at the end of last century been replaced by an elegant concept of halogen bond as a primarily electrostatic interaction between an electron-depleted region of a halogen atom (a σ -hole), corresponding to a positive electrostatic potential, and an electron-rich (negative) region of an acceptor.^[6] More recently however there has been growing body of evidence indicating that a $n \rightarrow \sigma^*$ charge transfer component also has a considerable contribution, in particular for strong halogen bonds.^[7] Indeed, recent studies of Rosokha *et al.*^[8] demonstrated that there is a continuous increase of covalent character of the N \cdots Br XB in binding of DABCO (1,4-diazabicyclo[2.2.2]octane) with reduction of XB length, and that, even in the case of weaker halogen bonds formed by haloethane molecules, the charge

transfer component is present.^[8b] Formigue *et al.* have reported an almost symmetric halogen bond between *N*-bromosaccharin and 4-methylpyridine with a considerable charge transfer (0.27 e) to the acceptor.^[9] On the other hand, Řezáč and de la Lande have determined that the charge transfer component, although present in XB-s, contributes only up to 10% to the overall energy even in strong halogen bonds.^[10]

As the question of the charge transfer in XB has primarily been addressed from the computational point of view, we have opted for experimental determination of charge density of a system including a strong, potentially partially covalent XB. Only a handful of experimental charge density studies of halogen bonding have been published to date.^[11] The strongest XB studied in this manner has been one between 1,4-diiodotetrafluorobenzene and 4-dimethylaminopyridine.^[11c] We have selected *N*-bromosuccinimide as the XB donor, since *N*-haloimides have been shown not only to form strong halogen bonds with bond energies approaching, and even surpassing the energies of equivalent hydrogen bonds, but also considerable elongations of the donor N–Br bond upon formation of XB with strong nucleophiles, indicating that these could be ideal systems for the study of charge transfer in XB.^[12] *N*-bromosuccinimide was crystallised with a 3,5-dimethylpyridine ($pK_a = 6.15$) to afford a 1:1 complex **2** connected *via* an expectedly strong N–Br \cdots N XB. For comparison, we have also studied the charge density of pure **1**, in which there is only a much weaker N–Br \cdots O contact. In addition, we have undertaken the first X-ray charge density study of a bromonium cation, bis(3-methylpyridine)bromonium, as its perchlorate salt (**3**). The perchlorate salt was conveniently chosen as the studied model, because the bromine atom is located in a general position and the bromonium cation does not have any crystallographically imposed symmetry. As the bond in halonium ions $[\text{R}–\text{X}–\text{R}]^+$ $[\text{R}–\text{X}–\text{R}]^-$ and polyhalogenides is commonly accepted as *covalent* (equivalent to the similarly partially covalent hydrogen bonds in ionic hydrogen bonded species such as H_5O_2^{+} ^[13] or HF_2^-),^[14] it should represent a benchmark for a Br \cdots N contact with an extreme charge transfer.



Scheme 1. The model compounds – NBS (**1**), NBS-lut (**2**), and [MePy₂Br]⁺ClO₄[–] (**3**).

The strength of the XB in **2** is implied by the geometry: the Br1 \cdots N2 distance (2.3194(4) Å) is by 1.08 Å (31.9%) shorter than the sum of van der Waals radii for N and Br and by almost 1 Å shorter than the average distance of Br \cdots N contacts (3.27(11) Å) in the CSD, while the N1–Br1 \cdots N2 fragment is perfectly linear,

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(179.8(9)°). The N1–Br1 bond of 1.9314(4) Å is almost 0.1 Å longer than the equivalent bond in **1** (1.8360(12) Å). Difference between the lengths of the "covalent bond" N1–Br and "intermolecular contact" Br⋯N2 of only 0.388 Å indicates that the two contacts may be rather similar in nature.

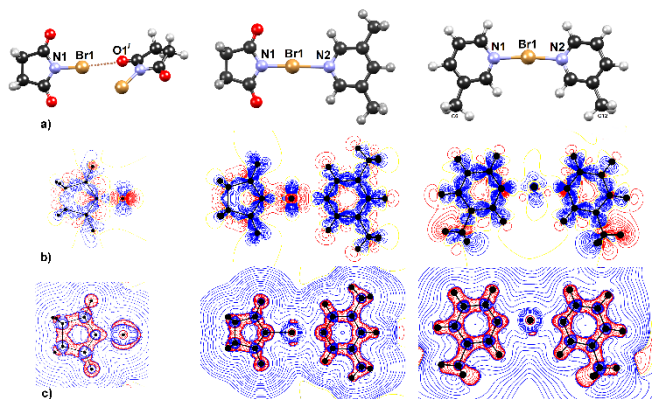


Figure 1. Comparison of experimental charge density in **1** (left), **2** (centre) and **3** (right): a) ball-and-stick representation; b) deformation density (blue: positive, red: negative, yellow: zero-density; contours represent electron density of 0.05 e Å⁻³); c) Laplacians of electron density (blue: positive, red: negative; contours at ±2 e Å⁻⁵) in the molecular plane.

Table 1. Topology of electron density in N–Br bonds, derived from electron-density after multipolar refinement.

Bond	Length (Å)	Electron density, ρ_{cp} (e Å ⁻³)	Laplacian (e Å ⁻⁵)	Ellipticity
1				
N1–Br	1.8360(12)	1.118	0.82	0.27
Br⋯O1	2.7575(11)	0.135	1.87	0.43
2				
N1–Br	1.9314(4)	0.908	5.36	0.59
Br⋯N2	2.3194(4)	0.379	3.63	0.33
3				
N1–Br	2.084(4)	0.722	5.90	0.25
N2–Br	2.105(4)	0.658	6.01	0.19

This supposition is borne out by the results of the AIM analysis of the experimental electron density. The deformation density (Fig. 1b) reveals that there is no significant qualitative difference between bonds N1–Br in the pure **1** and **2**, but also that the "intermolecular contact" Br⋯N2 is qualitatively similar to the former two. Even more conspicuous is the Laplacian map (Fig. 1c): valence-shell charge concentrations (VSCC-s; red areas in Fig 1c) point out to existence of three lone electron pairs at the Br atom in **1**, despite presence of a rather large σ -hole. While electron density in the direction of N–Br axis is diminished, the VSCC is nevertheless obviously present. In **2** the only VSCC-s are those normal to the N–Br axis. The VSCC, which was supposed to lie on the N–Br axis is conspicuously absent. This points out that the nature of the interactions in the "bond" N1–Br and "intermolecular contact" Br⋯N2 is qualitatively the same. Topology of electron density (Table 1) reveals that the bond N1–Br in **2** is considerably weakened compared to **1**, and both of them

can be classified as highly polar covalent. Positive values of the Laplacian also agree with the polar nature of the bond. However, the maximum electron density in the Br⋯N2 contact of almost 0.38 e Å⁻³ also indicates a considerable covalent component; in fact, this contact is much more similar to a weak covalent bond than a closed-shell interaction. *In vacuo* optimised geometry (Table 2) of **2** displays a significantly elongated N–Br bond (1.924 Å) with respect to that of optimised **1** (1.864 Å) and ρ_{max} at the critical point of 0.999 e Å⁻³. Computed ρ_{max} at the critical point for the Br⋯N2 contact is 0.31 e Å⁻³. For comparison, ρ_{max} in medium-strength hydrogen bonds is in the range 0.15–0.20 e Å⁻³.^[15] In spite of the significant contribution of the charge transfer in the halogen bond in **2**, the computed *in vacuo* energy of formation of **2**, corresponding to the energy of the Br1⋯N2 halogen bond was found to be 41.90 kJ mol⁻¹ – more comparable to an intermediate/strong O–H⋯O or O–H⋯N hydrogen bond than to a covalent bond. This is particularly emphasised when the halogen bond energy in **2** is compared to the Br⋯N bond energy in **3** which was calculated to be 146.49 kJ mol⁻¹, in accord with its covalent nature. On the other hand, the Br⋯O halogen bond energy in a dimer of **1** (*in vacuo*) can be estimated as ca. 10.46 kJ mol⁻¹.

Table 2. Computed geometries, energies of formation (B2PLYPD/aug-cc-pVDZ) and topology of electron density (B2PLYPD/aug-cc-pVTZ) in N–Br bonds.

Bond	Length (Å)	Electron density, ρ_{cp} (e Å ⁻³)	Laplacian (e Å ⁻⁵)	Ellipticity	Energy of formation (kJ mol ⁻¹)
1					
N1–Br	1.86417	1.131	-1.614	0.045	–20.92 [a]
Br⋯O1	3.06865	0.067	0.939	0.109	
2					
N1–Br	1.92408	0.999	-0.552	0.056	–41.90
Br⋯N2	2.44788	0.310	2.82	0.064	
3					
N1–Br	2.12407	0.655	1.92	0.051	–146.49
N2–Br	2.12407	0.655	1.92	0.051	

[a] Corresponds to the formation of two Br⋯O1 contacts in a centrosymmetric dimer.

Charge density of the bromonium cation in **3** (Fig. 1) shows two almost identical N–Br bonds in the (bis(3-methylpyridine)bromonium cation, which are approximately intermediate between the 'covalent' N1–Br1 and the 'non-covalent' Br1⋯N2 in **2**. Intermediate values of electron density, which are about 0.7 e Å⁻³ (Table 1) and positive values of Laplacian are consistent with weak, highly polar covalent bonds. In comparison, the *in vacuo* optimised geometry of the bromonium ion from **3** is symmetric, with both N⋯Br contacts having lengths of 2.124 Å and ρ_{max} of 0.655 e Å⁻³. Therefore, the N–Br–N fragment of the bromonium cation is analogous to the covalent/hydrogen bonded Zundel cation (H₂O⋯H⁺⋯OH₂), which comprises two weak covalent bonds of order 0.5.^[13b] Also, a systematic trend of reduction of VSCC-s around the Br atom can be noted, going from an almost isolated N–Br bond in **1** (only weak interactions with its environment) to the bromonium cation (Fig. 1c). This is consistent with an increasing cationic and divalent nature of the Br atom.

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The computed electron deformation density, NBO charges and NBO occupancies suggest that in the case of weak halogen bonding between two molecules of **NBS**, there is virtually no charge transfer from acceptor atom, while electron density on the bromine atom is deformed to increase its partially positive charge of the σ -hole. In case of the **NBS-lut** complex, the deformation of electron density on the bromine atom is accompanied by charge transfer from the lone pair of halogen bond acceptor to the antibonding $\sigma^*(\text{Br}-\text{N})$ orbital, giving an overall pattern of positive and negative deformation densities along the $\text{N}-\text{Br}\cdots\text{N}$ fragment, quite similar to that in the covalently bound bromonium ion (Fig. 2).

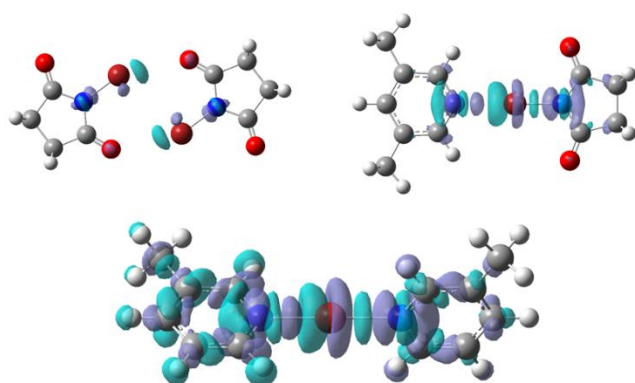


Figure 2. Electron deformation density (isodensity surfaces corresponding to the value of ± 0.002 a.u.) for optimised geometries of a dimer of **NBS**, the **NBS-lut** complex and the $[\text{MePy}_2\text{Br}]^+$ cation.

To further elucidate the nature of bonding in **2**, we have optimised a series of **NBS-lut** complexes with $\text{Br}\cdots\text{N}_2$ distances fixed in the range 1.6 – 9.0 Å (Fig 3). The energy of the complex follows a Morse-like curve with the minimum at 2.6 Å. More revealing on the nature of the bond, however, are the populations of the antibonding $\sigma^*(\text{N1}-\text{Br})$ orbital which are close to zero ($0.05 e^-$) and remain basically unchanged by the presence of the N_2 atom for $\text{Br}\cdots\text{N}_2$ distances above 4 Å. Below 4 Å, the population increases exponentially with the reduction of the distance, reaching $0.11 e^-$ at 2.6 Å and $0.21 e^-$ by 2.2 Å. This is exactly mirrored by the decrease of the population of the lone pair $n(\text{N}_2)$ orbital, indicating that there is a significant contribution of $n \rightarrow \sigma^*$ charge transfer only when **NBS** and **lut** approach each other closer than ca. 3 Å. Calculated ρ_{max} at the critical point follows the same trend, which validates the use of $\sigma^*(\text{N1}-\text{Br})$ populations as a measure for the bond covalent character. The charges (NBO) on the contact atoms, however, follow a quite different trend. There is a steady increase of the charge on the bromine (and corresponding decrease of the charges on both N_1 and N_2) with reduction of the $\text{Br}\cdots\text{N}_2$ distance starting at ca. 8 Å, which continues until the charge transfer becomes significant (ca. 3 Å), at which point the charge on the bromine atom starts decreasing with reduction of the $\text{Br}\cdots\text{N}_2$ distance (Fig 3). This reversal of the trend at 3 Å is followed by the charge of N_2 , but not by N_1 , the NBO charge of which continues to change monotonously.

This behaviour demonstrated a clear distinction between the polarisation effect and the charge transfer component in the halogen bond. The donor and acceptor molecule polarise each other at much larger distances than necessary for charge transfer,

which induces not only the increase of the σ -hole of the XB donor, but also the basicity of the XB acceptor. However, once the donor and the acceptor have become sufficiently close, the charge transfer takes over as the dominant effect and the bond becomes (partially) covalent.

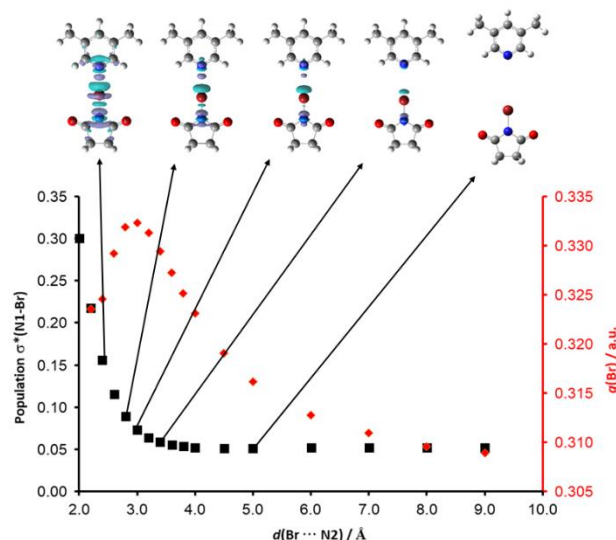


Figure 3. The population of the antibonding $\sigma^*(\text{N1}-\text{Br})$ orbital (black), NBO charge on the Br atom (red) and the optimised geometries with the electron deformation density (above; isodensity surfaces corresponding to the value of ± 0.002 a.u.) for **NBS-lut** complexes with $\text{Br}\cdots\text{N}_2$ distances in the range 2.0–9.0 Å.

It is noteworthy that the same general trend is followed by **NBS-lut** complexes at decreasing distances, as there is in the series of the three halogen bonds of increasing strength in **1**, **2** and **3**. This would seem to indicate that, in spite of a large variation of halogen bond energies from weak bond in **1** to covalent in **3**, there is no fundamental difference and no sharp cut-off line between the intermolecular 'non-bonding' halogen bond and a three center-two electron covalent bond, but rather that they represent two end-points of a continuum of interactions.

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Keywords: Noncovalent interactions • Supramolecular chemistry • Charge transfer • X-ray diffraction • Quantum Chemistry

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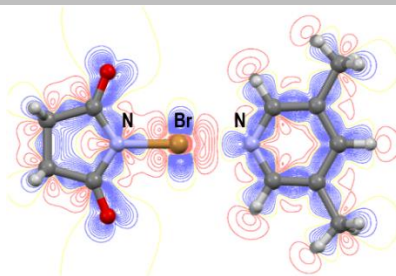
COMMUNICATION

Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Crystallographic charge density analysis of a strong N–Br \cdots N halogen bond reveals its partially covalent character.



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