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Halogen-bonded adduct of 1,2-dibromo-1,1,2,2-tetrafluoroethane and 1,4-diazabicyclo[2.2.2]octane

Alan K. Brisdon,^{a*} Abeer M. T. Muneer^a and Robin G. Pritchard^a

^aSchool of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, England

*Correspondence e-mail: alan.brisdon@manchester.ac.uk

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Halogen bonding is an intermolecular interaction capable of being used to direct extended structures. Typical halogen-bonding systems involve a noncovalent interaction between a Lewis base, such as an amine, as an acceptor and a halogen atom of a halofluorocarbon as a donor. Vapour-phase diffusion of 1,4-diazabicyclo[2.2.2]octane (DABCO) with 1,2-dibromotetrafluoroethane results in crystals of the 1:1 adduct, C₂Br₂F₄·C₆H₁₂N₂, which crystallizes as an infinite one-dimensional polymeric structure linked by intermolecular N...Br halogen bonds [2.829 (3) Å], which are 0.57 Å shorter than the sum of the van der Waals radii.

Keywords: halogen bonding; crystal structure; 1,4-diazabicyclo[2.2.2]octane; dibromotetrafluoroethane; extended structures; phase change; one-dimensional polymeric structure; bromofluorocarbon trapping.

CCDC reference: 1422107

1. Introduction

Halogen bonding (XB) has become recognized as an intermolecular interaction, comparable to hydrogen bonding (Metrangolo *et al.*, 2005), capable of being used to direct extended structures, and there are examples of its application ranging from crystal engineering (Cavallo *et al.*, 2010) to organocatalysis (Knip *et al.*, 2013). Very recently, halogen bonding has also been used as a method of converting highly volatile organofluorine compounds, which are difficult to handle, into a more easily handled form by halogen-bond adduct formation (Aakeröy *et al.*, 2015).

Prototypical halogen-bonding systems involve a noncovalent interaction between a Lewis base, such as an amine, as a halogen-bond acceptor, and a halogen, most often iodine, of a halofluorocarbon, which acts as a donor (Desiraju *et al.*, 2013). The halide of the fluorocarbon is able to act in this way because of the distortion of the electron density of the R_f-X bond (R_f is a perfluorinated organic group), caused by the strongly electron-withdrawing R_f group, resulting in an area of reduced electron density on the X atom opposite the $C-X$ bond, called a σ -hole. This linear, or near-linear, arrangement is described as a type I halogen bond (Desiraju & Parthasarathy, 1989).

Because iodine is more readily polarized than bromine, the strength of the halogen-bond interaction is greater between amines and iodine acceptors than it is in the bromo analogues, and so, typically, $C-I\cdots N$ halogen-bonded interactions are frequently stronger than those in $C-Br\cdots N$ systems. However, the $C-Br\cdots N$ halogen-bonded systems are of considerable interest because they offer a potential method of trapping and holding small bromofluorocarbons that are volatile and ozone-depleting substances. It was thus of interest to investigate the halogen bonding in the 1:1 adduct, (I), of 1,4-diazabicyclo[2.2.2]octane (DABCO) with 1,2-dibromotetrafluoroethane, the structure of which is reported here.

2. Experimental

1,4-Diazabicyclo[2.2.2]octane and $BrCF_2CF_2Br$ were obtained from commercial sources and were used without further purification.

2.1. Synthesis and crystallization

Preparation of the title compound was by vapour diffusion in a sealed system consisting of two concentric glass vials. In the smaller inner vial was placed DABCO (0.1 g), with $BrCF_2CF_2Br$ (0.5 ml) in the outer vial. Crystals suitable for X-ray diffraction studies formed within 24 h at room temperature on the surface of the inner vial. IR (ν , cm^{-1}): 2934.9, 2871.0 (C—H), 1149.4, 1097.5 (C—F).

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Adduct (I) crystallized in the monoclinic space group $I2/a$, with half a molecule per asymmetric unit. H atoms were visible in difference maps and were allowed for as riding atoms, with $C-H = 0.97 \text{ \AA}$ and $U_{iso}(H) = 1.2U_{eq}(C)$.

Table 1

Experimental details

Crystal data	
Chemical formula	$C_2Br_2F_4 \cdot C_6H_{12}N_2$
M_r	372.02
Crystal system, space group	Monoclinic, $I2/a$
Temperature (K)	150
a, b, c ($\text{\AA}$)	10.9815 (9), 10.8697 (10), 11.1525 (9)

β (°)	111.135 (9)
V (Å ³)	1241.68 (19)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	6.55
Crystal size (mm)	0.20 × 0.13 × 0.07
Data collection	
Diffractometer	Agilent SuperNova Single Source diffractometer with an Eos detector
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Agilent, 2014)
$T_{\min}$, $T_{\max}$	0.159, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2416, 1282, 1028
R_{int}	0.032
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.627
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.069, 1.03
No. of reflections	1282
No. of parameters	73
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.61, -0.64

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXS87* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

3. Results and discussion

The asymmetric unit of the title adduct, (I), comprises half a molecule of both DABCO and BrCF₂CF₂Br. Both the DABCO and BrCF₂CF₂Br molecules possess crystallographic C_2 symmetry. The complete molecular structure of (I) is shown in Fig. 1. The bond lengths and angles (Table 2) are largely as expected. DABCO undergoes a phase change at 351 K under atmospheric pressure (Chang & Westrum, 1960; Trowbridge & Westrum, 1963). The low-temperature phase (Sauvajol, 1980), *i.e.* phase II, data reports N—C and C—C bond lengths of 1.4834 and 1.5355 Å, respectively, and C—N—C angles of 107.29°, which compare with the corresponding average values of 1.471 (5), 1.548 (5) Å and 108.4 (3)° in (I). Similarly, the average parameters obtained for the BrCF₂CF₂Br unit here [Br—C = 1.939 (4) Å, C—C = 1.516 (8) Å and C—F = 1.337 (5) Å] are comparable to those obtained previously from a neutron diffraction study (Pawley & Whitley, 1988).

Table 2

Selected geometric parameters (Å, °)

Br1—C4	1.939 (4)	N1—C3	1.477 (5)
F2—C4	1.336 (4)	C4—C4 ⁱ	1.516 (8)
F1—C4	1.338 (5)	C1—C1 ⁱⁱ	1.535 (6)
N1—C1	1.471 (5)	C2—C3 ⁱⁱ	1.553 (4)
N1—C2	1.466 (5)	C3—C2 ⁱⁱ	1.553 (4)

C1—N1—C3	108.7 (3)	F2—C4—Br1	109.2 (3)
C2—N1—C1	108.8 (3)	F2—C4—F1	107.6 (3)
C2—N1—C3	107.6 (3)	F1—C4—Br1	109.5 (3)

Symmetry codes: (i) $-x + \frac{1}{2}, y, -z + 1$; (ii) $-x - \frac{1}{2}, y, -z$.

Figure 1

A view of the components of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x + \frac{1}{2}, y, -z + 1$; (ii) $-x - \frac{1}{2}, y, -z$.]

The extended structure displays near-linear interactions [$\text{N}\cdots\text{Br}-\text{C}$ angle = $175.6(1)^\circ$] of the N atoms of the DABCO molecule with the Br atoms of $\text{BrCF}_2\text{CF}_2\text{Br}$, resulting in an extended one-dimensional polymeric structure based on the formation of $\text{Br}\cdots\text{N}$ contacts (Fig. 2). The $\text{N}\cdots\text{Br}$ distance of $2.829(3) \text{ \AA}$, is $0.57 \text{ \AA}$ (16.8%) shorter than the sum of the van der Waals radii for nitrogen and bromine ($3.40 \text{ \AA}$). Taken together, the short $\text{N}\cdots\text{Br}$ distance and collinear alignment indicate the presence of a type I halogen-bonding interaction. This is further supported by a reduction in the C—F stretching frequencies (ν_{max} 1149.4 and 1097.5 cm^{-1}) in (I), compared with the values 1158.6 and 1109.8 cm^{-1} observed for $\text{BrCF}_2\text{CF}_2\text{Br}$.

Figure 2

A view of the intermolecular halogen bonds (dashed lines) in the crystal structure of (I).

Interestingly, there are no other obvious direction-specific interactions in the structure of (I). There are no classical hydrogen bonds formed, indeed the shortest intermolecular $\text{H}\cdots\text{F}$ distance is $2.66 \text{ \AA}$, and although some short $\text{F}\cdots\text{F}$ and $\text{F}\cdots\text{Br}$ interactions are observed, these are intramolecular rather than intermolecular in nature.

A search of the Cambridge Structural Database (CSD, Version 5.36; Groom & Allen, 2014) was undertaken for contacts between a tertiary N atom and an organic-bound Br atom less than the sum of their van der Waals radii. Of the 37 hits returned, the C—N $\cdots$ Br distances were found to lie between 2.531 and $3.379 \text{ \AA}$, with the average being $3.138 \text{ \AA}$. By comparison, searches carried out for the analogous iodine, rather than bromine, system results in a slightly larger number of hits (47), with C—N $\cdots$ I distances in the range 2.715 – $3.452 \text{ \AA}$, and a shorter average distance ($2.932 \text{ \AA}$), which is

consistent with a greater degree of interaction for the more polarizable iodine centre, in agreement with the current understanding of halogen bonding.

It is noteworthy that of the crystallographically characterized C—N $\cdots$ Br—C adducts, only two have DABCO as the halogen-bond acceptor. In the structure of the adduct formed between DABCO and 1,4-

dibromotetrafluorobenzene (CSD refcode DIVDUI; Cinčić *et al.*, 2008), a one-dimensional polymeric arrangement is also formed, with C—N $\cdots$ Br = 2.894 (2) and 2.910 (2) Å. The shorter of these distances is still significantly longer (20 σ) than observed in (I), where the halogen-bond distance is 2.829 (3) Å. Whilst in the only reported BrCF₂CF₂Br adducts of nitrogen-containing compounds, namely Me₂NCH₂CH₂NMe₂ (REMBOB; Huang *et al.*, 2006) and 1,4-dimethylpiperazine (ULOJUA; Chu *et al.*, 2003), the C—N $\cdots$ Br distances are remarkably similar at 2.864 (3) and 2.863 (5) Å, respectively, but both distances are longer than the equivalent interaction found in (I).

In conclusion, the adduct formed between DABCO and BrCF₂CF₂Br results in a method of trapping the volatile (and ozone-depleting) bromofluorocarbon. The resulting crystals adopt a one-dimensional polymeric structure in which the C—N $\cdots$ Br halogen-bond length is shorter than the average for related type I C—N $\cdots$ Br—C halogen-bonded systems, and shorter than found in the two other reported crystal structures of related Br₂C₂F₄ adducts.

Supporting information

CCDC reference: [1422107](#)

Crystal structure: contains datablock I. DOI: [10.1107/S2053229615016472/yf3093sup1.cif](#)

Structure factors: contains datablock I. DOI: [10.1107/S2053229615016472/yf3093Isup2.hkl](#)

Supporting information file. DOI: [10.1107/S2053229615016472/yf3093Isup3.mol](#)

Supporting information file. DOI: [10.1107/S2053229615016472/yf3093Isup4.cml](#)

Supplementary crystallographic information

[3D view](#)

► **Supporting crystallographic data**

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