Article

Halogen Interactions in 2,4,5-Tribromoimidazolium Salts

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Abstract: The crystal structures of 2,4,5-tribromo-1-(prop-2-ynyl)imidazole and seven new 1,3-dialkyl-2,4,5-tribromoimidazolium salts (R^1 = propenyl, propynyl, dibromopropenyl; R^2 = Me, Et) with halogen-containing anions (tetrafluoroborate, hexafluorophosphate, triflimide) were determined. The structures revealed halogen···halogen and anion···π interactions. Contacts of the type Br···Br, Br···F, Br···O, Br···N, F···F, H···Br, H···F, F···π and O···π were identified. Specific interactions were quantified by Hirshfeld surface analysis.

Keywords: bromine; fluorine; halogen interaction; Hirshfeld surface analysis; imidazole
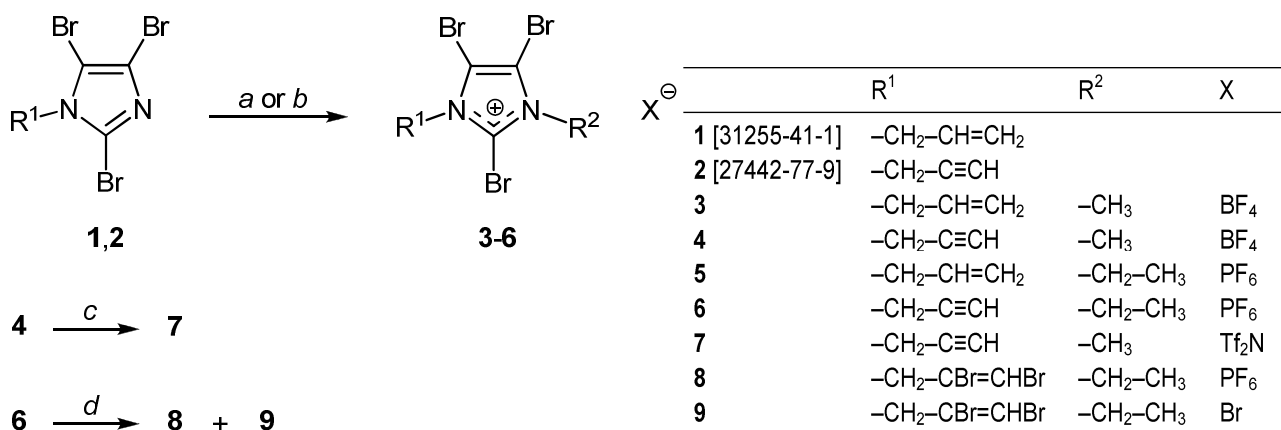
1. Introduction

2,4,5-Tribromoimidazole [CARN 2034-22-2], first described in 1877 [1], is readily prepared by bromination of imidazole [2–7]. It has been found in nature [8] and is an effective fire-retardant agent [9]. It has been used as starting material for the synthesis of quaternary salts as high-density ionic liquids [10]. Halogenated imidazoles exhibit insecticidal [11], parasiticidal [12], acaricidal [13], and herbicidal [14] activity. Only few crystal structures of partially brominated imidazole [15] and quaternary imidazolium salts [16–18] have been reported. A cobalt complex of 2,4,5-tribromoimidazole has been published [19]. To our knowledge, no other crystal structures of 2,4,5-tribromoimidazole

derivatives are known to date. Here we present the structures of eight new compounds of this kind. The quaternary salts are intended for application as non-volatile fire retardants. The olefinic substituents allow the preparation of new materials by polymerization.

2. Results and Discussion

The synthesis (Figure 1) of the propenyl and propynyl derivatives 1 and 2 was carried out by known methods. The salts 3–6 were prepared by quaternization of 1 and 2. Compound 7 was obtained by ion metathesis from 4, and compounds 8 and 9 by bromination of 6. The choice of fluorine-containing anions such as tetrafluoroborate, hexafluorophosphate, and bis(trifluoromethanesulfonyl)imide ("triflimide") provided an opportunity to study non-covalent hetero-halogen, homo-halogen, hydrogen-halogen, and other interactions. Crystal data and structure refinement details are summarized in Table 1. Charge transfer complexes of halogens and electron-donor molecules have been the subject of the 1970 Nobel Prize lecture by Odd Hassel [20]. Today it is known that halogen atoms can act as electron-acceptors (X-bond donors) and electron donors (X-bond acceptors). Theoretical calculations predicted negative ring and positive end cap domains of halogen atoms due to their polarizability [21], even for fluorine [22]. In fact, hetero halogen–halogen interactions in both directions, *i.e.*, Cl→F and F→Cl, have been observed recently [22]. As expected, a classic Br···N interaction was found in 2 (Table 2). Some typical examples of this interaction, displayed by brominated N-heterocycles, are found in the Cambridge Structural Database (CSD) [23–26].

Figure 1. Synthesis of 2,4,5-tribromoimidazolium salts. Reagents and solvents: *a*: $(CH_3)_3O^+BF_4^-/CH_2Cl_2$; *b*: $(C_2H_5)_3O^+PF_6^-/CH_2Cl_2$; *c*: $Li^+Tf_2N^-/MeOH$; *d*: Br_2/CH_2Cl_2.

	R^1	R^2	X
1 [31255-41-1]	$-CH_2-CH=CH_2$		
2 [27442-77-9]	$-CH_2-C\equiv CH$		
3	$-CH_2-CH=CH_2$	$-CH_3$	BF$_4$
4	$-CH_2-C\equiv CH$	$-CH_3$	BF$_4$
5	$-CH_2-CH=CH_2$	$-CH_2-CH_3$	PF$_6$
6	$-CH_2-C\equiv CH$	$-CH_2-CH_3$	PF$_6$
7	$-CH_2-C\equiv CH$	$-CH_3$	Tf$_2$N
8	$-CH_2-CBr=CHBr$	$-CH_2-CH_3$	PF$_6$
9	$-CH_2-CBr=CHBr$	$-CH_2-CH_3$	Br

The role of fluorine, which exhibits the lowest polarizability and highest electronegativity of the halogens, in crystal structures of organic compounds has been reviewed [27]. After some controversy, it has been concluded that short C–H···F contacts between oppositely charged molecules are genuine interionic hydrogen bonds [28]. Non-Linear allylic C–H···F interactions [28] were observed in compound 8. Short interactions between covalent halogen atoms (Br···F and Br···Br) [21] were observed in compounds 3–9. Classic H···Br$^-$ and Br···Br$^-$ bonds were found in the bromide 9. Similar Br···Br$^-$ interactions have been observed in the structures of 2-bromoimidazolium bromides [16,18,29–31], a related Br···F contact in a 2-bromoimidazolium hexafluorophosphate [30], and a typical Br···Br interaction for example in pentabromoferrocene [32].

Table 1. Crystal data and structure refinement details.

Compound	2	3	4	5	6	7	8	9
CCDC no.	881953	881952	881955	881951	881954	881956	881957	881958
Chemical formula	$C_6H_3Br_3N_2$	$C_7H_8Br_3N_2 \cdot BF_4$	$C_7H_6Br_3N_2 \cdot BF_4$	$C_8H_{10}Br_3N_2 \cdot F_6P$	$C_8H_8Br_3N_2 \cdot F_6P$	$C_7H_6Br_3N_2 \cdot C_2F_6NO_4S_2$	$C_8H_8Br_5N_2 \cdot F_6P$	$C_8H_8Br_5N_2 \cdot Br$
M_r	342.83	446.69	444.68	518.88	516.86	638.02	676.68	611.62
Crystal size/mm^3	$0.48 \times 0.08 \times 0.08$	$0.28 \times 0.24 \times 0.20$	$0.27 \times 0.24 \times 0.17$	$0.32 \times 0.20 \times 0.02$	$0.16 \times 0.12 \times 0.01$	$0.24 \times 0.24 \times 0.02$	$0.28 \times 0.20 \times 0.08$	$0.32 \times 0.08 \times 0.08$
Crystal system	Orthorhombic	Tetragonal	Tetragonal	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$Pbc2_1$	$I4_1/a$	$I4_1/a$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	7.1109(2)	23.6138(3)	23.4674(4)	7.5434(3)	8.2368(5)	7.5438(4)	7.6729(4)	7.3200(7)
b/Å	7.8014(2)	23.6138(3)	23.4674(4)	15.5493(7)	13.4522(8)	8.6311(5)	7.8858(5)	11.5867(12)
c/Å	15.6397(5)	18.8371(4)	18.6531(4)	12.7552(4)	13.6605(6)	15.9716(7)	15.8383(7)	18.1972(16)
α/°	90	90	90	90	92.476(4)	75.020(4)	90.001(4)	87.611(8)
β/°	90	90	90	90.198(3)	100.965(4)	87.083(4)	88.104(4)	81.121(8)
γ/°	90	90	90	90	92.884(5)	66.580(5)	62.169(8)	86.375(8)
V/Å^3	867.61(4)	10503.8(3)	10272.6(3)	1496.11(10)	1481.96(14)	920.25(8)	846.88(9)	1521.0(3)
Z	4	32	32	4	4	2	2	4
D_x/g·cm^{-3}	2.63	2.26	2.30	2.30	2.32	2.30	2.65	2.67
μ/mm^{-1}	13.88	9.24	9.45	8.25	11.70	6.88	12.01	15.81
$F(000)$/e	632	6720	6656	984	976	608	628	1120
$\sin\theta_{max}/\lambda$	0.60	0.60	0.60	0.60	0.60	0.60	0.67	0.60
h, k, l range	$-8 \leq h \leq 8$	$-28 \leq h \leq 26$	$-28 \leq h \leq 24$	$-9 \leq h \leq 8$	$-9 \leq h \leq 9$	$-9 \leq h \leq 6$	$-9 \leq h \leq 10$	$-8 \leq h \leq 8$
	$-9 \leq k \leq 9$	$-28 \leq k \leq 28$	$-28 \leq k \leq 23$	$-18 \leq k \leq 15$	$-16 \leq k \leq 15$	$-10 \leq k \leq 9$	$-10 \leq k \leq 10$	$-12 \leq k \leq 13$
	$-18 \leq l \leq 15$	$-14 \leq l \leq 22$	$-22 \leq l \leq 21$	$-15 \leq l \leq 15$	$-16 \leq l \leq 12$	$-19 \leq l \leq 19$	$-20 \leq l \leq 14$	$-21 \leq l \leq 18$
Absorption correction	Multi-scan	Multi-scan	Analytical	Multi-scan	Multi-scan	Gaussian	Multi-scan	Multi-scan
Measured reflections	4789	32072	31973	9203	16144	5550	5619	12598
Independent reflections	1276	4811	4684	2715	5289	3329	3506	5551
(R_{int})	(0.031)	(0.052)	(0.068)	(0.066)	(0.038)	(0.040)	(0.023)	(0.052)

Table 1. *Cont.*

Observed reflections [$I \geq 2\sigma(I)$]	1243	3786	3838	2078	4748	2302	2920	4184
Restraints/parameters	1/104	10/315	14/315	15/188	0/363	1/243	7/204	0/291
R_1/wR_2 [$I \geq 2\sigma(I)$]	0.019/0.042	0.043/0.097	0.044, 0.103	0.055/0.121	0.039/0.102	0.039/0.091	0.043/0.102	0.040/0.062
R_1/wR_2 (all data)	0.021/0.043	0.060/0.105	0.057, 0.110	0.0810.138	0.043/0.106	0.061/0.095	0.057/0.110	0.065/0.071
Goodness of fit	1.09	1.04	1.07	1.04	1.03	0.94	1.07	1.00
$\Delta\rho_{max/min}$/e Å^{-3}	0.53/−0.48	1.59/−0.76	1.96/−1.03	1.26/−0.88	1.82/−0.79	1.01/−0.88	1.73/−1.49	0.86/−0.77

Table 2. Halogen bonding and hydrogen bonding in 2–9.

Compound	Interaction	Distance (d/Å)	$d - \sum r_{vdW}$ (Å)	Angle (°)	Symmetry Operator
2	C–Br3⋯N2	3.089(4)	−0.311	159.8(2)	$1 + x, y, z$
3	C–Br11⋯F5	2.869(5)	−0.451	166.1(2)	x, y, z
	C–Br31⋯F7	2.869(4)	−0.451	168.9(2)	$-1/2 + x, y, 1/2 - z$
	C–Br21⋯F4	2.906(5)	−0.414	179.5(2)	$3/4 + y, 3/4 - x, -1/4 + z$
	C–Br12⋯F3	3.041(6)	−0.279	158.1(2)	x, y, z
	C–Br22⋯F8	3.090(5)	−0.230	172.2(2)	$5/4 + y, 5/4 - x, 1/4 + z$
	C–Br32⋯F3	3.137(6)	−0.183	147.4(2)	$5/4 + y, 5/4 - x, 1/4 + z$
4	C–Br22⋯F2	2.822(5)	−0.498	167.8(2)	$1/4 + y, 1/4 - x, 1/4 + z$
	C–Br12⋯F5	2.826(6)	−0.494	166.1(2)	$-1/2 + x, y, 3/2 - z$
	C–Br32⋯F6	2.944(5)	−0.376	165.3(2)	x, y, z
	C–Br11⋯F3	2.972(7)	−0.348	161.7(2)	$1 - x, -y, 1 - z$
	C–Br21⋯F7	3.094(5)	−0.226	167.2(2)	$1/4 - y, -1/4 + x, -1/4 + z$
	C–Br32⋯F7	3.141(7)	−0.179	151.6(2)	x, y, z
	C–Br31⋯F3	3.244(7)	−0.076	152.2(2)	$1/4 + y, 3/4 - x, 3/4 - z$
5	C–Br2⋯F3A	2.927(10)	−0.393	161.5(4)	$1 - x, -y, 2 - z$
	C–Br3⋯F2	2.989(5)	−0.331	160.0(3)	$3/2 + x, 1/2 - y, 1/2 + z$
6	C–Br21⋯F13	3.010(3)	−0.310	160.9(1)	$1 - x, 1 - y, 1 - z$
	C–Br31⋯F22	3.060(4)	−0.260	161.1(2)	x, y, z
	C–Br22⋯F14	3.084(3)	−0.236	158.9(1)	x, y, z
	C–Br11⋯F23	3.157(5)	−0.163	154.9(2)	$x, y, 1 + z$
	C–Br12⋯F21	3.209(6)	−0.111	127.0(2)	$1 - x, -y, -z$
	C–Br32⋯F15	3.255(4)	−0.065	171.0(1)	$1 - x, 1 - y, 1 - z$
7	C–Br3⋯O3	2.943(4)	−0.427	167.1(2)	$-1 + x, 1 + y, z$
	C–Br2⋯O3	3.201(3)	−0.169	152.9(2)	$1 - x, 1 - y, 1 - z$
	C–H6⋯O1	2.32(5)	−0.402	160(5)	$-x, 1 - y, 2 - z$
	C–F3⋯F3	2.700(7)	−0.240	163.7(4)	$1 - x, 1 - y, 2 - z$
8	C–Br3⋯F2	3.017(6)	−0.303	173.6(2)	$x, 1 + y, z$
	C–Br5⋯Br5	3.517(1)	−0.183	143.6(2)	$3 - x, -y, 2 - z$
	C–Br2⋯Br2	3.575(1)	−0.125	129.6(2)	$2 - x, 1 - y, 1 - z$
	C–H6⋯F6	2.38(3)	−0.290	164(4)	x, y, z
	C–H6⋯F2	2.50(6)	−0.174	140(4)	x, y, z
9	C–Br1⋯Br6	3.032(1)	−0.668	177.7(2)	$1 - x, -y, -z$
	C–Br7⋯Br12	3.092(1)	−0.608	177.6(2)	$1 - x, 1 - y, 1 - z$
	C–Br8⋯Br6	3.201(1)	−0.499	176.6(2)	$1 + x, y, z$
	C–Br9⋯Br12	3.230(1)	−0.470	175.2(2)	$1 - x, -y, 1 - z$
	C–Br3⋯Br12	3.291(1)	−0.409	175.6(2)	x, y, z
	C–Br4⋯Br4	3.474(1)	−0.226	152.9(2)	$2 - x, -1 - y, -z$
	C–H8⋯Br6	2.756(1)	−0.294	148.3(4)	x, y, z
	C–H16⋯Br12	2.812(1)	−0.238	155.1(4)	x, y, z

Lately, attractive anion⋯π interactions have been recognized as supramolecular forces between anions and electron-deficient heterocyclic ring system [33,34]. We indeed observed interactions of the tetrafluoroborate, hexafluorophosphate, and triflimide anions with the tribromoimidazolium system. The cut-off for anion⋯π interactions has not been clearly established [33]. We judged such an

interaction as existing when at least three interactions with the atoms of a five-membered ring shorter than the sum of van der Waals (vdW) radii were found, as in compounds 3–5 and 7 (Table 3).

Table 3. Anion···π interactions in 3, 4, 5 and 7.

Compound	Interaction	Distance (*d*/Å)	$d - \sum r_{vdW}$ (Å)	Symmetry Operator
3	C11···F5	2.900(7)	−0.270	$3/4 + y, 5/4 - x, 1/4 - z$
	C21···F5	3.084(7)	−0.086	$3/4 + y, 5/4 - x, 1/4 - z$
	N21···F5	2.935(6)	−0.085	$3/4 + y, 5/4 - x, 1/4 - z$
	C31···F5	3.137(7)	−0.033	$3/4 + y, 5/4 - x, 1/4 - z$
	N11···F5	3.025(7)	+0.005	$3/4 + y, 5/4 - x, 1/4 - z$
	centroid···F5	2.790		
4	C32···F5	3.162(9)	−0.008	$1/4 - y, -1/4 + x, -1/4 + z$
	N22···F5	2.957(7)	−0.063	$1/4 - y, -1/4 + x, -1/4 + z$
	C12···F5	2.940(8)	−0.230	$1/4 - y, -1/4 + x, -1/4 + z$
	C22···F5	3.109(8)	−0.061	$1/4 - y, -1/4 + x, -1/4 + z$
	N12···F5	3.073(8)	+0.053	$1/4 - y, -1/4 + x, -1/4 + z$
	centroid···F5	2.824		
5	C3···F4B	3.10(1)	−0.068	$1/2 + x, 1/2 - y, 1/2 + z$
	C1···F4B	3.11(1)	−0.055	$1/2 + x, 1/2 - y, 1/2 + z$
	C2···F4B	3.13(1)	−0.044	$1/2 + x, 1/2 - y, 1/2 + z$
	N1···F4B	3.10(1)	+0.080	$1/2 + x, 1/2 - y, 1/2 + z$
	N2···F4B	3.16(1)	+0.140	$1/2 + x, 1/2 - y, 1/2 + z$
	centroid···F4B	2.901		
7	C3···O2	2.901(6)	−0.319	x, y, z
	C2···O2	3.054(7)	−0.166	x, y, z
	N1···O2	3.041(7)	−0.029	x, y, z
	C1···O2	3.255(8)	+0.035	x, y, z
	N2···O2	3.278(7)	+0.208	x, y, z
	centroid···O2	2.887		

Table 4. Percent contributions of selected interactions relative to the whole Hirshfeld surface. Independent cations are termed A and B.

Interaction	Compound											
	2	3A	3B	4A	4B	5	6A	6B	7	8	9A	9B
Br···Br	12.0	9.4	9.5	11.1	10.1	7.3	5.8	5.2	5.6	19.0	22.4	22.7
Br···H/H···Br	36.3	24.4	27.0	23.1	21.8	22.3	20.5	18.5	13.5	29.2	54.7	55.4
Br···C/C···Br	18.8	1.6	0.9	1.8	4.2	1.1	3.2	3.5	4.0	5.9	8.9	6.9
Br···N/N···Br	10.5	0.2	0.2	0.2	0.4	0	0	0	0.2	0	1.3	1.3
Br···O	-	-	-	-	-	-	-	-	8.9	-	-	-
Br···F	-	13.3	13.2	16.5	13.7	13.8	17.5	15.8	14.4	13.7	-	-
C···H/H···C	12.9	4.0	5.1	16.6	9.9	1.7	15.2	12.4	0.7	0	3.2	4.5
C···O	-	-	-	-	-	-	-	-	6.3	-	-	-
C···F	-	4.9	4.5	7.6	9.2	5.1	5.3	5.8	6.8	4.4	-	-
H···F	-	20.9	16.8	7.6	16.3	26.6	18.7	24.7	17.2	19.6	-	-
H···H	1.1	19.1	20.6	5.5	11.8	20.4	11.4	11.7	4.2	6.5	9.6	9.1
H···O	-	-	-	-	-	-	-	-	11.9	-	-	-

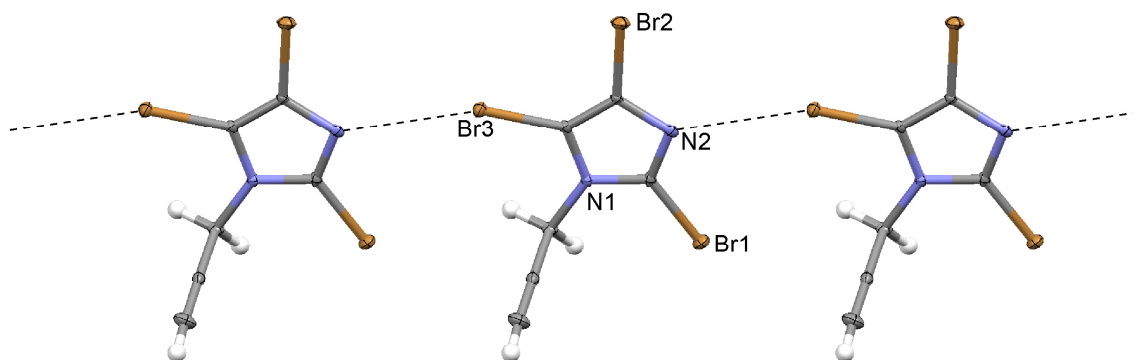A few imidazolium tetrafluoroborates which also exhibit this type of interaction with short F⋯centroid distances have been located in the CSD [35–37], although not described as such by the respective authors. Likewise, examples of PF$_6$⋯π [38–40] and S=O⋯π [30,41,42] interactions in imidazolium hexafluorophosphates, triflimides, and triflates should be mentioned.

Commonly accepted van der Waals radii [43,44] were used in this work, although the radii of anionic species may be considered to be larger [33]. Finally, Hirshfeld surface analysis [45–48] was performed to obtain quantitative insight into the cation–anion interactions (Table 4).

2.1. 2,4,5-Tribromo-1-(prop-2-ynyl)imidazole (2)

The imidazole molecules are arranged in chains in the [1 0 0] direction by short Br⋯N interactions, as shown in Figure 2. Distance and angle of this directed interaction are in the typical range. Being the only neutral molecule in this study, electrostatic N⋯H interactions are found by Hirshfeld surface analysis, whereas the ionic compounds show zero interactions of this kind. On the other hand, H⋯H interactions are negligible in 2 compared to the salt structures 3–9.

Figure 2. Chains of molecules of 2 in the direction of the crystallographic *a* axis.

2.2. 2,4,5-Tribromo-3-methyl-1-(prop-2-enyl)imidazolium Tetrafluoroborate (3)

Two independent ion pairs are found in the asymmetric unit. Short Br⋯F contacts are clearly detected between the tribromoimidazolium cations and the tetrafluoroborate anions (Figure 3). The C–Br⋯F angles are nearly linear, exceptions are probably due to packing effects. There are indisputable interactions of the anion with the aromatic π system observed, with a short anion⋯centroid distance. Evidently, the anion is located on top of the aromatic ring, fixed by four contacts shorter than the sum of van der Waals radii (Table 3). These weak interactions can be overridden by packing effects [49], and it has been remarked that it is still not possible to predict anion⋯π interactions [49]. Thus, it is not surprising that the π-system of the second cation does not exhibit perceptible interactions with an anion.

**Figure 3.** (**a**) Typical Br···F interactions; and (**b**) the anion···π interactions in the propenyl imidazolium tetrafluoroborate 3. Only one of the two independent cations is shown. The other one exhibits very similar Br···F contacts.

(**a**)   (**b**)
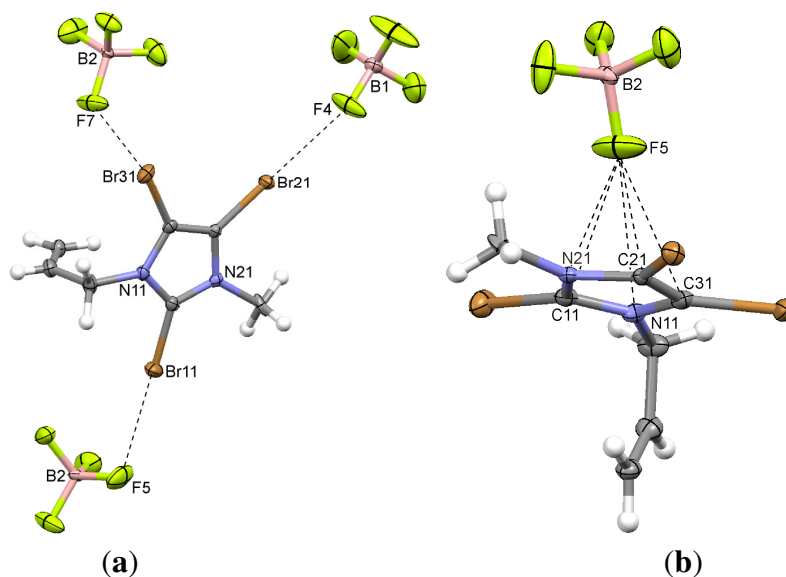
2.3. 2,4,5-Tribromo-3-methyl-1-(prop-2-ynyl)imidazolium Tetrafluoroborate (4)

The unit cell is very similar to that of the previous compound 3. Again, two ion pairs are in the asymmetric unit. The Br···F contacts, with angles between 152 and 168° (Table 2) are slightly different, one bromine atom exhibiting a bifurcated Br···F interaction (Figure 4a). The π-system of one imidazolium cation is involved in four short contacts with a tetrafluoroborate anion (Table 3). In contrast to 3, a surprisingly high contribution of C···H interactions is revealed by Hirshfeld surface analysis which, everything else being equal, can only be attributed to the propynyl substituent.

Figure 4. (**a**) Typical Br···F interactions; and (**b**) the anion···π interactions in the propenyl imidazolium tetrafluoroborate 4. Only one of the two independent cations is shown. The other one exhibits very similar Br···F contacts.

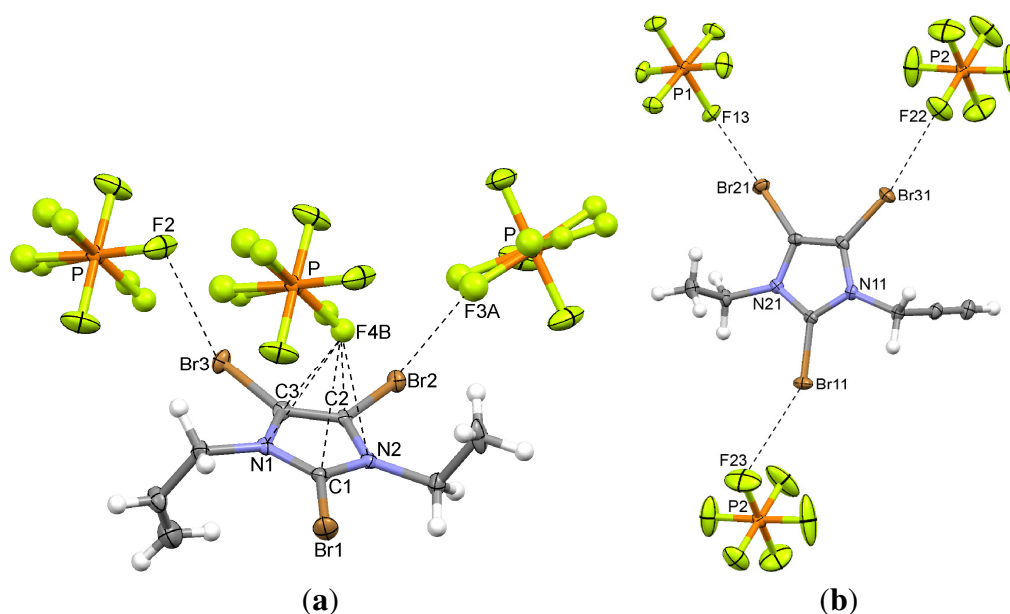(**a**)   (**b**)
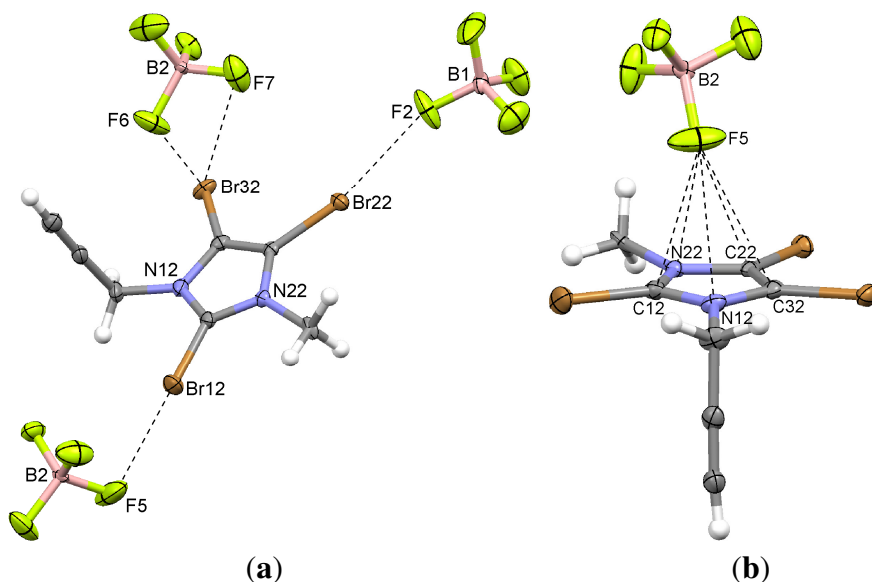
2.4. 2,4,5-Tribromo-3-ethyl-1-(prop-2-enyl)imidazolium Hexafluorophosphate (5)

In this structure, the two alkyl substituents of the imidazolium cation adopt an anti conformation. The pronounced prolate shape of the thermal ellipsoids of some of the fluorine atoms of the PF_6 anion indicated the presence of a disorder that was modeled by introducing split positions (A and B with occupancy factors of 0.50) for the F1, F3 and F4 atoms, which were refined isotropically. Since no temperature dependent measurements were performed the question remains whether the disorder is static or dynamic. Two short Br···F contacts with C–Br···F angles around 160° are observed. A skewed anion···π interaction (Figure 5a) is found with a short F···centroid distance (Table 3). Obviously, the anion is not located exactly over the center of the ring, only three contacts shorter than the sum of van der Waals radii are found in this case. The anion is interacting predominantly with the carbon atoms of the heterocyclic ring system.

Figure 5. Interionic interactions in the hexafluorophosphates of (**a**) the propenyl imidazolium salt 5 (Br···F and anion···π) and (**b**) the propynyl imidazolium salt 6 (Br···F). Only one of the two independent cations in 6 is shown.


(**a**)   (**b**)

2.5. 2,4,5-Tribromo-3-ethyl-1-(prop-2-ynyl)imidazolium Hexafluorophosphate (6)

Two ion pairs are located in the asymmetric unit. Again, the two alkyl substituents adopt the anti conformation. In this instance, no anion···π interaction is detected, but the typical Br···F contacts (Figure 5b) are found in both ion pairs. The C–Br···F angles range from 155 to 171° (Table 2) which is the typical angular preference [28]. One interaction (C–Br12···F21) exhibits a suspiciously small angle. However, this contact is three percent shorter than the sum of van der Waals radii and cannot be ignored. Once again, a surprisingly high contribution of C···H interactions is revealed by Hirshfeld surface analysis.

2.6. 2,4,5-Tribromo-3-methyl-1-(prop-2-ynyl)imidazolium Triflimide (7)

The triflimide ion adopts the anti conformation (C–S···S–C torsion angle of 170.6°); this conformation is preferred in metal-free triflimide structures [50]. The angle C–C≡C is found to be 175.8°. A "classic" C_{sp}–H···O hydrogen bond between H6 and O1 is observed, thus forming a cyclic dimer (Figure 6). Interestingly, in this structure no Br···Br or Br···F interactions are found, but Br···O contacts to the sulfonyl group, as noticed earlier in related structures [17,51,52], and a F···F contact across a symmetry center. However, an anion···π interaction is observed. This time one partially negatively charged oxygen atom of a sulfonyl group is involved in three contacts shorter than the sum of van der Waals radii. Again, the interacting atom of the anion is shifted from the center of the π system and is located over the rim of the heterocycle, exhibiting short contacts with N1, C2, and C3 of the imidazolium ring.

**Figure 6.** Classic C–H···O hydrogen bonds forming a cyclic dimer and anion···π interaction in the propynyl imidazolium triflimide 7.
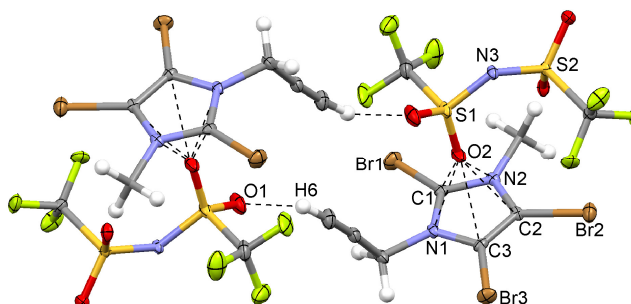
2.7. 2,4,5-Tribromo-1-(2,3-dibromoprop-2-enyl)-3-ethylimidazolium Hexafluorophosphate (8)

As before, there are almost linear Br···F contacts between the ions. The structure also exhibits Br2···Br2 interactions in the ring plane, forming layers which are connected by Br5···Br5 contacts to give a three-dimensional network (Figure 7). The Br···Br contacts are both across a symmetry center, deviate from linearity due to packing (Table 2), and are also found prominently in the Hirshfeld surface analysis (Table 4). The allylic C–H···F interactions are also detected in the Hirshfeld analysis.

Figure 7. The halogen···halogen interactions in 2,4,5-tribromo-1-(2,3-dibromoprop-2-enyl)-imidazolium hexafluorophosphate (8).
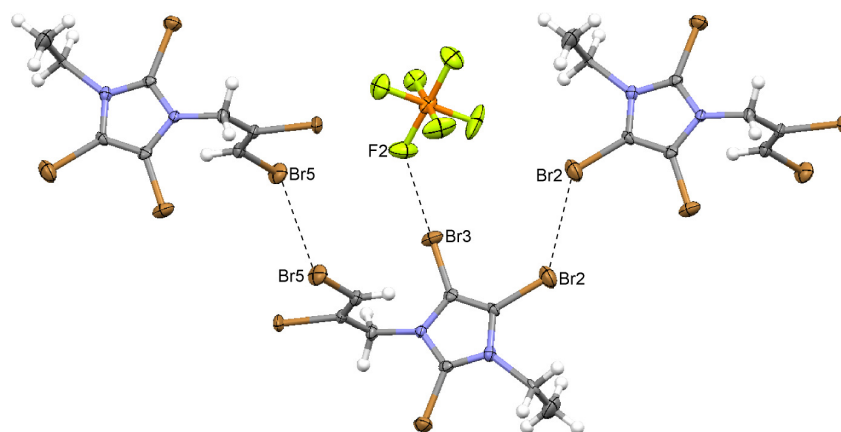
2.8. 2,4,5-Tribromo-1-(2,3-dibromoprop-2-enyl)-3-ethylimidazolium Bromide (9)

Two independent ion pairs are located in the asymmetric unit. The presence of the brominated side chain results in an increased number of Br···Br contacts such as short Br4···Br4 and weak Br1···Br1 and Br9···Br9 contacts across a symmetry center. Strong bromine···bromide contacts exist in the crystal which are significantly shorter than the sum of van der Waals radii, even without taking into account the fact that bromide has a larger van der Waals radius than covalently bound bromine [33]. The C–Br···Br⁻ angles are close to 180°, indicating linearity of the X-bonds. The coordination around the two independent bromide ions is shown in Figure 8. It is not unexpected that, due to the brominated side chain, contacts involving Br atoms are quite dominant in the Hirshfeld surface analysis. According to this analysis, C–H···Br contacts by far represent the majority of interactions, obviously due to the relatively strong C_{sp2}–H···Br⁻ interactions, followed by Br···Br contacts. Some examples of similar situations are found in the Cambridge Structural Database [53–56].

Figure 8. Bromine···Bromide and hydrogen···bromide coordination of the two independent bromide ions (**a**) Br6 and (**b**) Br12 in the structure of 2,4,5-tribromo-(2,3-dibromoprop-2-enyl)-3-ethylimidazolium bromide (9).

(**a**)

(**b**)
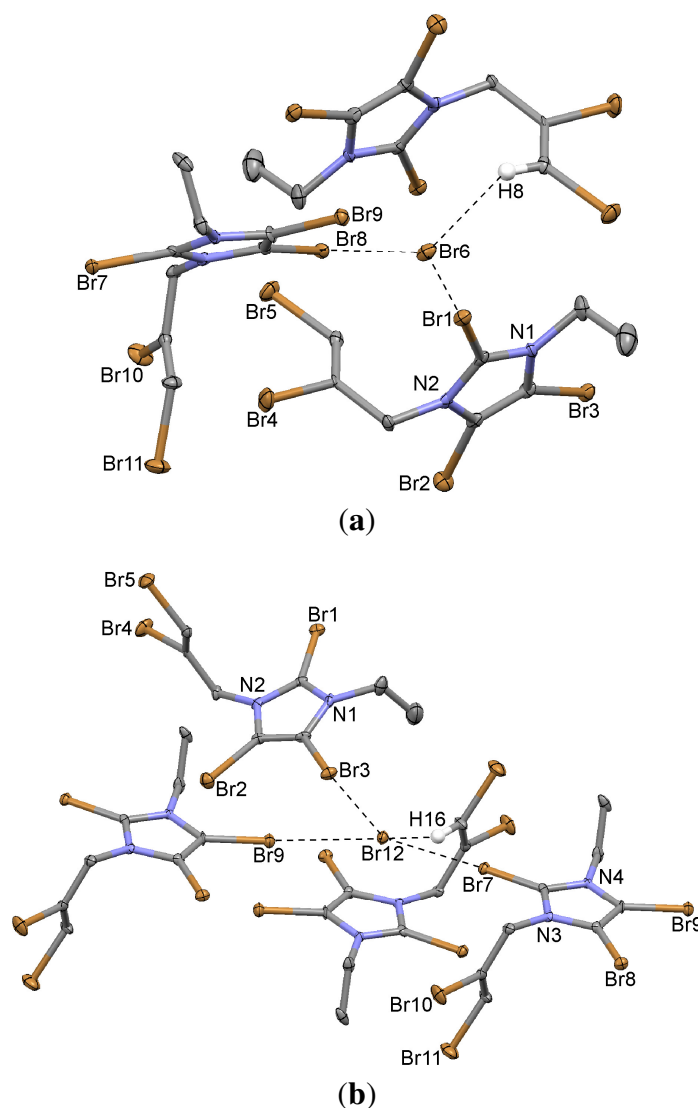
3. Experimental Section

Chemicals and solvents were purchased from Sigma-Aldrich and used as received. 2,4,5-Tribromo-1-(prop-2-enyl)imidazole (1) [CARN 31255-41-1] and 2,4,5-tribromo-1-(prop-2-ynyl) imidazole (2) [CARN 27442-77-9] were prepared according to published procedures [12,13,57].

3.1. Data of 2,4,5-Tribromo-1-(Prop-2-Ynyl)Imidazole (2)

m.p. 123 °C. IR (neat): ν 3288 (m), 2129 (w), 1494 (m), 1433 (m), 1410 (m), 1380 (m), 1335 (m), 1214 (m), 1192 (m), 1121 (m), 985 (m), 937 (m), 758 (m), 682 (s), 651 (s)·cm^{-1}. ^{13}C NMR (DMSO-d$_6$, 75 MHz): δ 37.7, 76.4, 76.8, 105.9, 116.0, 118.9 ppm. Single crystals were obtained from MeOH.

3.2. General Procedure for the Alkylation of 1-Alkylimidazoles (3–6)

To a solution of trimethyloxonium tetrafluoroborate or triethyloxonium hexafluorophosphate (16 mmol) in anhydrous CH$_2$Cl$_2$ (5 mL) the respective 2,4,5-tribromo-1-alkylimidazole (1.0 eq.) was added and stirred overnight at room temperature. Et$_2$O was added, and the resulting colorless solid was filtered and dried under reduced pressure. Single crystals were obtained from MeOH.

2,4,5-Tribromo-3-methyl-1-(prop-2-enyl)imidazolium tetrafluoroborate (3): m.p. 179 °C. IR (neat): ν 1553 (w), 1501 (w), 1049 (s), 1035 (s), 946 (w), 669 (w)·cm^{-1}. ^{13}C NMR (DMSO-d$_6$, 75 MHz): δ 37.8, 52.4, 110.8, 112.5, 118.9, 124.5, 129.1 ppm.

2,4,5-Tribromo-3-methyl-1-(prop-2-ynyl)imidazolium tetrafluoroborate (4): m.p. 203 °C. IR (neat): ν 2135 (w), 1554 (w), 1498 (w), 1050 (s), 1035 (s), 816 (w), 679 (w), 652 (w)·cm^{-1}.

2,4,5-Tribromo-3-ethyl-1-(prop-2-enyl)imidazolium hexafluorophosphate (5): m.p. 228 °C (dec). IR (neat): ν 1496 (w), 1122 (w), 936 (w), 831 (s), 669 (w)·cm^{-1}.

2,4,5-Tribromo-3-ethyl-1-(prop-2-ynyl)imidazolium hexafluorophosphate (6): m.p. 232 °C (dec). IR (neat): ν 2135 (w), 1559 (w), 1494 (w), 1118 (m), 1051 (s), 833 (s), 710 (s)·cm^{-1}.

3.3. 2,4,5-Tribromo-3-methyl-1-(prop-2-ynyl)imidazolium Triflimide (7)

A solution of 2,4,5-tribromo-3-methyl-1-(prop-2-ynyl)imidazolium tetrafluoroborate (4) and lithium triflimide (1.05 eq.) in MeOH was stirred for 18 h. After evaporation of the solvent, the residual solid was suspended in H$_2$O. The mixture was extracted twice with CH$_2$Cl$_2$. The organic phase was washed three times with H$_2$O and dried under reduced pressure to give a colorless solid. m.p. 122 °C. IR (neat): ν 2135 (w), 1556 (w), 1500 (w), 1351 (s), 1333 (m), 1190 (s), 1178 (s), 1137 (s), 1116 (m), 1046 (s), 1033 (s), 959 (w), 819 (w), 794 (w), 743 (w), 694 (w), 613 (s)·cm^{-1}. Single crystals were obtained from MeOH.

3.4. 2,4,5-Tribromo-1-(2,3-dibromoprop-2-enyl)-3-ethylimidazolium Hexafluorophosphate (8)

Bromine (1.0 eq.) was added to an ice-cooled suspension of 6 in CH$_2$Cl$_2$. The mixture was stirred at room temperature for 18 h, and the colorless precipitate was filtered, washed with CH$_2$Cl$_2$, and dried

under reduced pressure. m.p. 206 °C. IR (neat): ν 837 (s), 673 (w)·cm^{-1}. Single crystals were obtained from MeOH.

3.5. 2,4,5-Tribromo-1-(2,3-dibromoprop-2-enyl)-3-ethylimidazolium Bromide (9)

Crystals of this minor byproduct were spotted in the major product 8.

3.6. X-ray Crystal Structure Determination

Intensity data were recorded with an Oxford Diffraction Gemini-R Ultra diffractometer using Mo-*K*α radiation at *T* = 173(2) K. For 6, Cu-*K*α radiation was used. Experimental details are summarized in Table 1. Structure solution and refinement was performed with the programs SIR2002 (direct methods) [58] and SHELXL-97 [59]. A Flack parameter of 0.03(2) was obtained for the non-centrosymmetric structure of 2. The crystals of 8 were subject to non-merohedral twinning which was taken into consideration during data reduction, integration and refinement. Visualization of the structures and measurements of distances and angles was performed with the program Mercury [60]. CCDC reference numbers: 881951–881958. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

4. Conclusions

The crystal structures of eight *N*-alkylated 2,4,5-tribromoimidazole compounds were determined. Halogen interactions and anion···π interactions were detected. Hirshfeld surface analysis (Figure 9) yielded quantitative information about these interactions. These results are supposed to further our understanding of halogen interactions in the solid state.

Figure 9. (**a**) Normalized Hirshfeld surface of the cation in 5 and associated fingerprint plots highlighting specific interactions; (**b**) Br···Br; (**c**) Br···H (reciprocal interactions included); (**d**) Br···F and (**e**) H···F. The full fingerprint appears as a grey shadow.
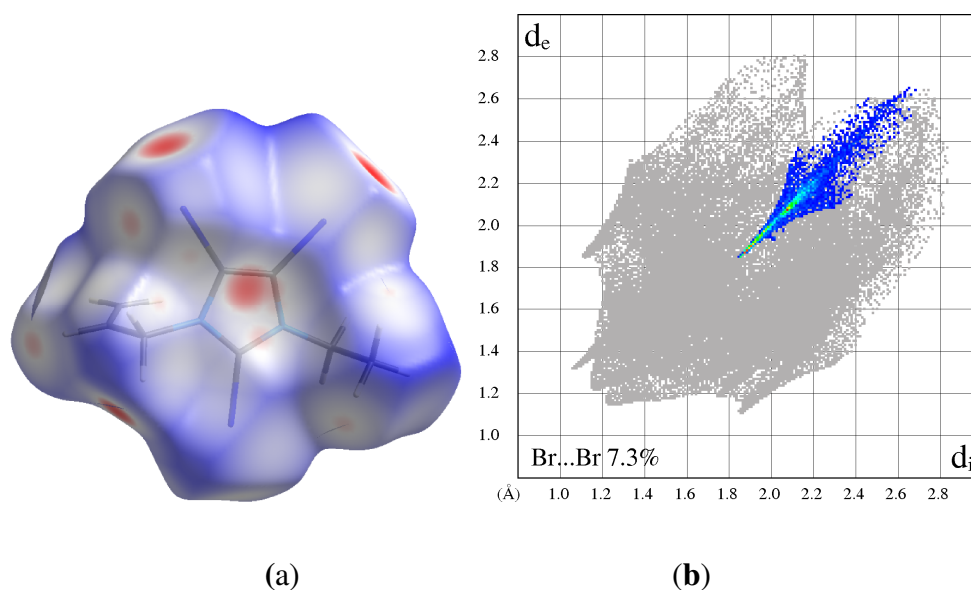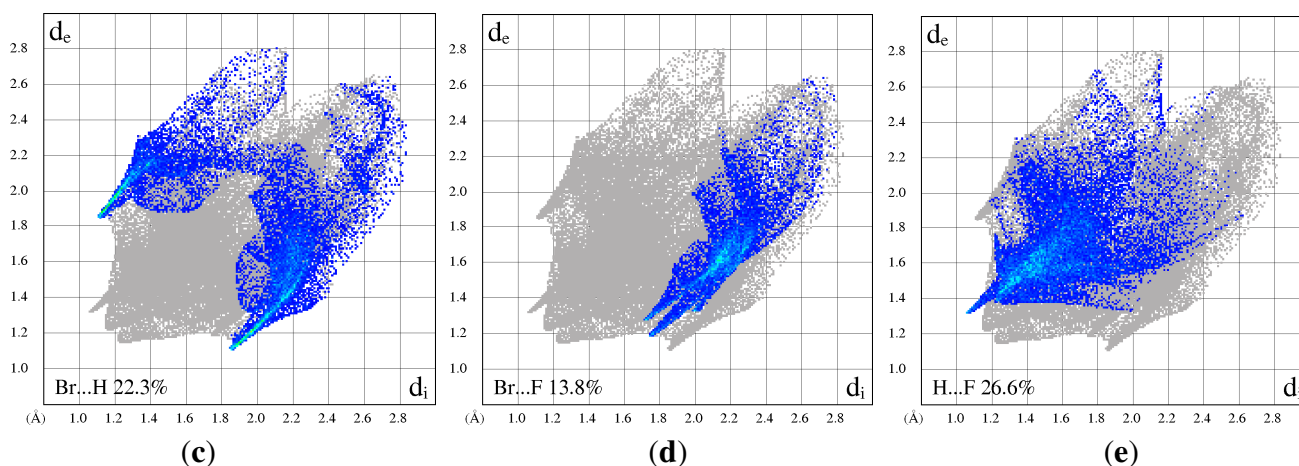
(a)   (b)

Figure 9. *Cont.*

(c)   (d)   (e)

Acknowledgments

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