

Electronic Supplementary Information

Noncovalent Interactions in Halogenated Ionic Liquids: Theoretical Study and Crystallographic Implications

Haiying Li,^a Yunxiang Lu,^{*a} Weihong Wu, Yingtao Liu,^b Changjun Peng,^a Honglai Liu,^a and Weiliang Zhu^b

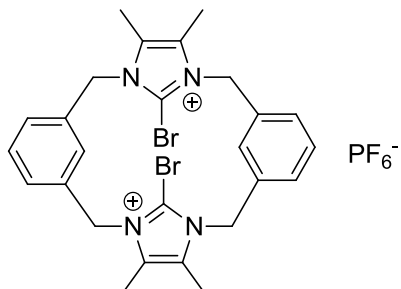
^a *Key Laboratory for Advanced Materials and Department of Chemistry, East China University of Science and Technology, Shanghai, 200237, China. E-mail: yxlu@ecust.edu.cn*

^b *Drug Discovery and Design Center, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai, 201203, China*

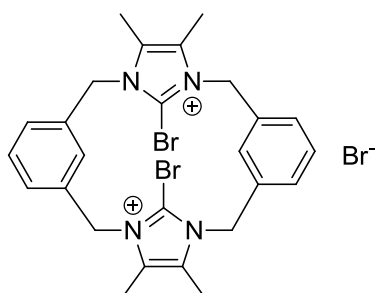
The results of the CSD search:

1. Halogen substituents in the 2 position (15 crystal structures)

ALOKIW: Angew. Chem. Int. Ed., 2011, 50, 1845.

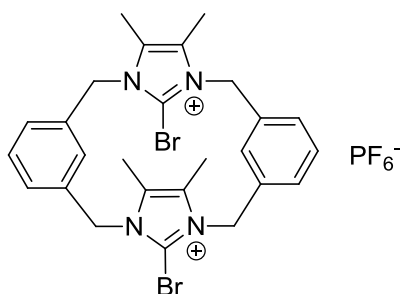


ALOKOC: Angew. Chem. Int. Ed., 2011, 50, 1845.



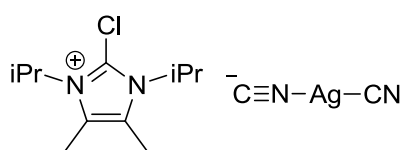
XB ($\text{C}-\text{Br}\cdots\text{Br}^-$): $R(\text{Br}\cdots\text{Br}^-) = 3.2 \text{ \AA}$; $\angle(\text{C}-\text{Br}\cdots\text{Br}^-) = 174.2^\circ$

ALOLAP: Angew. Chem. Int. Ed., 2011, 50, 1845

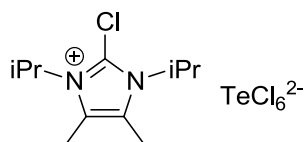


XB ($\text{C}-\text{Br}\cdots\text{F}$): $R(\text{Br}\cdots\text{F}) = 3.1 \text{ \AA}$; $\angle(\text{C}-\text{Br}\cdots\text{F}) = 160.0^\circ$

ASAZAW: Z. Naturforsch. B: Chem. Sci., 2011, 66, 545

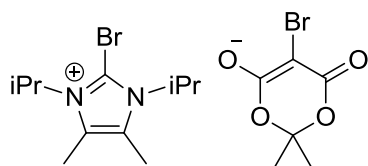


AXEFOY: Z. Anorg. Allg. Chem., 2004, 630, 495



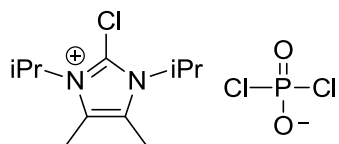
XB (C–Cl $\cdots$ Cl): $R(\text{Cl}\cdots\text{Cl}) = 3.2 \text{ \AA}$; $\angle(\text{C}-\text{Cl}\cdots\text{Cl}) = 161.9^\circ$

AYEHOB: Z. Naturforsch. B: Chem. Sci., 2004, 59, 129.



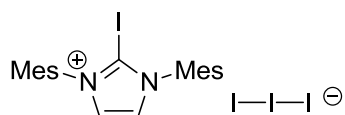
XB (C–Br $\cdots$ O): $R(\text{Br}\cdots\text{O}) = 2.9 \text{ \AA}$; $\angle(\text{C}-\text{Br}\cdots\text{O}) = 153.9^\circ$

EHENIO: Z. Anorg. Allg. Chem., 2002, 628, 2251.



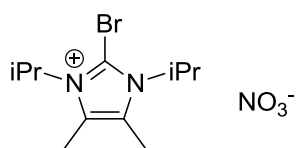
XB (C–Cl $\cdots$ O): $R(\text{Cl}\cdots\text{O}) = 2.8 \text{ \AA}$; $\angle(\text{C}-\text{Cl}\cdots\text{O}) = 180.0^\circ$

FAJCID: Dalton. Trans., 2004, 3909



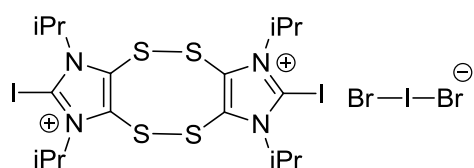
XB (C–I⋯I): $R(\text{I} \cdots \text{I}) = 3.4 \text{ \AA}$; $\angle(\text{C} - \text{I} \cdots \text{I}) = 177.9^\circ$

FALCIF: Z. Anorg. Allg. Chem., 2004, 630, 2054



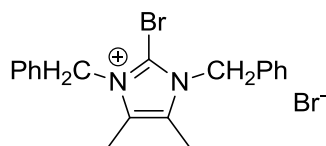
XB (C–Br⋯O): $R(\text{Br} \cdots \text{O}) = 3.0 \text{ \AA}$; $\angle(\text{C} - \text{Br} \cdots \text{O}) = 159.1^\circ$

GAZQIH: Inorg. Chim. Acta., 198, 273, 175.



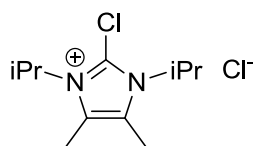
XB (C–I⋯Br): $R(\text{I} \cdots \text{Br}) = 3.3 \text{ \AA}$; $\angle(\text{C} - \text{I} \cdots \text{Br}) = 163.2^\circ$

HABNAB: Angew. Chem. Int. Ed., 2010, 49, 5322

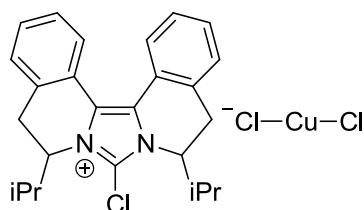


XB (C–Br⋯Br[−]): $R(\text{Br} \cdots \text{Br}^-) = 3.3 \text{ \AA}$; $\angle(\text{C} - \text{Br} \cdots \text{Br}^-) = 172.6^\circ$

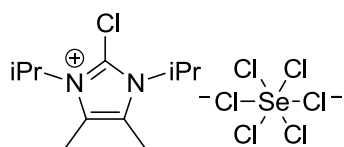
HILMEU: Z. Naturforsch. B: Chem. Sci., 1998, 53, 720



POXMUL: Chem. Commun., 2009, 2475.

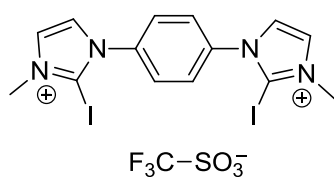


QIVPOB: Inorg. Chem., 2007, 46, 8594.



XB (C–Cl⋯Cl): $R(\text{Cl} \cdots \text{Cl}) = 3.2 \text{ \AA}$; $\angle(\text{C} - \text{Cl} \cdots \text{Cl}) = 165.2^\circ$

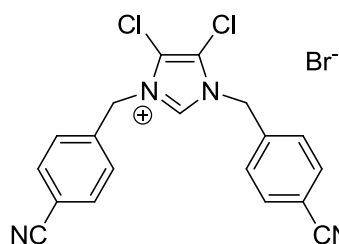
ITUPAP: Angew. Chem. Int. Ed., 2011, 50, 7187.



XB (C–I⋯O): $R(\text{I} \cdots \text{O}) = 3.2 \text{ \AA}$; $\angle(\text{C} - \text{I} \cdots \text{O}) = 174.2^\circ$

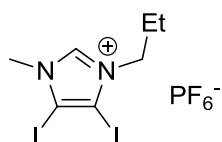
2. Halogen substituents in the 4 or 5 position (10 crystal structures)

EJEMAI: Appl. Organomet. Chem., 2010, 24, 781.



XB (C–Cl $\cdots$ Br $^-$): $R(\text{Cl}\cdots\text{Br}^-) = 3.2 \text{ \AA}$; $\angle(\text{C}-\text{Cl}\cdots\text{Br}^-) = 166.9^\circ$

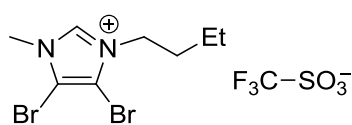
PUZZIU: X-ray. Str. Anal. Online., 2010, 26, 39.



XB (C–I $\cdots$ F): $R(\text{I}\cdots\text{F}) = 3.1 \text{ \AA}$; $\angle(\text{C}-\text{I}\cdots\text{F}) = 174.9^\circ$

$R(\text{I}\cdots\text{F}) = 3.2 \text{ \AA}$; $\angle(\text{C}-\text{I}\cdots\text{F}) = 159.6^\circ$

VURKUP: Solid. State. Sci., 2010, 12, 783.



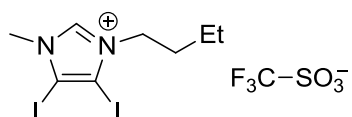
XB (C–Br $\cdots$ O): $R(\text{Br}\cdots\text{O}) = 3.2 \text{ \AA}$; $\angle(\text{C}-\text{Br}\cdots\text{O}) = 147.8^\circ$

$R(\text{Br}\cdots\text{O}) = 3.0 \text{ \AA}$; $\angle(\text{C}-\text{Br}\cdots\text{O}) = 165.7^\circ$

$R(\text{Br}\cdots\text{O}) = 3.2 \text{ \AA}$; $\angle(\text{C}-\text{Br}\cdots\text{O}) = 147.7^\circ$

$R(\text{Br}\cdots\text{O}) = 3.0 \text{ \AA}$; $\angle(\text{C}-\text{Br}\cdots\text{O}) = 165.6^\circ$

VURLAW: Solid. State. Sci., 2010, 12, 783.



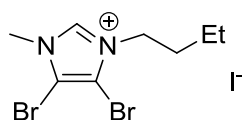
XB (C–I $\cdots$ O): $R(\text{I}\cdots\text{O}) = 2.9 \text{ \AA}$; $\angle(\text{C-I}\cdots\text{O}) = 171.4^\circ$

$R(\text{I}\cdots\text{O}) = 2.9 \text{ \AA}$; $\angle(\text{C-I}\cdots\text{O}) = 174.3^\circ$

$R(\text{I}\cdots\text{O}) = 2.9 \text{ \AA}$; $\angle(\text{C-I}\cdots\text{O}) = 171.4^\circ$

$R(\text{I}\cdots\text{O}) = 2.9 \text{ \AA}$; $\angle(\text{C-I}\cdots\text{O}) = 174.4^\circ$

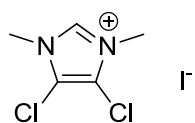
VUSNIH: X-ray. Str. Anal. Online., 2010, 26, 31.



XB (C–Br $\cdots$ I $^-$): $R(\text{Br}\cdots\text{I}^-) = 3.6 \text{ \AA}$; $\angle(\text{C-Br}\cdots\text{I}^-) = 175.6^\circ$

$R(\text{Br}\cdots\text{I}^-) = 3.6 \text{ \AA}$; $\angle(\text{C-Br}\cdots\text{I}^-) = 171.5^\circ$

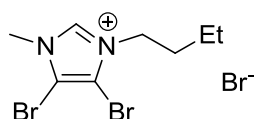
WOMYED: J. Med. Chem., 2008, 51, 1577.



XB (C–Cl $\cdots$ I $^-$): $R(\text{Cl}\cdots\text{I}^-) = 3.6 \text{ \AA}$; $\angle(\text{C-Cl}\cdots\text{I}^-) = 168.5^\circ$

$R(\text{Cl}\cdots\text{I}^-) = 3.6 \text{ \AA}$; $\angle(\text{C-Cl}\cdots\text{I}^-) = 155.0^\circ$

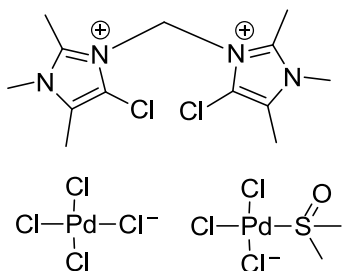
YOXWAK: Chem. Lett., 2009, 38, 402.



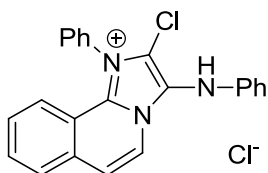
XB (C–Br⋯Br[−]): $R(\text{Br}\cdots\text{Br}^-) = 3.2 \text{ \AA}$; $\angle(\text{C}-\text{Br}\cdots\text{Br}^-) = 174.7^\circ$

$R(\text{Br}\cdots\text{Br}^-) = 3.2 \text{ \AA}$; $\angle(\text{C}-\text{Br}\cdots\text{Br}^-) = 168.8^\circ$

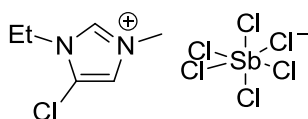
CUPPEJ: Chem. Eur. J., 2009, 15, 9375.



DUVCIG: ACA Abstr. Papers (Winter), 1986, 14, 62.



FUDFUG: Z. Anorg. Allg. Chem., 2009, 635, 1036.



XB (C–Cl⋯Cl): $R(\text{Cl}\cdots\text{Cl}) = 3.3 \text{ \AA}$; $\angle(\text{C}-\text{Cl}\cdots\text{Cl}) = 161.8^\circ$

Table S1 Selected MK and Chelpg charges of atoms and groups for the cations **1-5**.^a

Atoms	1		2		3		4		5	
/Groups	MK	Chelpg	MK	Chelpg	MK	Chelpg	MK	Chelpg	MK	Chelpg
N ₁	0.238	0.173	0.299	0.190	0.347	0.213	-0.390	0.198	0.500	0.216
C ₂	-0.146	-0.123	-0.214	-0.073	-0.319	-0.175	0.312	-0.134	-0.372	-0.123
N ₃	0.225	0.173	0.299	0.190	0.347	0.213	-0.390	0.198	0.488	0.215
C ₄	-0.182	-0.126	-0.194	-0.124	-0.202	-0.123	0.010	-0.057	-0.290	-0.12
C ₅	-0.188	-0.126	-0.194	-0.124	-0.202	-0.123	0.010	-0.057	-0.299	-0.119
H/X(C ₂)	0.227	0.214	0.210	0.195	0.293	0.289	0.254	0.197	0.230	0.178
H/X(C ₄)	0.236	0.199	0.228	0.190	0.223	0.182	0.243	0.136	0.247	0.202
H/X(C ₅)	0.237	0.199	0.228	0.190	0.223	0.182	0.243	0.136	0.248	0.202
C ₂ -H/X	0.081	0.091	-0.004	0.122	-0.026	0.114	0.566	0.063	-0.142	0.055
C ₄ -H/X	0.054	0.372	0.034	0.380	0.570	0.395	0.253	0.334	0.735	0.417
C ₅ -H/X	0.049	0.073	0.034	0.066	0.021	0.059	0.253	0.079	-0.042	0.082

^aAll values are given in a.u. The atomic labels are given in Fig. 1.

Table S2 Observed XBs in retrieved crystal structures of organic salts

Codes	Acceptors	Donors	Distances (Å)	Angles (°)
ALOKOC	Br	Br(C ²)	3.2	174.2
ALOLAP	F	Br(C ²)	3.1	160.6
AXEFOY	Cl	Cl(C ²)	3.2	161.9
AYEHOB	O	Br(C ²)	2.9	153.9
EHENIO	O	Cl(C ²)	2.8	180.0
FAJCID	I	I(C ²)	3.4	177.9
FALCIF	O	Br(C ²)	3.0	159.1
GAZQIH	Br	I(C ²)	3.3	163.2
HABNAB	Br	Br(C ²)	3.3	172.6
ITUPAP	O	I(C ²)	2.8	168.7

QIVPOB	Cl	Cl(C ²)	3.2	165.2
EJEMAI	Br	Cl(C ⁴ /C ⁵)	3.2	166.9
FUDFUG	Cl	Cl(C ⁴ /C ⁵)	3.3	161.8
PUZZIU	F	I(C ⁴ /C ⁵)	3.1	174.9
			3.2	159.6
VURKUP	O	Br(C ⁴ /C ⁵)	3.0	165.7
			3.0	165.6
			2.9	171.4
VURLAW	O	I(C ⁴ /C ⁵)	2.9	174.3
			2.9	171.4
			2.9	174.4
VUSNIH	I	Br(C ⁴ /C ⁵)	3.6	175.6
			3.6	171.5
WOMYED	I	Cl(C ⁴ /C ⁵)	3.6	168.5
			3.6	155.0
YOXWAK	Br	Br(C ⁴ /C ⁵)	3.2	174.7
			3.2	168.8

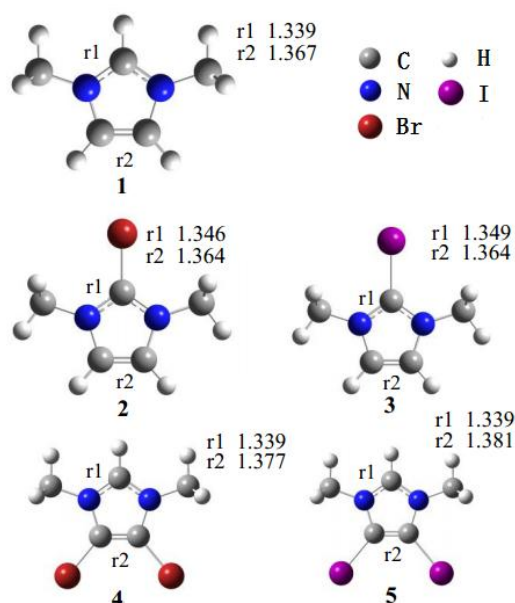


Fig. S1 Optimized geometries of the cations **1-5** at the B3LYP level of theory. Distances in angstroms.

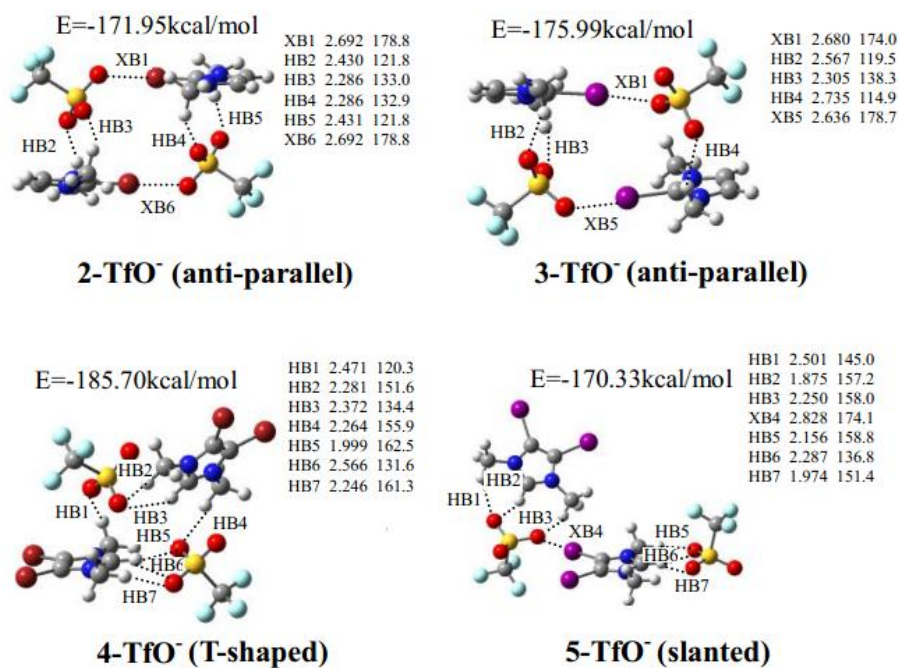


Fig. S2 Other optimized geometries of two ion pairs at the B3LYP level of theory. Distances in angstroms and angles in degrees.