Crystal Structure of Unusual $[CH_3SI_2][SbF_6]$ Salt

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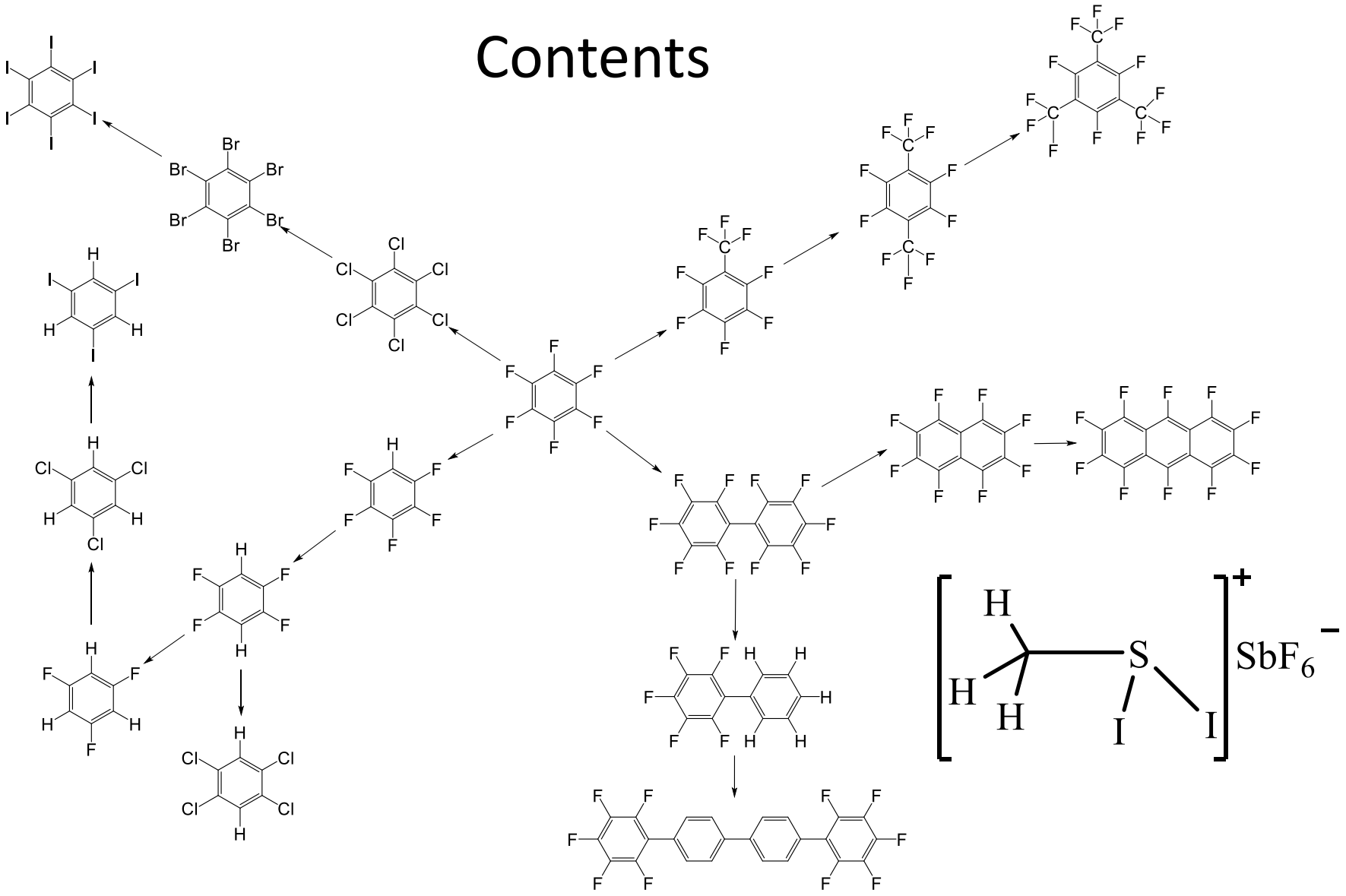
Contents



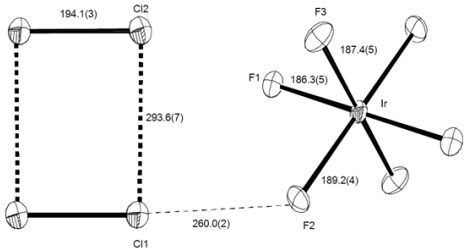
Introduction

Structural determination of metal hexafluorides

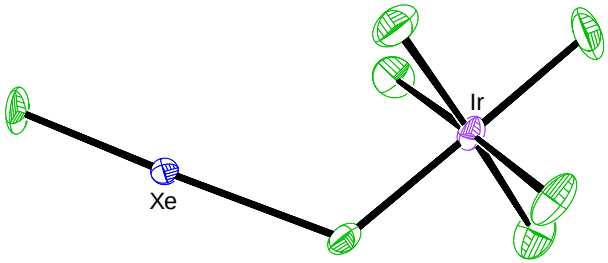
$$O_2 + PtF_6 \longrightarrow O_2^+ PtF_6^-$$

$$Xe + 2\ PtF_6 \longrightarrow XeF^+ Pt_2F_{11}^-$$

$$2\ Cl_2 + IrF_6 \xrightarrow{-80°C\ aHF} Cl_4^+ IrF_6^-$$



$$Xe + 2\ IrF_6 \xrightarrow{RT} XeF^+ IrF_6^- + IrF_5$$



Introduction

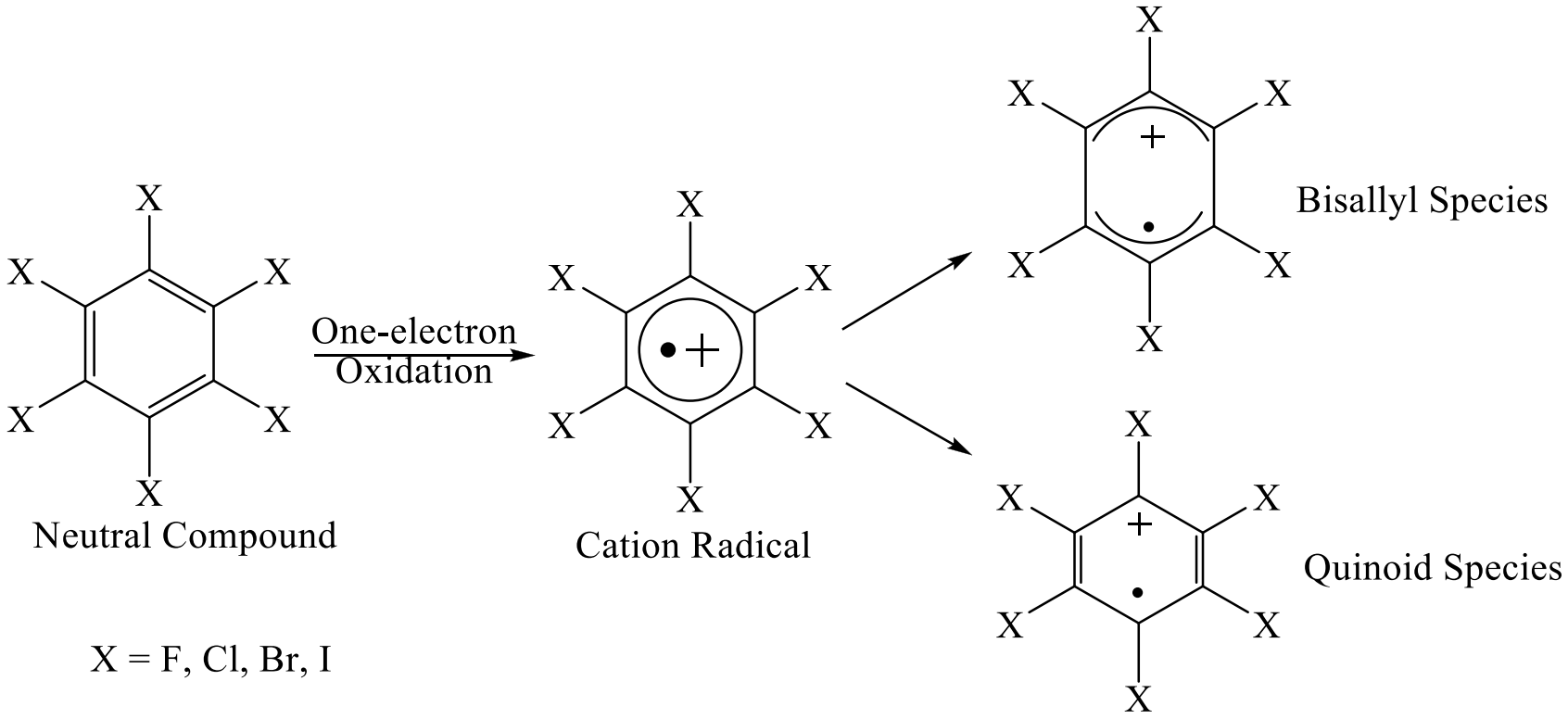
Oxidation power of some MF_6

MoF_6 4,0	TcF_6 5,5	RuF_6 7,0	RhF_6 6,5	EA in eV
WF_6 3,0	ReF_6 4,0	OsF_6 5,0	IrF_6 6,0	PtF_6 7,0

Which may oxidize hardly oxidizable substrates

C_6I_6 7,9	C_6H_6 9,2	C_6F_6 9,9	Cl_2 11,6	O_2 12,1	Xe 12,1	IE in eV

Concepts



- oxidation from π–system
- D_{6h} symmetric ring geometry is not retained (Jahn–Teller effect)

Preparation of $C_6F_6^{+\bullet}$ $Os_2F_{11}^-$

IP(C_6F_6) = 9.9 eV

EA(OsF_6) = 5.0 eV

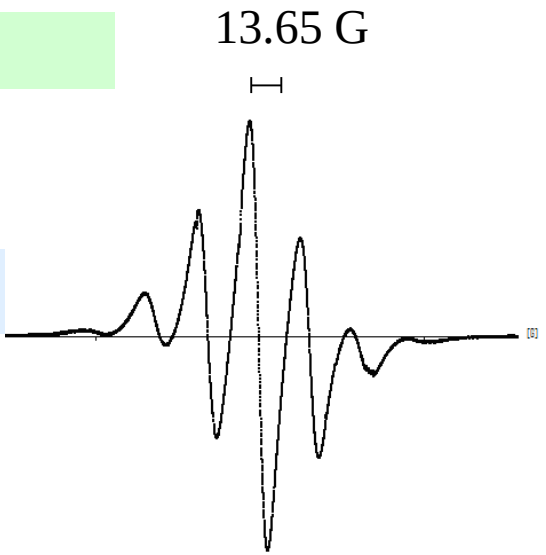
$$C_6F_6 + OsF_6 \xrightarrow[\text{in aHF}]{\times} C_6F_6^{+\bullet}\,Os_2F_{11}^-$$

EA(OsF_6 + SbF_5) > 5.0 eV

$$C_6F_6 + OsF_6 \xrightarrow{SbF_5 \text{ in aHF}} C_6F_6^{+\bullet}\,Os_2F_{11}^-$$

Stable at room temperature,

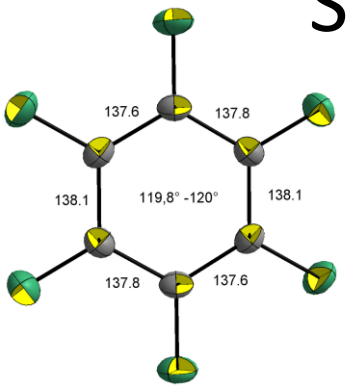
non-volatile in Vacuum

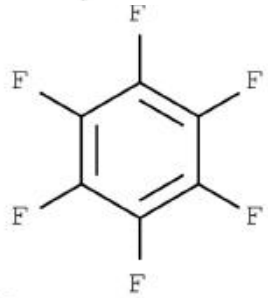


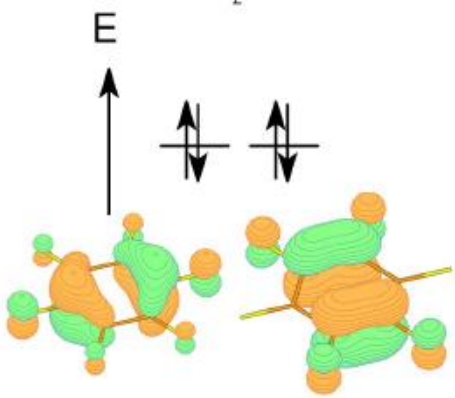
measured in SO_2ClF at RT, g = 2.0022

H. Shorafa, *et al*, *Angew. Chem. Int. Ed.*, ***2009, 48, 5845;***

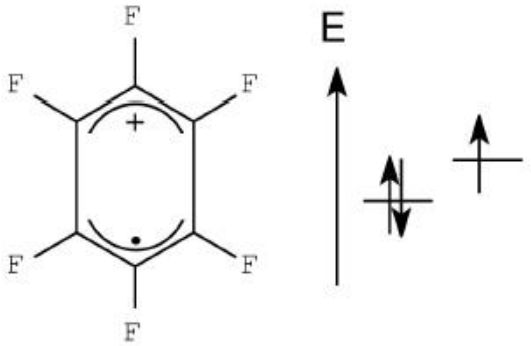
Structure of $C_6F_6^{+\bullet}$ $Sb_2F_{11}^-$

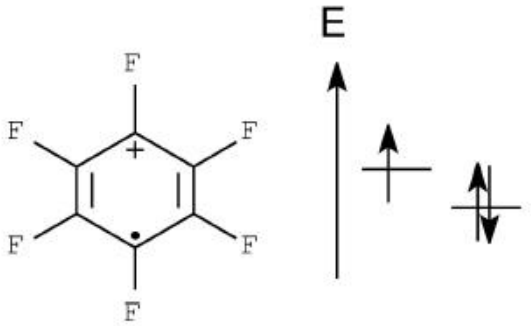




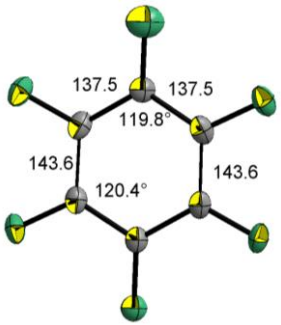


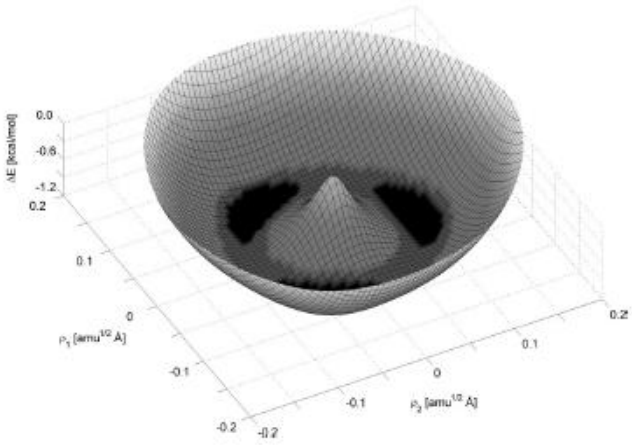
Bisallyl isomer

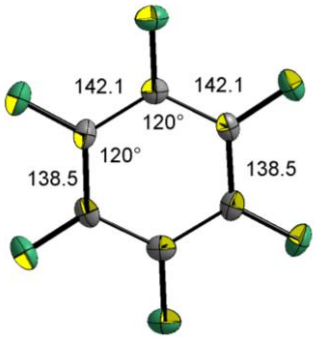




Quinoid isomer

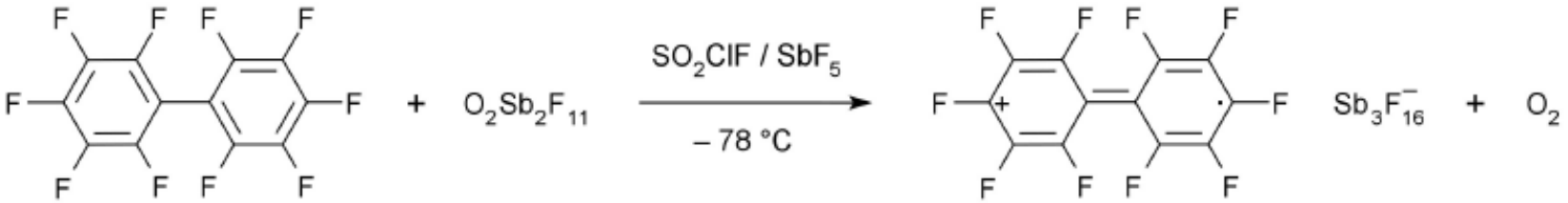






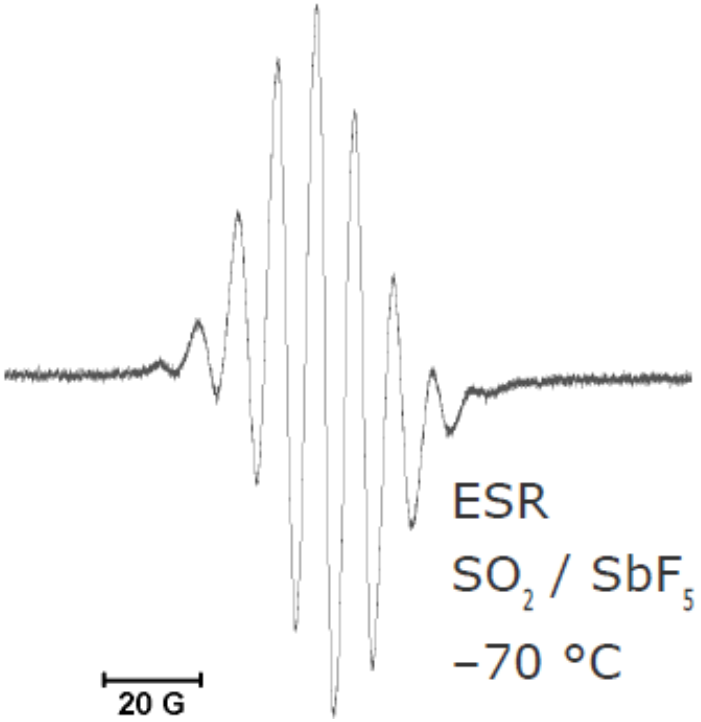
H. Shorafa, *et al*, *Angew. Chem. Int. Ed.*, ***2009, 48, 5845;***

Oxidation of perfluorinated Biphenyl

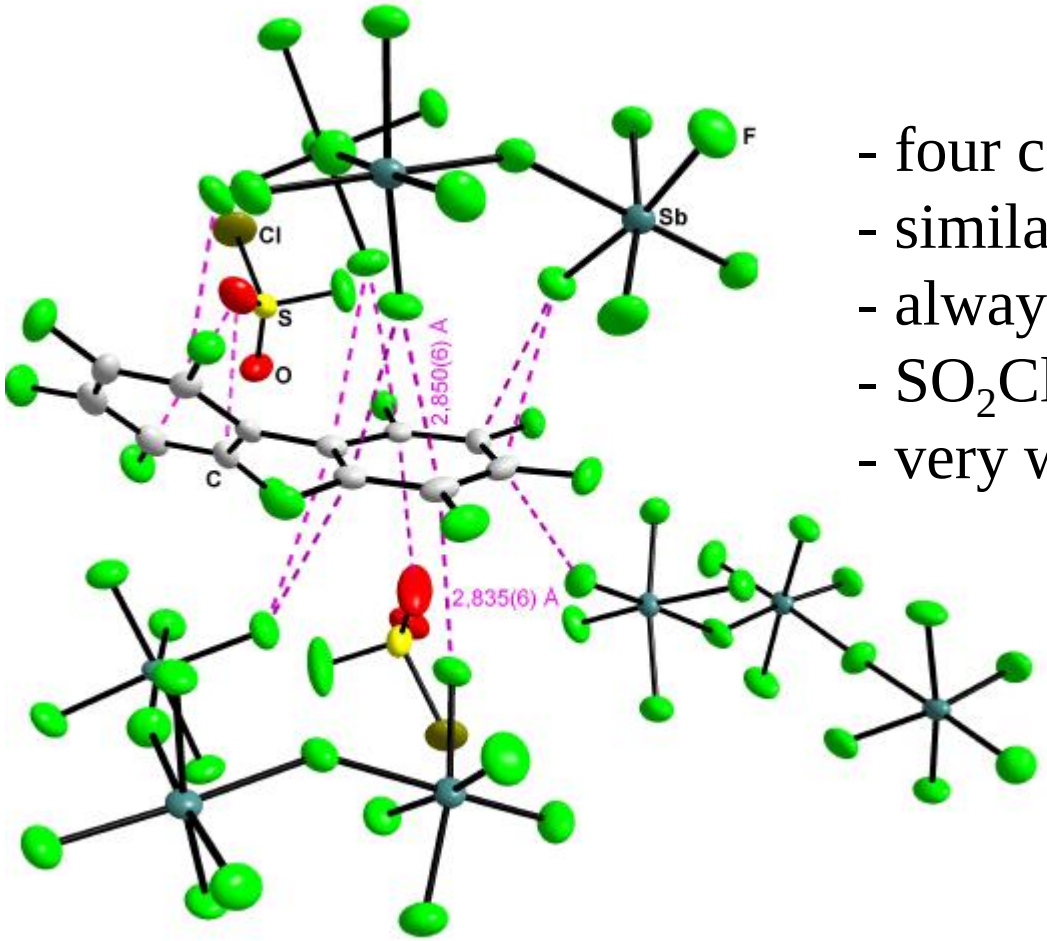


- green needles

- high solubility at low temp.

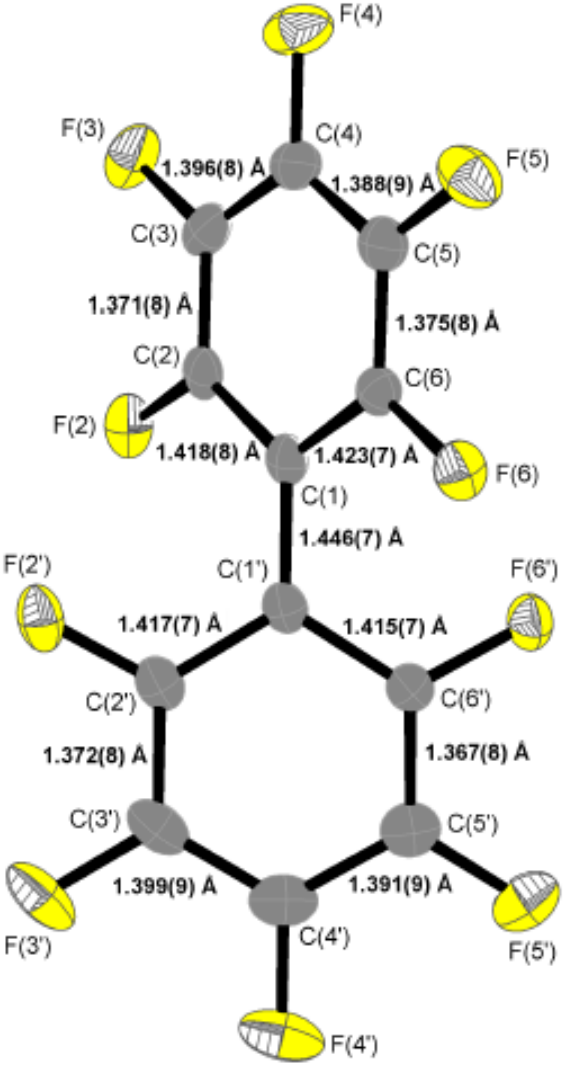


Isolation of perfluorinated Biphenyl radical cation

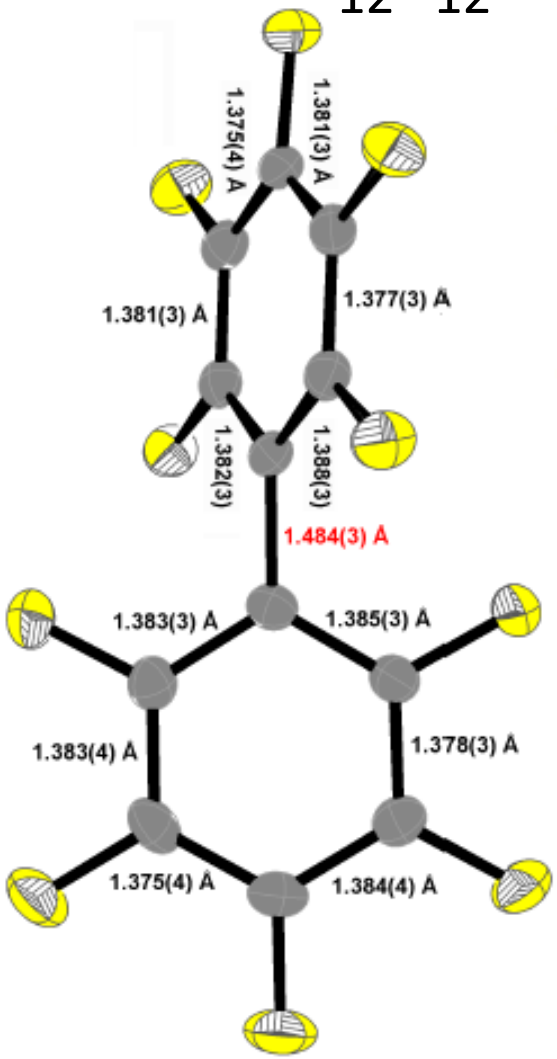


- four cations
- similar coordination sphere
- always 2-3 SO_2ClF coordinated
- SO_2ClF is reason for solubility
- very weak anion

Structure of $C_{12}F_{12}^{+\cdot}$



$[C_{12}F_{10}^{+\cdot}][Sb_3F_{16}^{-}]$

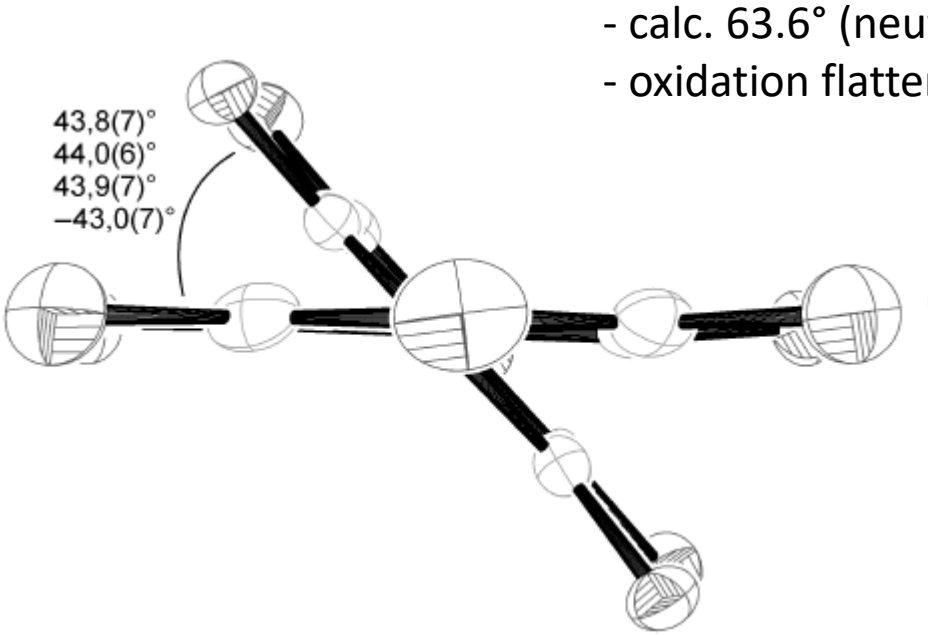


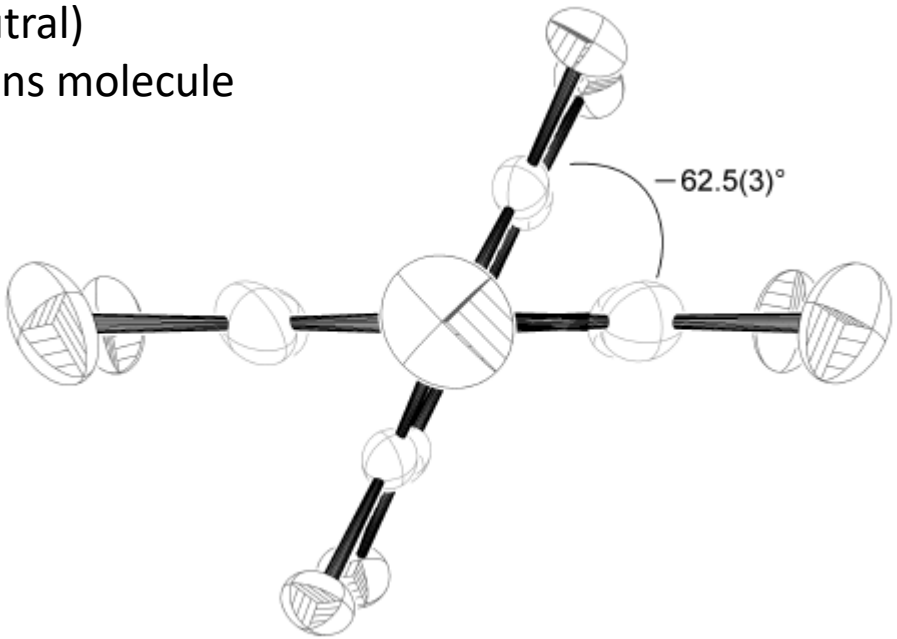
$C_{12}F_{10}$

- central bond ~4 pm shorter
- many CC bonds elongated (~2-4 pm)
- three groups of CC bonds
- angles similar

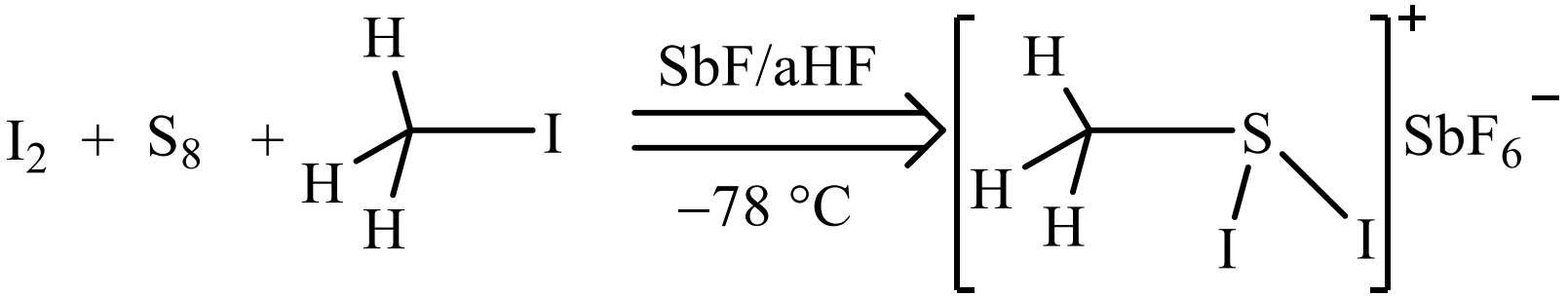
Structure of $C_{12}F_{12}^{+\cdot}$

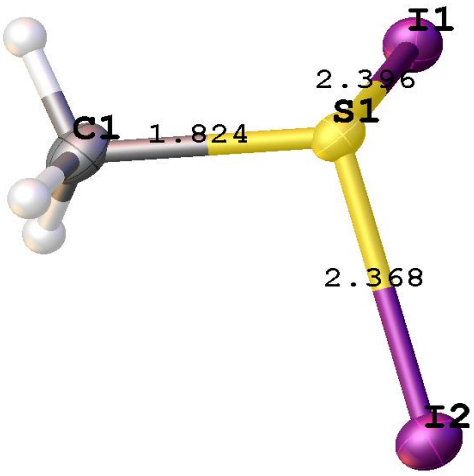
- calc. 46.1° (cation)
- calc. 63.6° (neutral)
- oxidation flattens molecule

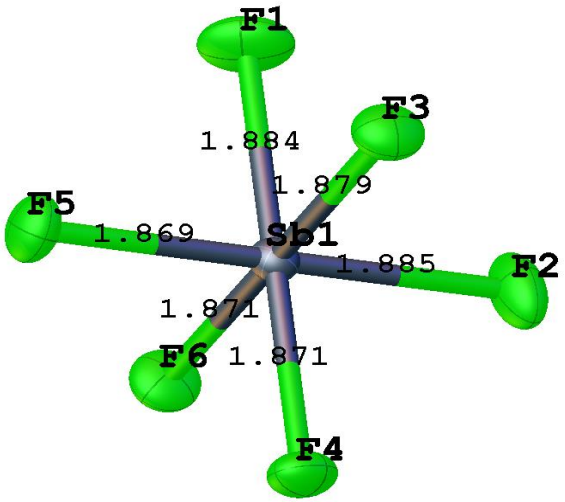




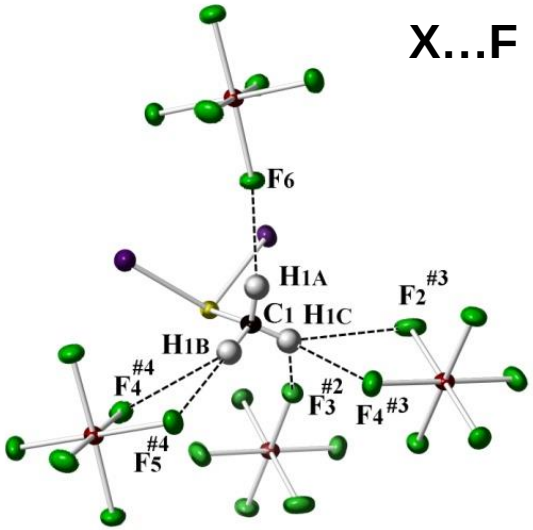
Preparation

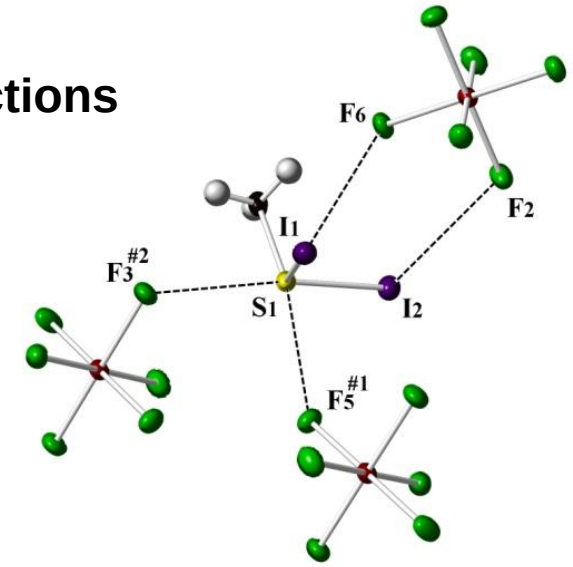




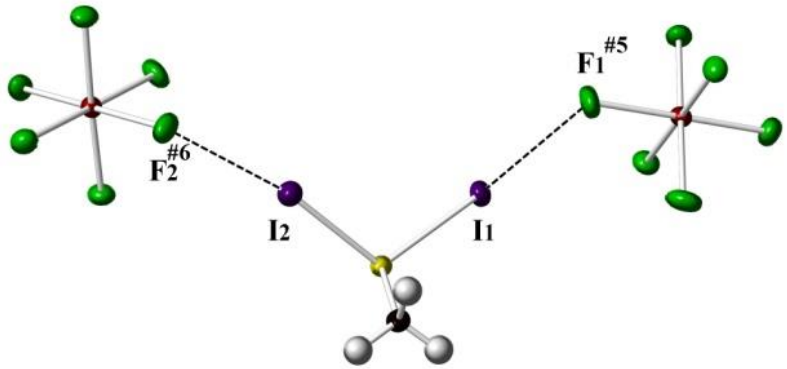


X…F , C…F and F…S interactions



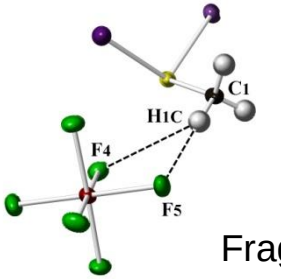


Interaction	(X…F) / Å	
$I_1…F_6$	3.504 (1)	
$I_2…F_2$	3.501 (2)	
$I_1…F_1^{\#5}$	2.782 (1)	
$I_2…F_2^{\#6}$	2.795 (1)	
$S_1…F_3^{\#2}$	2.935 (2)	
$S_1…F_5^{\#1}$	2.968 (1)	
Interaction	**(C…F), (C-H) / Å**	**(C-H…F) / deg**
$C_1-H_{1A}…F_6$	3.261 (2), 2.365 (1)	155.20
$C_1-H_{1B}…F_2^{\#3}$	3.741 (1), 2.873 (1)	151.00
$C_1-H_{1B}…F_4^{\#3}$	3.209 (1), 2.506 (1)	130.08
$C_1-H_{1B}…F_3^{\#2}$	3.209 (2), 2.676 (2)	115.40
$C_1-H_{1C}…F_5^{\#4}$	3.425 (2), 2.467 (1)	175.59
$C_1-H_{1C}…F_4^{\#4}$	3.526 (1), 2.881 (1)	125.45

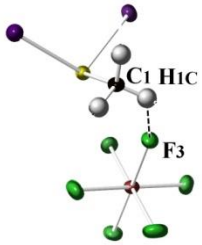


#1 1-x,+1/2+y,+1/2-z, #2 -1+x,+1/2-y,-1/2+z,
#3-1+x,y,z,
#4 1-x,1/2+y,1/2-z, #5 x, 1/2-y, -1/2+z,
#6 1-x, 1-y, 1-z

Crystal Structure of Unusual $[CH_3SI_2][SbF_6]$ Salt



Frag1



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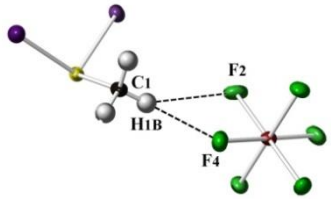

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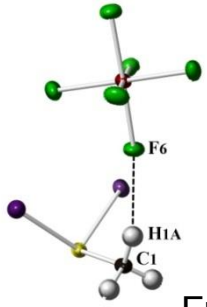

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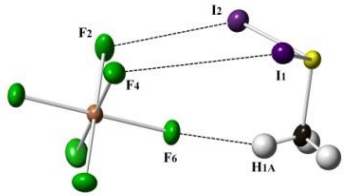

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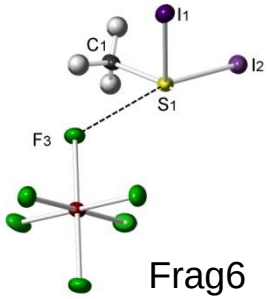
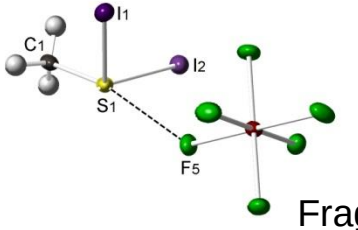


Frag6



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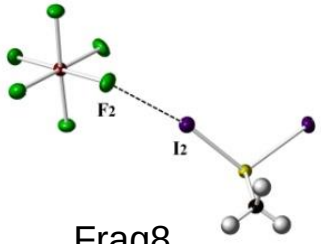

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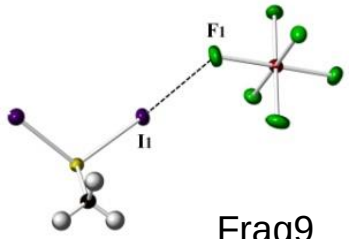

Frag9

	Interaction energy (kcal/mol)
Frag1	-210
Frag2	-547
Frag3	-566
Frag4	-210
Frag5	-291
Frag6	-567
Frag7	-211
Frag8	-484
Frag9	-382

Interactions are ionic

Professor Dr. Konrad Seppelt

Dr. Hashem Shorafa
Dr. Matthias Molski

The DFG
The DAAD
The Deanship of Research at the University of Jordan

THANK YOU

شُكراً لَكُم