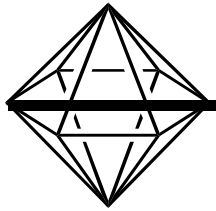
F-Cl-Br-I-F-Cl-Br-F-Cl-Br-F

Halogen Bonding: Exploration of a New Horizon

Wynter Eve Gilson
January 14, 2009

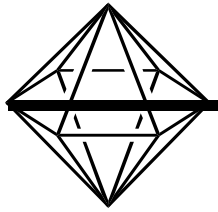
F-Cl-Br-I-F-Cl-Br-F-Cl-Br-F

Outline



- Discovery and types of halogen bonding (XB).
- Halogen bonding used in Liquid Crystals (LC), LC polymers and Molecular Imprinted Polymers (MIP).
- Use of halogen bonds in molecular conductors and formation of Borromean Rings (BR) .

Outline



- Discovery and types of halogen bonding (XB).
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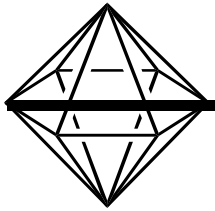
Progress of Halogen Bonding



Late 19th Century

Halogen interaction with electron donors recognized in dihalogens and halocarbons.

1949

First intermolecular donor-acceptor complex formed.

1970

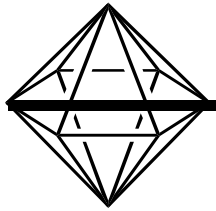
Hassel stressed importance of halogens for directing molecular self-assembly phenomena.

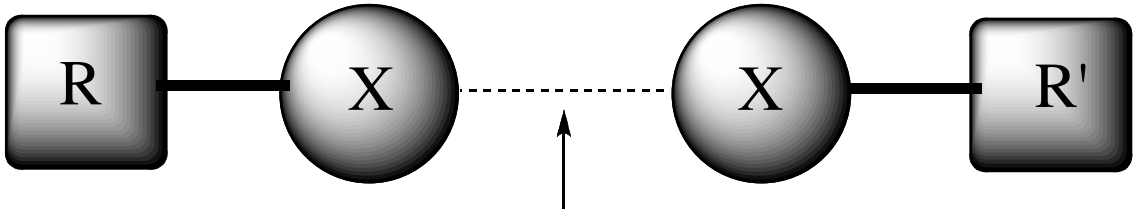
1990's

Halogens drew attention for their ability to direct intermolecular recognition processes.

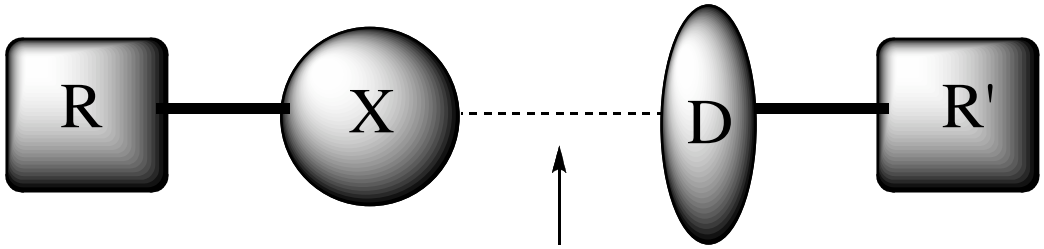
Metrangolo, P.; Meyer, F. Pilati, T.; Resnati, G.; Terraneo, G. *Angew. Chem. Int. Ed.* **2008**, *47*, 6114-6127.

Types of Halogen Bonding





Halogen-Halogen Bonding

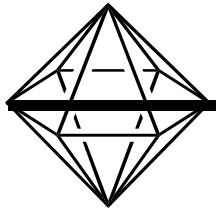


Halogen-Lewis Base Bonding

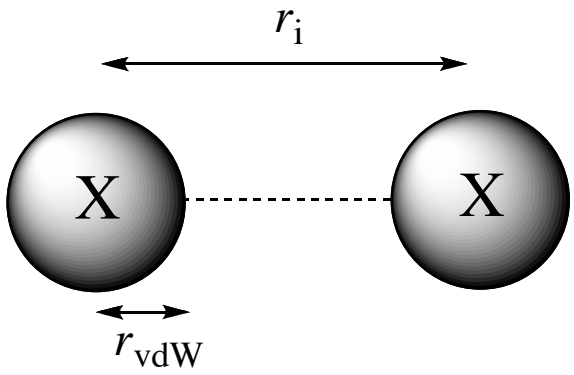
R, R' = Carbon, Halogen, or Nitrogen
X = Electrophilic Halogen
D = Donor of Electron Density

Awwadi, F.; Willett, R.; Peterson, K.; Twamley, B. *Chem. Eur. J.* **2006**, *12*, 8952-8960.
Metrangolo, P.; Meyer, F. Pilati, T.; Resnati, G.; Terraneo, G. *Angew. Chem. Int. Ed.* **2008**, *47*, 6114-6127.

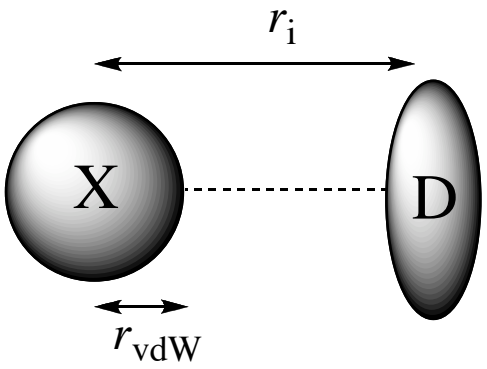
Halogen Bond: Definition



Halogen-Halogen Bond



Halogen-Lewis Base Bond

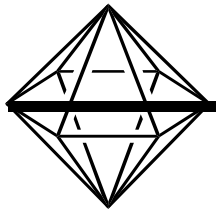


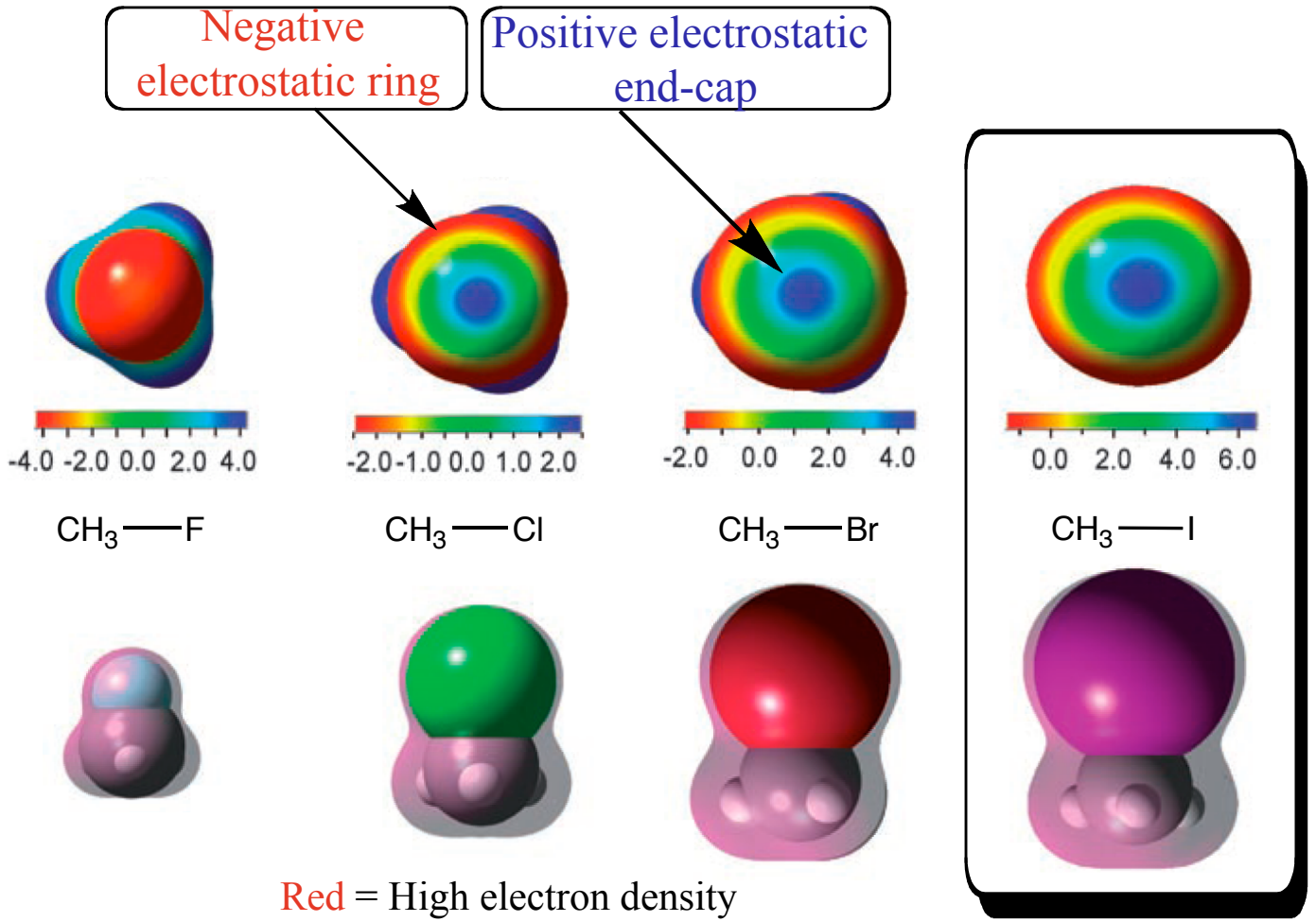
X	Radius (Å)
F	1.47
Cl	1.75
Br	1.85
I	1.98

A halogen bond is characterized by an interatomic distance (r_i) that is less than the sum of the van der Waals radii (r_{vdW}).

Awwadi, F.; Willett, R.; Peterson, K.; Twamley, B. *Chem. Eur. J.* **2006**, *12*, 8952-8960.
Cambridge Crystallographic Data Centre www.ccdc.cam.ac.uk/

Electrostatic Model of Halogens





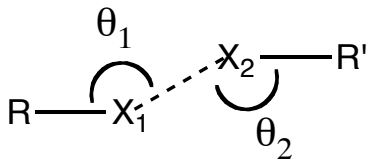
Red = High electron density
Blue = Low electron density

Awwadi, F.; Willett, R.; Peterson, K.; Twamley, B. *Chem. Eur. J.* **2006**, *12*, 8952-8960.

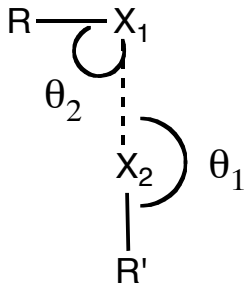
Halogen-Halogen Bonding: Geometries

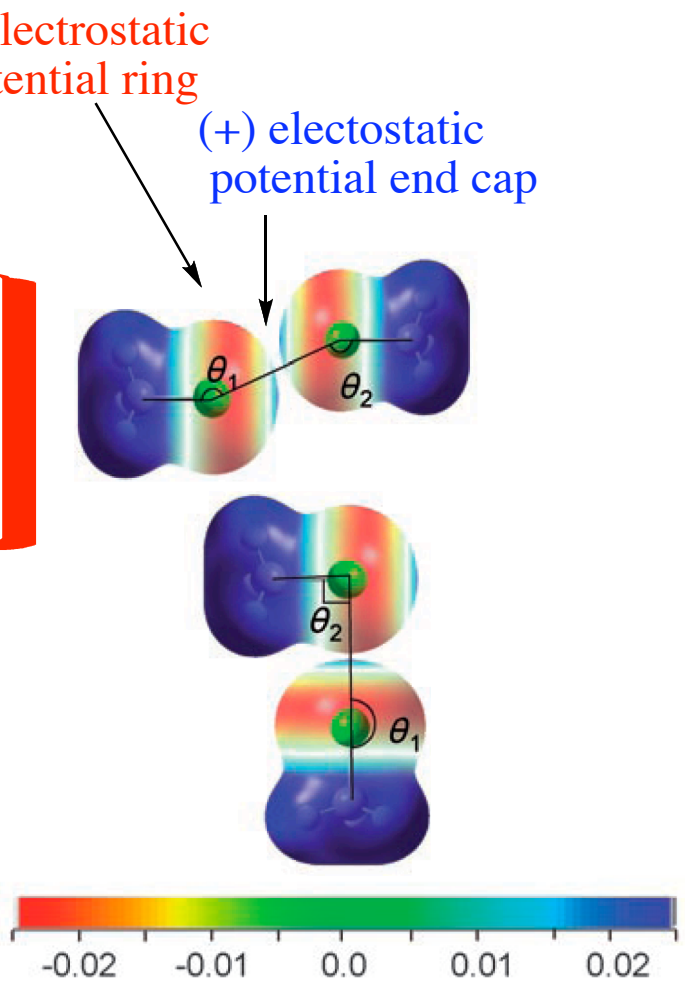
Calculated electrostatic potential

$\theta_1 = \theta_2$
Interaction maxima occur between 140-160°



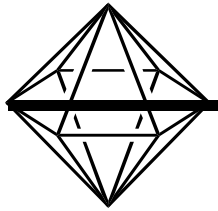
$\theta_1 = 180°$
$\theta_2 = 90°$

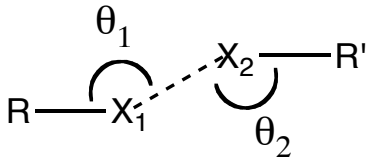




Awwadi, F.; Willett, R.; Peterson, K.; Twamley, B. *Chem. Eur. J.* **2006**, *12*, 8952-8960.

Halogen Bonding Between Dimers





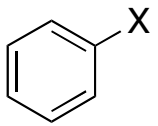
$\theta_1 = \theta_2$
(140-160°)

H_3C-X

1a = Cl

1b = Br

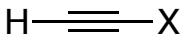
1c = I



2a = Cl

2b = Br

2c = I



3a = Cl

3b = Br

3c = I

	Angle (°)	Distance (Å)		Angle (°)	Distance (Å)		Angle (°)	Distance (Å)
1a	156	3.71	2a	152	3.46	3a	142	3.66
1b	153	3.82	2b	150	3.72	3b	140	3.85
1c	147	4.15	2c	148	3.96	3c	144	4.11

Awwadi, F.; Willett, R.; Peterson, K.; Twamley, B. *Chem. Eur. J.* **2006**, *12*, 8952-8960.

Halogen-Halogen Bonding: Geometries

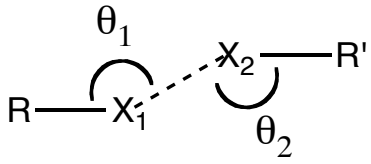
Calculated electrostatic potential

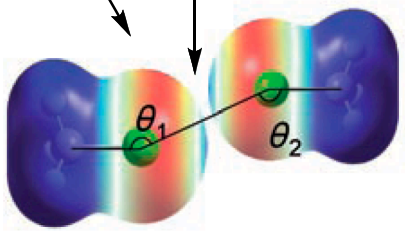
(-) electrostatic potential ring

(+) electostatic potential end cap

$\theta_1 = \theta_2$

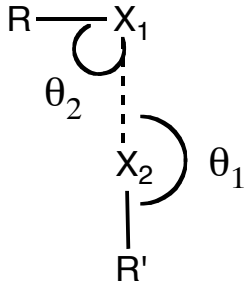
Interaction maxima occur between 140-160°

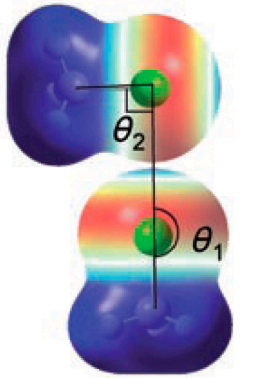


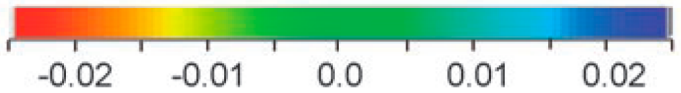


$\theta_1 = 180°$

$\theta_2 = 90°$

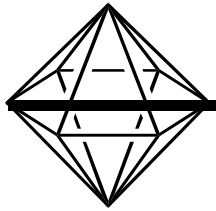


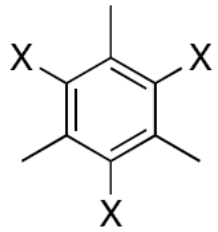




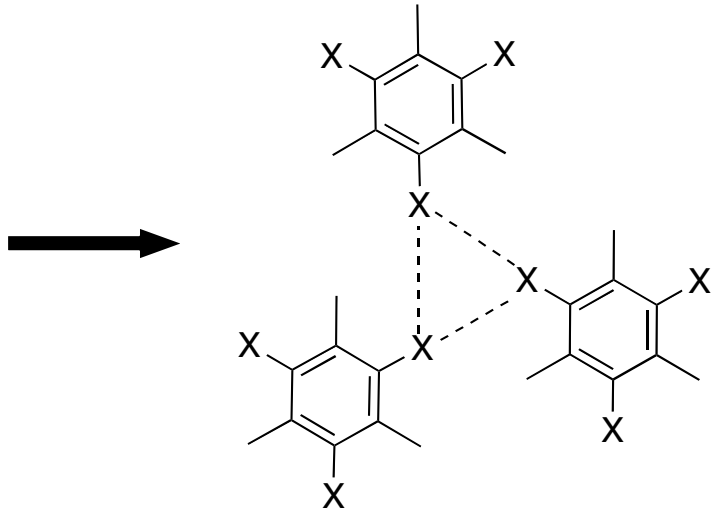
Awwadi, F.; Willett, R.; Peterson, K.; Twamley, B. *Chem. Eur. J.* **2006**, *12*, 8952-8960.

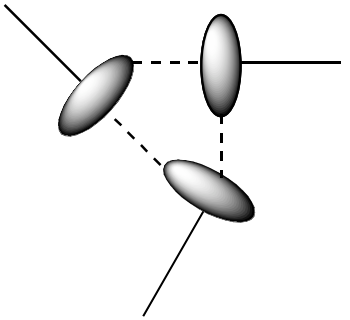
Trihalomesitylenes in triangular halogen-halogen-halogen bonding

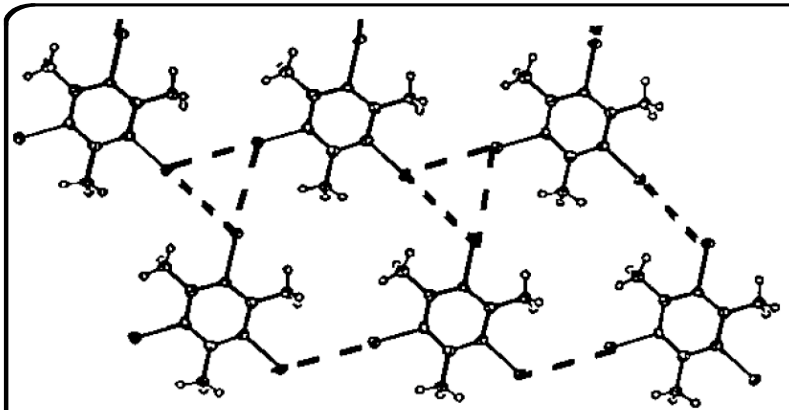




Trihalomesitylene
X = (I, Br, Cl)





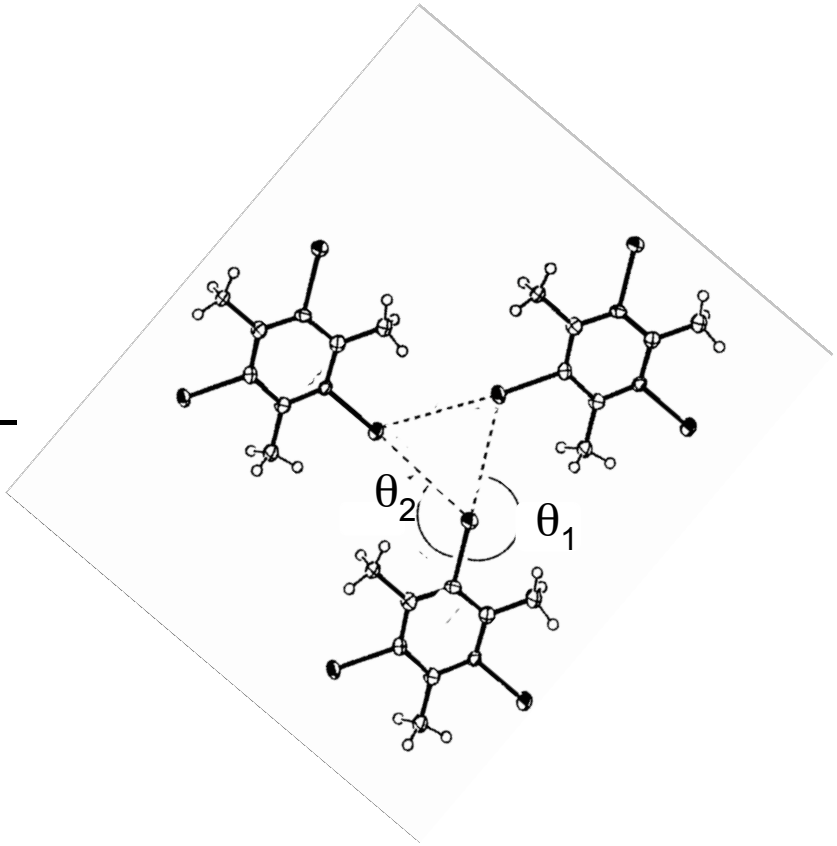


Triiodomesitylene molecules arranged triangularly.

Bosch, E.; Barnes, L. *Cryst. Growth Des.***2002**, *2*, 299-302.

Angles in Triangular System

	X_1		X_2		X_3	
X	θ_1	θ_2	θ_1	θ_2	θ_1	θ_2
I	173.0	119.8	173.5	118.6	165.7	119.7
Br	170.7	124.6	174.6	124.4	169.9	124.9
Cl	167.3	128.8	168.8	129.4	170.2	128.0



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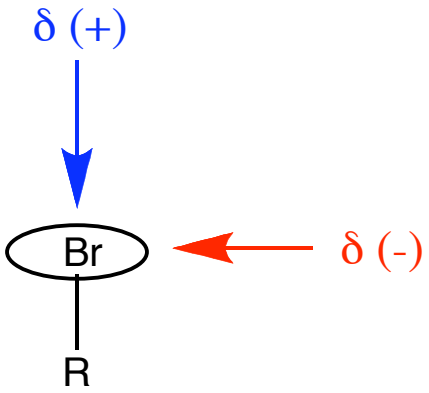
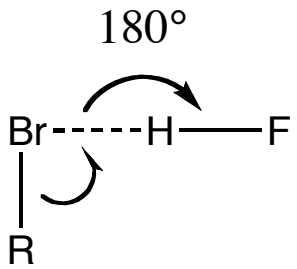
Halogen-Hydrogen Bond Geometry

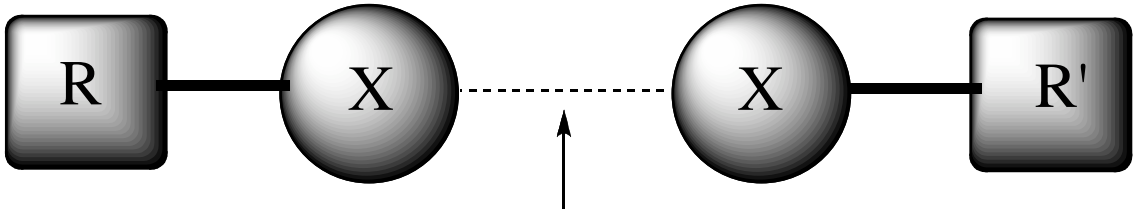




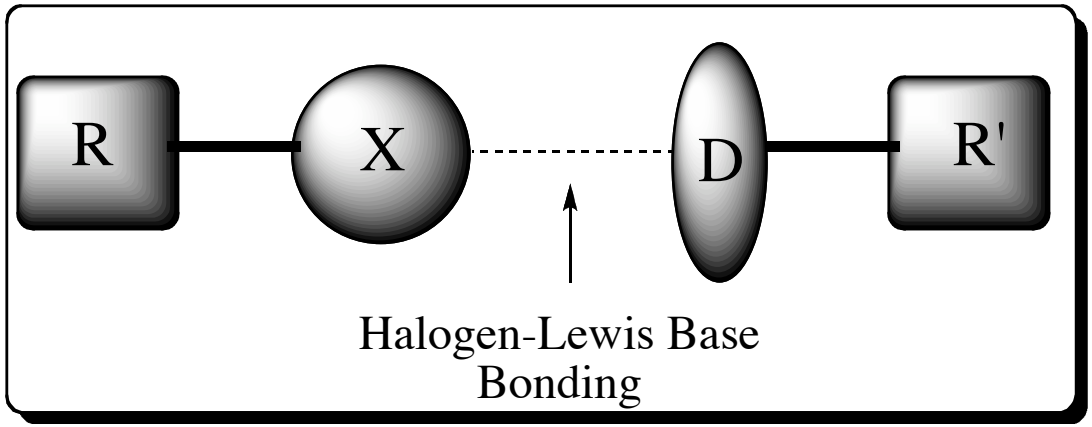
R	*d* (Br•••H) (Å)	∠ (R-Br•••H) (°)
F-	2.6076	94.1
Cl-	2.5278	89.2
Br-	2.4974	87.2
HO-	2.5420	91.3
H_2N-	2.4571	89.2
H-	2.4891	94.5
H_3C-	2.3750	93.2

Lu, Y.; Zou, J.; Wang, Y.; Zhang, H.; Yu, Q.; Jiang, Y. *J. Mol. Struc.: THEOCHEM* **2006**, *766*, 119-124.

Types of Halogen Bonding



Halogen-Halogen Bonding



Halogen-Lewis Base Bonding

R, R' = Carbon, Halogen, or Nitrogen
X = Electrophilic Halogen
D = Donor of Electron Density

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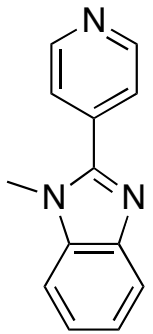
Metrangolo, P.; Meyer, F. Pilati, T.; Resnati, G.; Terraneo, G. *Angew. Chem. Int. Ed.* **2008**, *47*, 6114-6127.

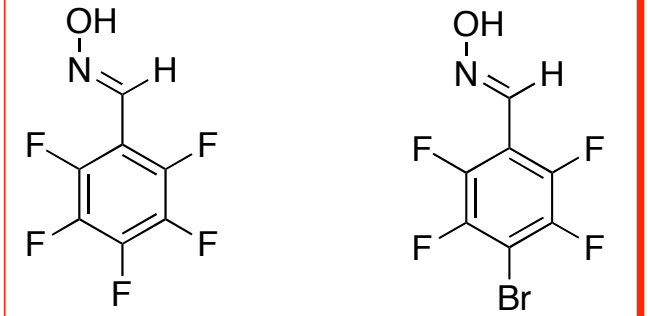
Competition of Hydrogen and Halogen Bonding

Pyridal and benzimidazole nitrogen (hydrogen/ halogen acceptor)



1*

Oximes with varying halogens (hydrogen/ halogen donor)



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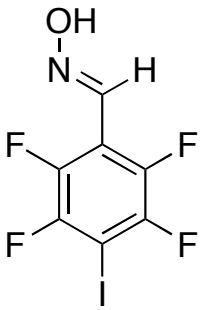
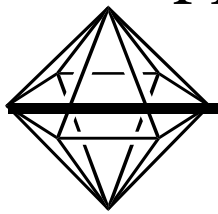
2

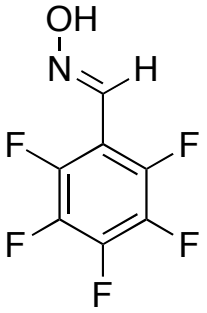


3

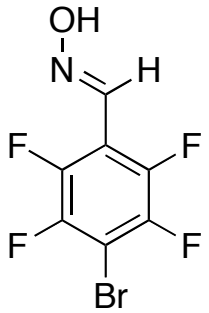
Aakeroy, C. B.; Fasulo, M.; Schultheiss, N.; Desper, J.; Moore, C. *J. Am. Chem. Soc.***2007***, 129*, 13772-13773.

Absence of Halogen Bonding with F and Br





1



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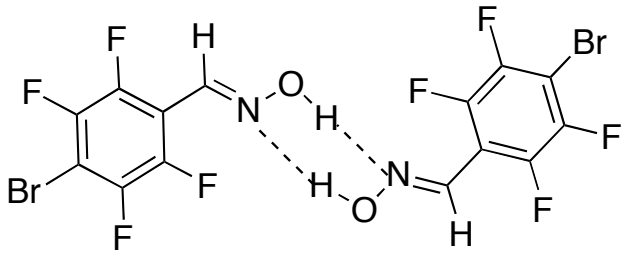
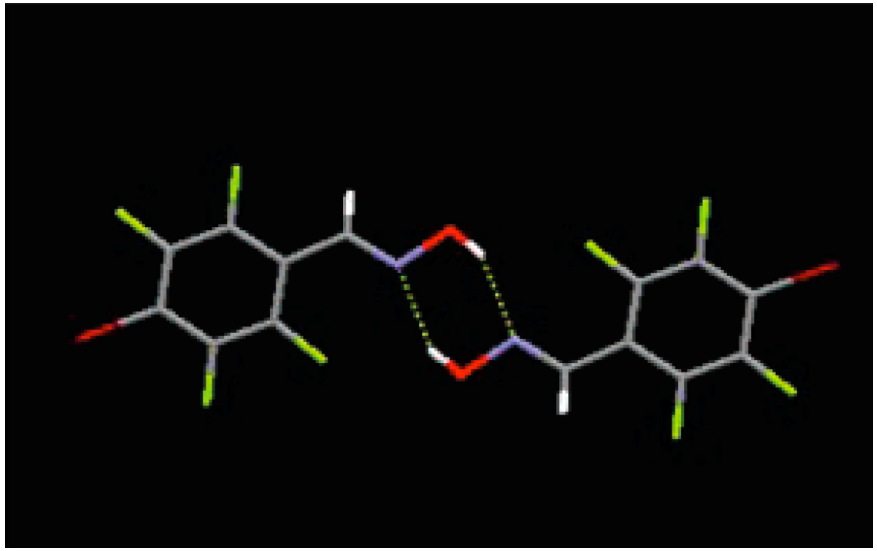


No Halogen Bonding between compound **1** or compound **2** dimers.

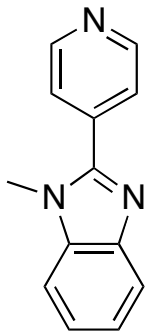


Aakeroy, C. B.; Fasulo, M.; Schultheiss, N.; Desper, J.; Moore, C. *J. Am. Chem. Soc.***2007***, 129*, 13772-13773.

Competition of Hydrogen and Halogen Bonding

Pyridal and benzimidazole nitrogen (hydrogen/ halogen acceptor)

Oximes with varying halogens (hydrogen/ halogen donor)



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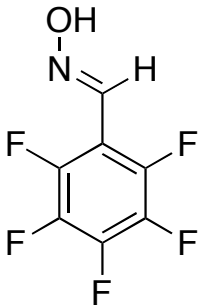

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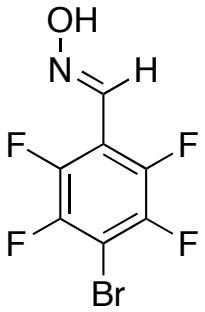

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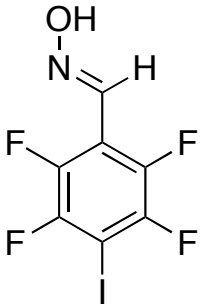
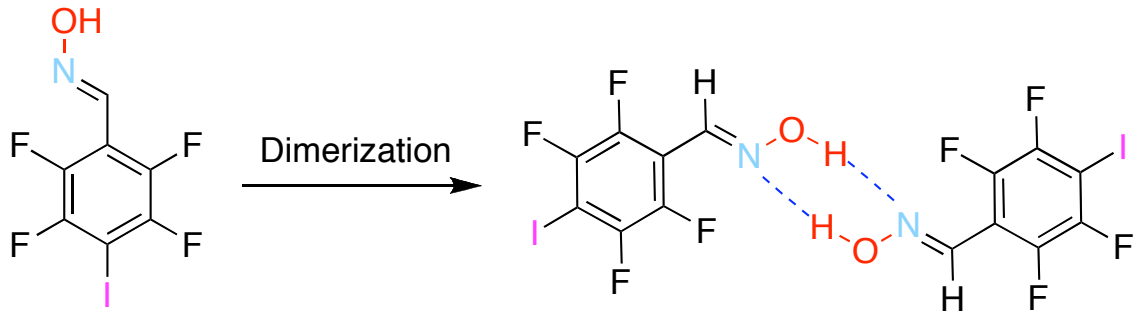
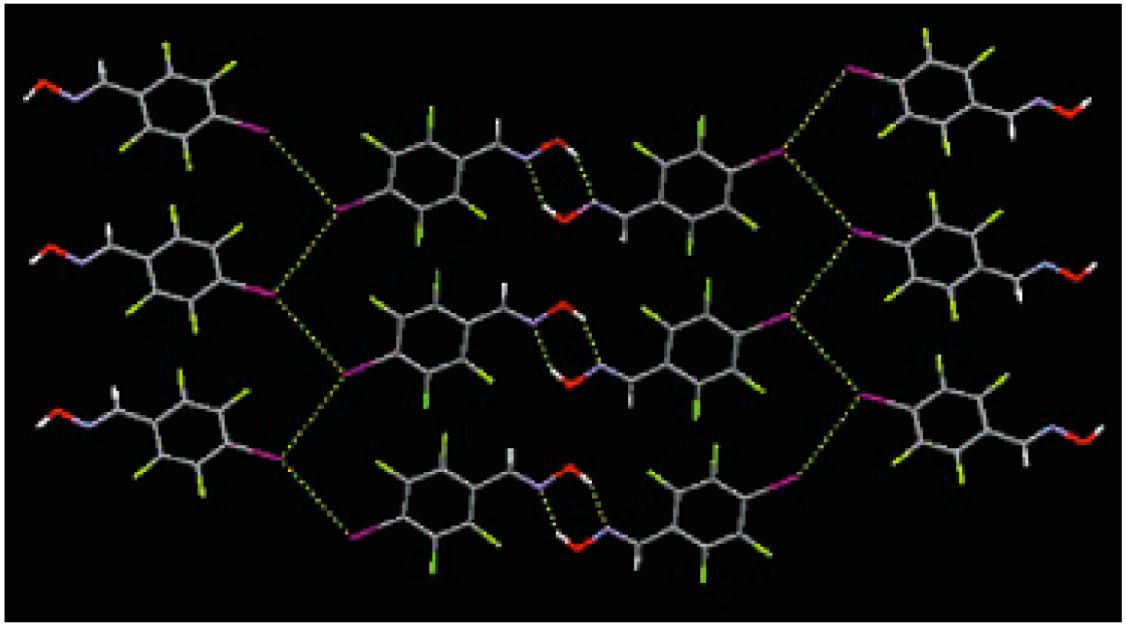


3

Aakeroy, C. B.; Fasulo, M.; Schultheiss, N.; Desper, J.; Moore, C. *J. Am. Chem. Soc.***2007***, 129*, 13772-13773.

Halogen and Hydrogen Bonding Coexisting





N•••O = 2.872 Å

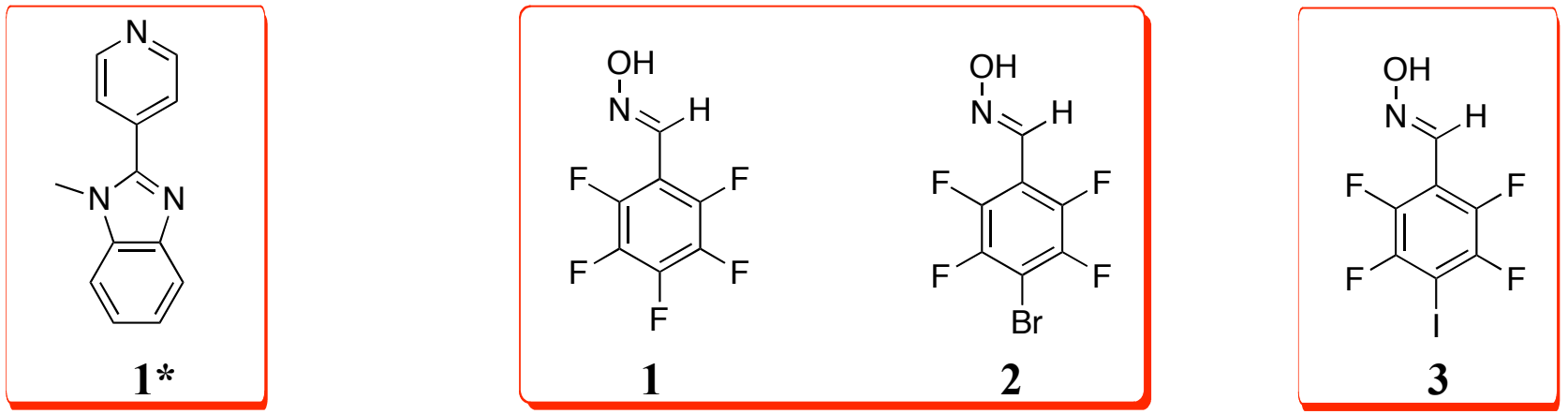
I•••I = 3.944 Å

Aakeroy, C. B.; Fasulo, M.; Schultheiss, N.; Desper, J.; Moore, C. *J. Am. Chem. Soc.***2007***, 129*, 13772-13773.

Competition of Hydrogen and Halogen Bonding

Pyridal and benzimidazole nitrogen (hydrogen/ halogen acceptor)

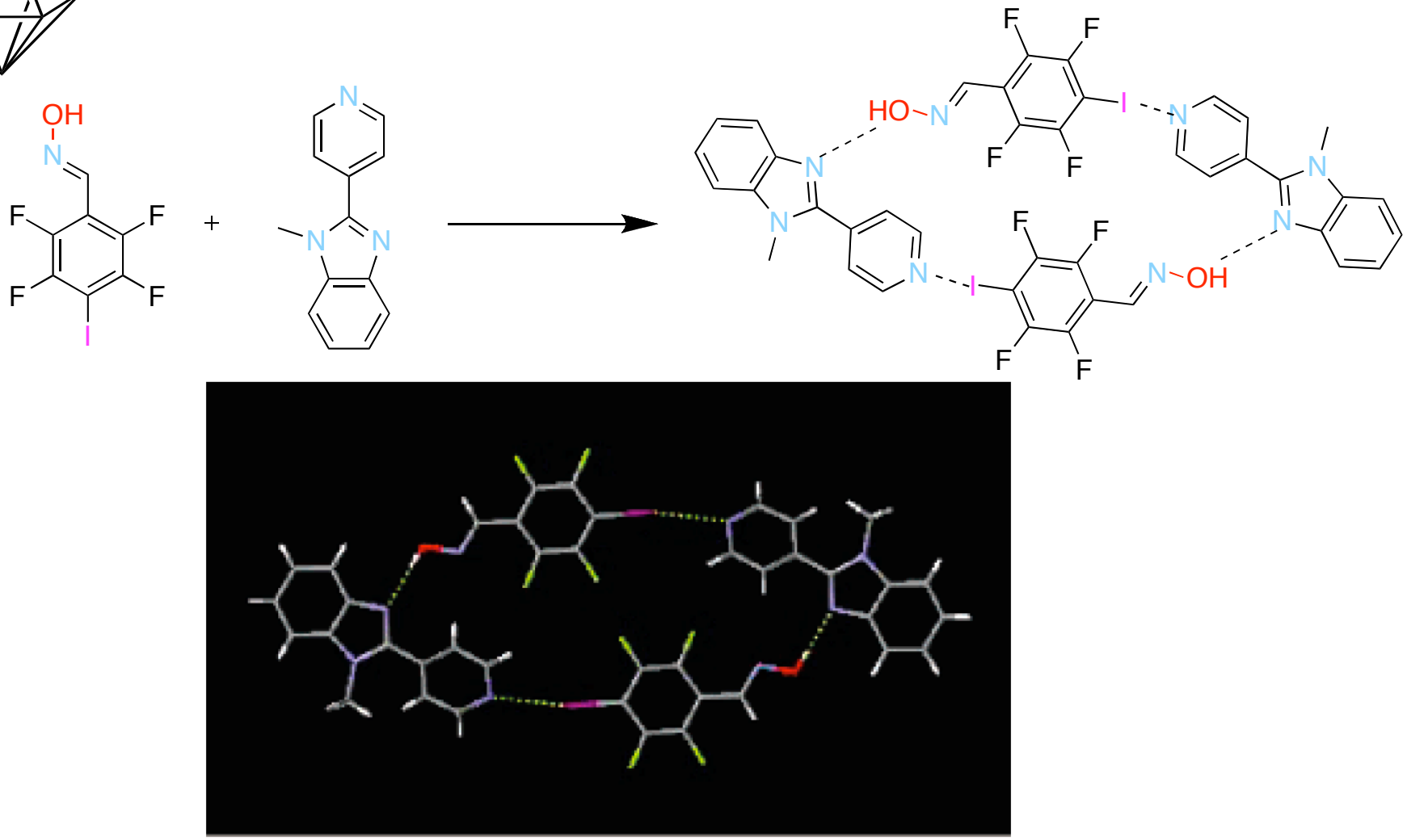
Oximes with varying halogens (hydrogen/ halogen donor)



No halogen bonding between either **1*** and **1** or **1*** and **2.**

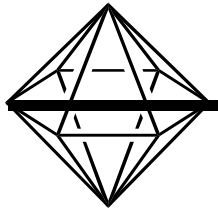
Aakeroy, C. B.; Fasulo, M.; Schultheiss, N.; Desper, J.; Moore, C. *J. Am. Chem. Soc.***2007***, 129*, 13772-13773.

Hydrogen and Halogen Bonding to Non-Bonding Electrons

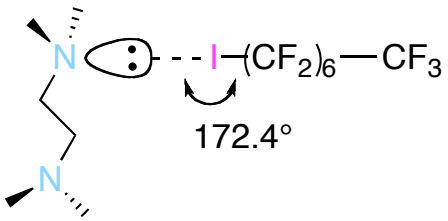


Aakeroy, C. B.; Fasulo, M.; Schultheiss, N.; Desper, J.; Moore, C. *J. Am. Chem. Soc.***2007**, *129*, 13772-13773.

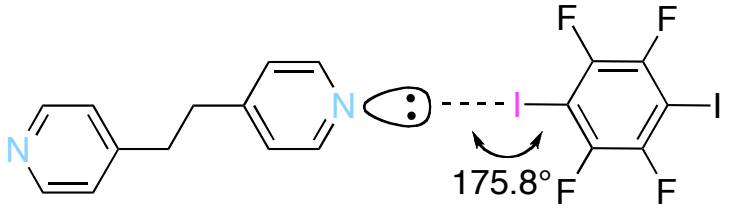
Halogen-Nitrogen Bonding Geometries



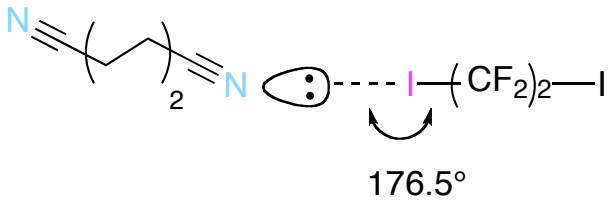
sp^3



sp^2



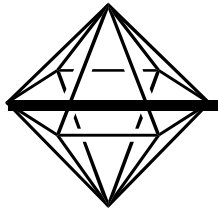
sp

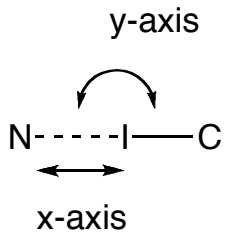


Linearity Increases:
$sp^3 < sp^2 < sp$

Cardillo, P.; Corradi, E.; Lunghi, A.; Meille, S. V.; Messina, M. T.; Metrangolo, P.; Resnati, G. Tetrahedron **2000**, *56,* 5535-5550.
Metrangolo, P.; Pilati, T.; Resnati, G.; Stevenazzi, A. *Chem Commun* **2004**, 1492-1493.

Nitrogen-Halogen Bond Angle *vs* Distance

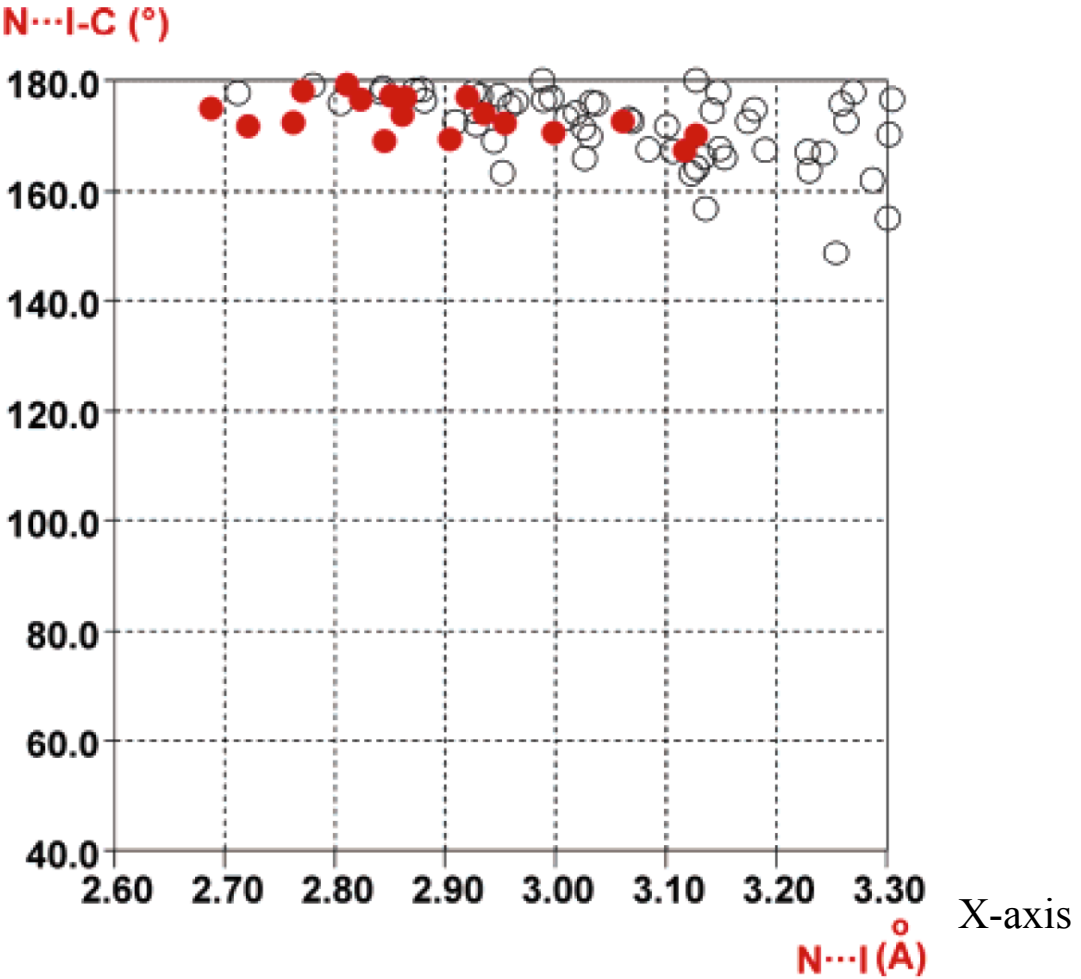




Red Dots: Crystal Structures Involving Iodoperfluorocarbons

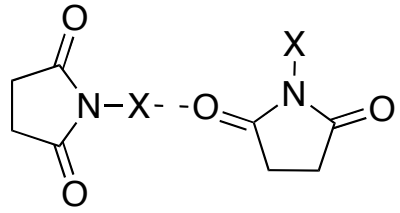
White Dots: non-fluorinated carbons

Linearity Increases as Bond Distance Decreases



Metrangolo P.; Resnati, G.; Pilati, T.; Liantonio, R.; Meyer, F. *J. Polym. Sci. Part A: Polym Chem.* **2007**, *45*, 1-15.

Oxygen-Halogen Bond Angle *vs* Distance

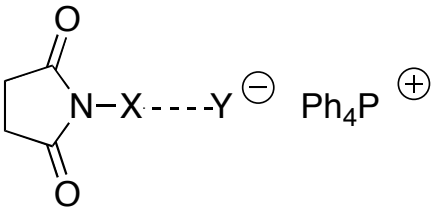


X	N-X•••O (Å)	N–X•••O (°)
Cl	2.880	168.87
Br	2.802	169.54
I	2.580	175.71

Linearity increases as bond distance decrease.

Ghassemzadeh, M.; Harms, K.; Dehnicke, K.; Goesmann, H.; Fenske, D. Z. Naturforsch B: *Chem. Sci.* **1994**, *49*, 602.

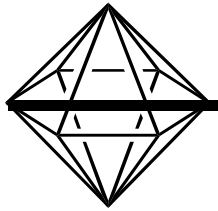
Anion-Halogen Bond Angle *vs* Distance

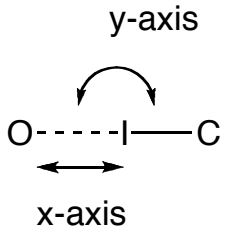


X	Y^-	N-X•••Y^- (Å)	N-X•••Y^- (°)
I	Cl^-	2.845	177.59
I	Br^-	2.933	177.19
I	I^-	3.103	176.87
Cl	Cl^-	2.892	178.64
Br	Cl^-	2.822	177.50
Br	Br^-	2.900	177.52

Ghassemzadeh, M.; Harms, K.; Dehnicke, K.; Goesmann, H.; Fenske, D. Z. Naturforsch B: *Chem. Sci.* **1994**, *49*, 602.

Oxygen-Halogen Bond Angle *vs* Distance

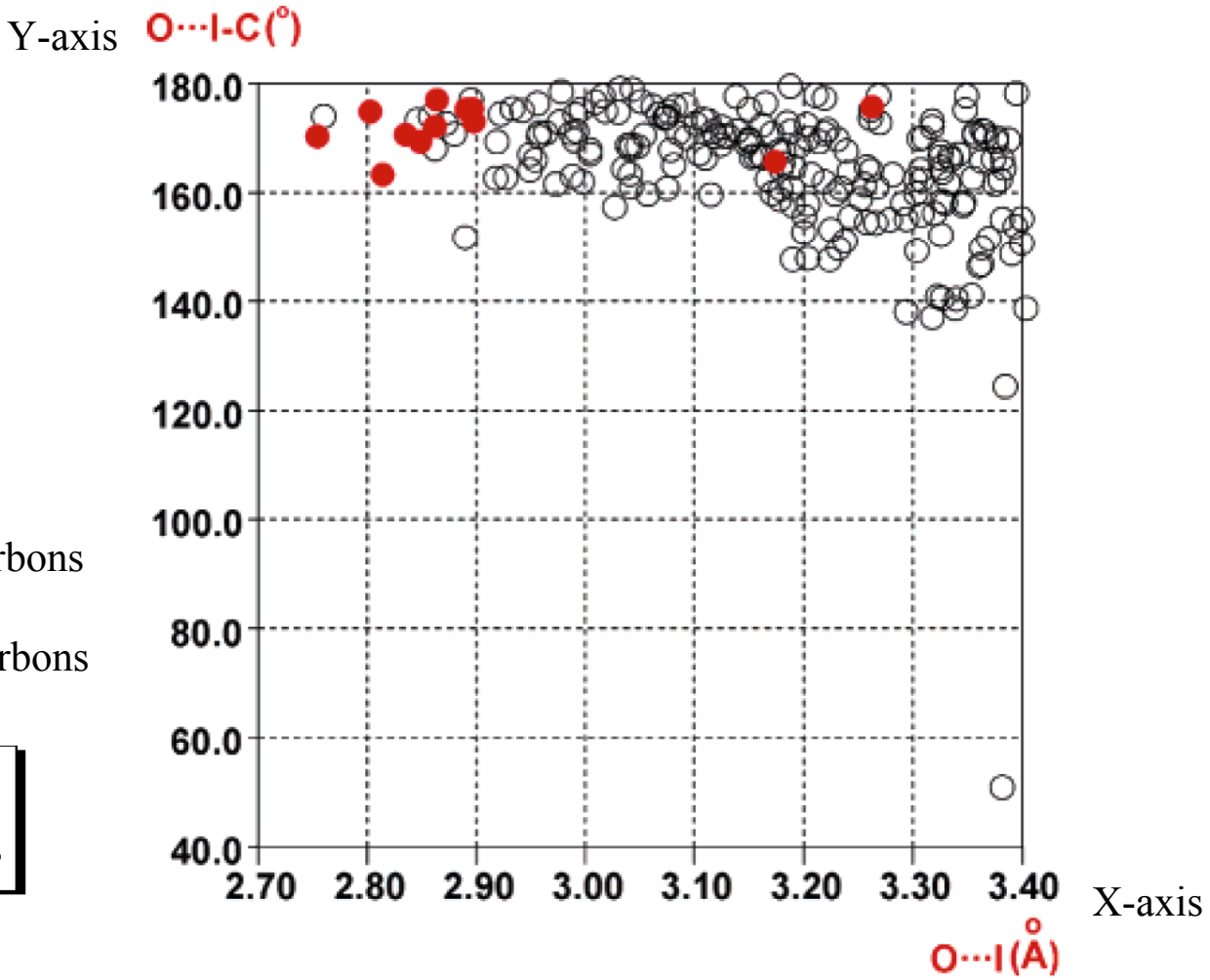




Red Dots: Crystal Structures Involving Iodoperfluorocarbons

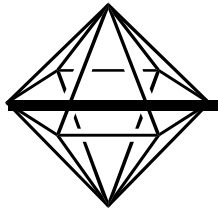
White Dots: non-fluorinated carbons

Linearity Increases as Bond Distance Decreases



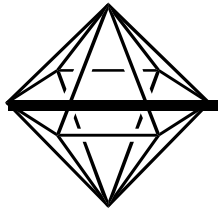
Metrangolo P.; Resnati, G.; Pilati, T.; Liantonio, R.; Meyer, F. *J. Polym. Sci. Part A: Polym Chem.* **2007**, *45*, 1-15.

Outline



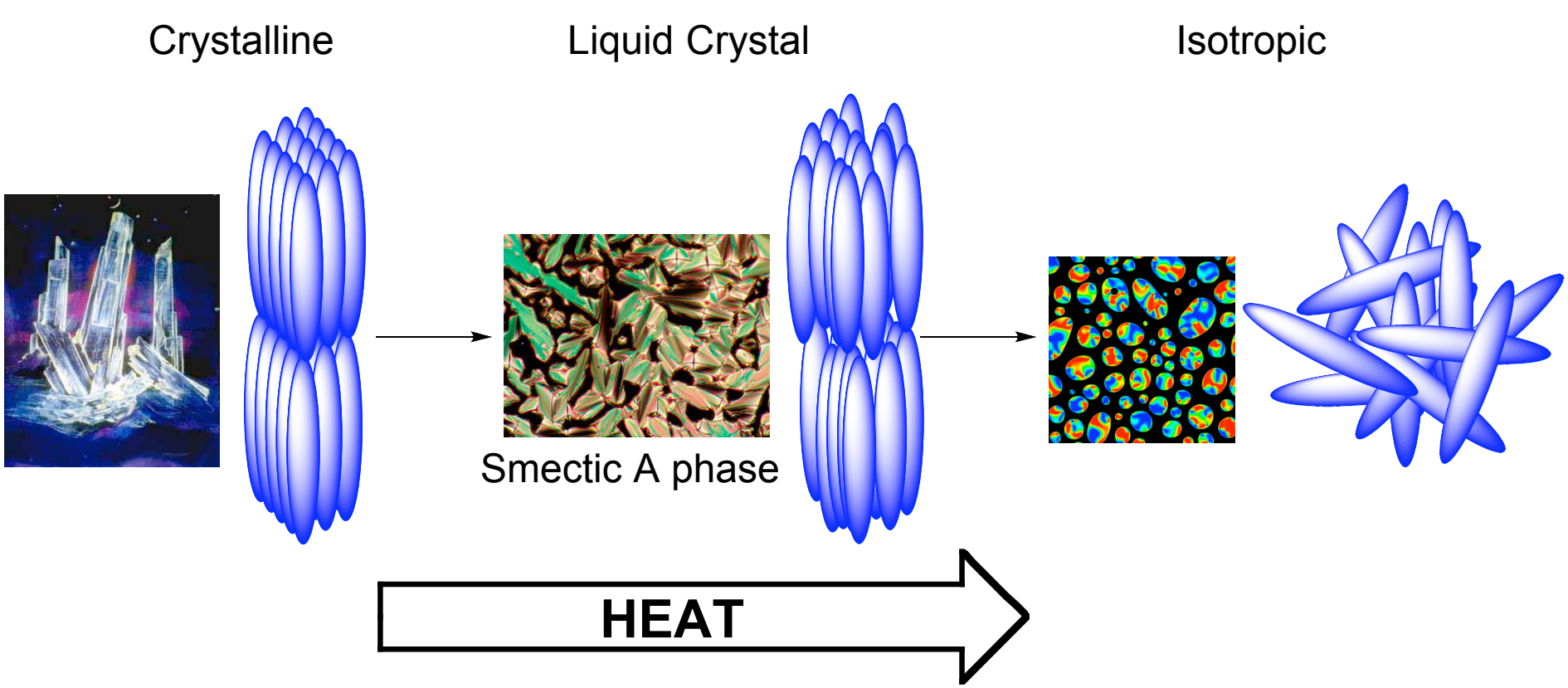
- Discovery and types of halogen bonding (XB).
- Halogen bonding used in Liquid Crystals (LC), LC polymers and Molecular Imprinted Polymers (MIP).
- Use of halogen bonds in molecular conductors and formation of Borromean Rings (BR) .

Outline



- Discovery and types of halogen bonding (XB).
- Halogen bonding used in Liquid Crystals (LC), LC polymers and Molecular Imprinted Polymers (MIP).
- Use of halogen bonds in molecular conductors and formation of Borromean Rings (BR) .

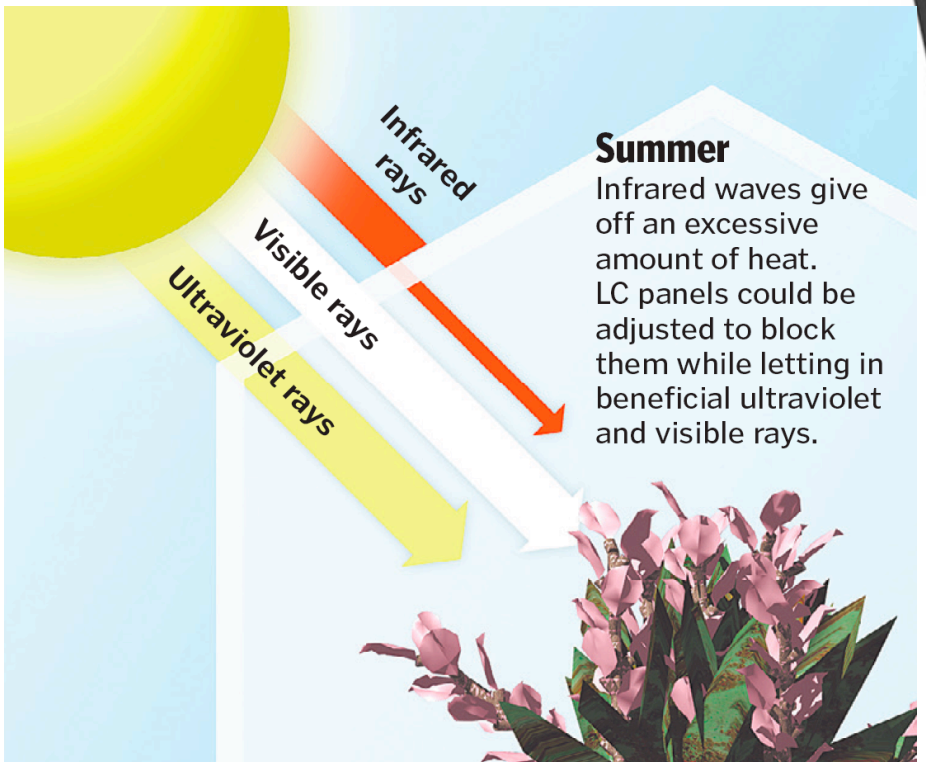
Liquid Crystals (LC)



http://htw4.iis.u-tokyo.ac.jp/research/Poly-LC-Col-Mem-Protein_E.html

Importance of Liquid Crystals

Green Houses



Monitors

Watches

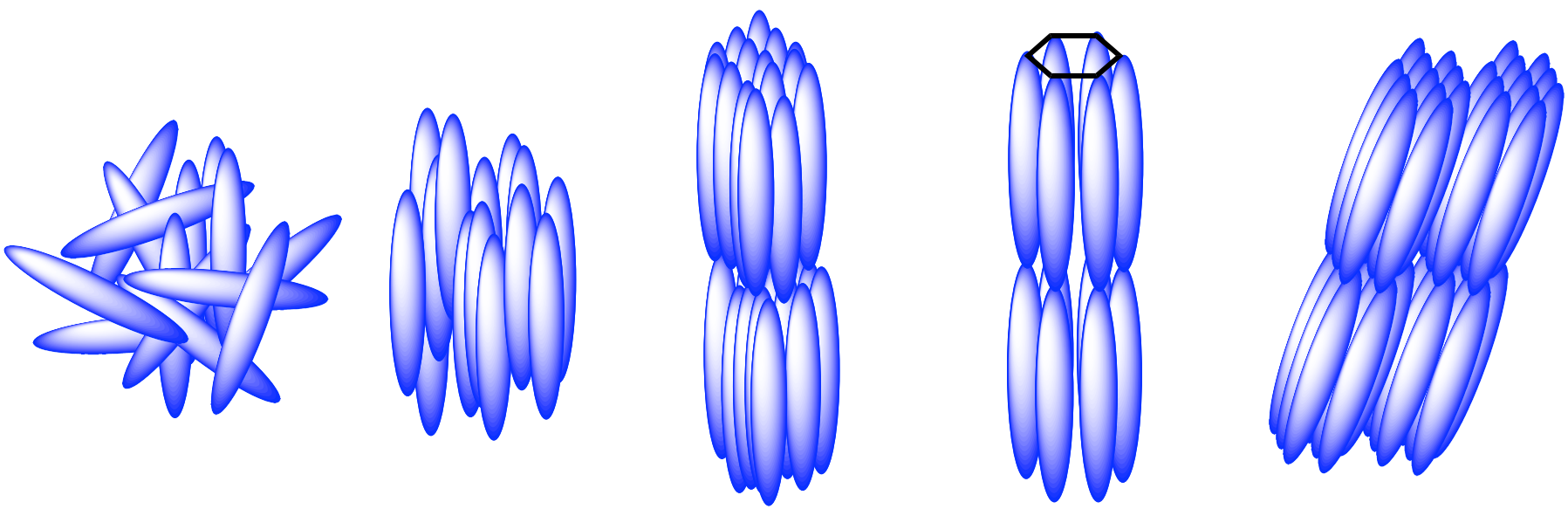
Televisions

Cell Phones

Prada Dressing Rooms

http://blog.cleveland.com/business/2008/01/greenhouse_experiment_to_use_1.html

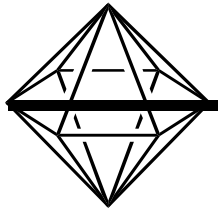
Liquid Crystal Phases



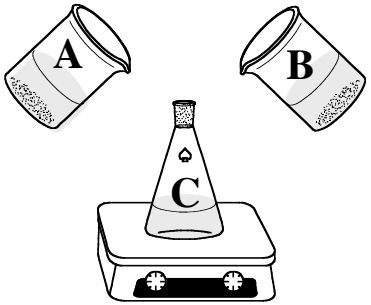
Isotropic Nematic Smectic A Smectic B Smectic C

http://atom.physics.calpoly.edu/~jfernsler/Research/Liquid%20Crystals/LCResearch.html

Formation of Liquid Crystals *via* Halogen Bonding

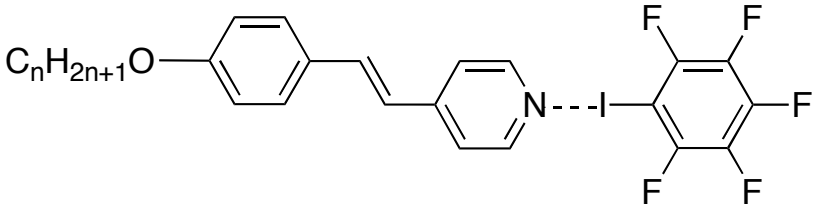


(Clear) (Clear)

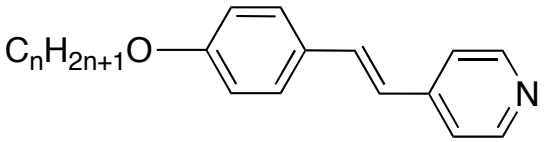


1. Stir 3 h

2. Evaporate solvent

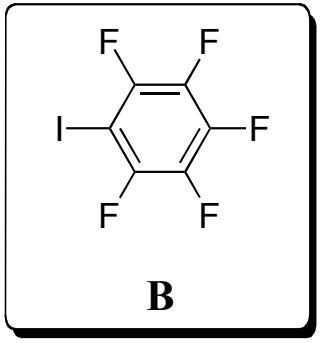


Liquid Crystal
(Yellow)



A

n = 2, 4, 6, 8



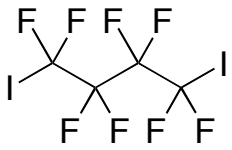
B

C = Low b.p. Solvent (i.e. acetone or dichloromethane)

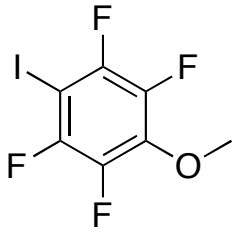
Nguyen, H. L.; Horton, P. N.; Hursthouse, M. B.; Legon, A. C.; Bruce, D. W.*J. Am. Chem. Soc.* **2004**, *126*, 16-17.

Effects of Electronegative Atoms on Halogen Compounds

Mulliken atomic charges are estimations of the partial atomic charges calculated using computational chemistry. These partial atomic charges can then be used to calculate electrostatic interaction energies.

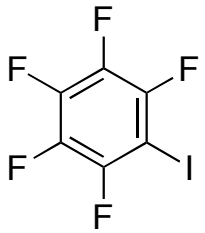


+ 0.85

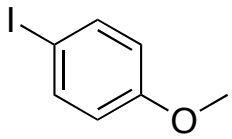


+ 0.122

B



+ 0.144



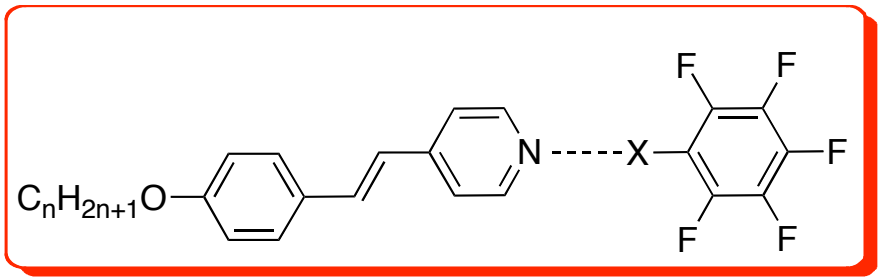
- 0.008

Non fluoro-substituted

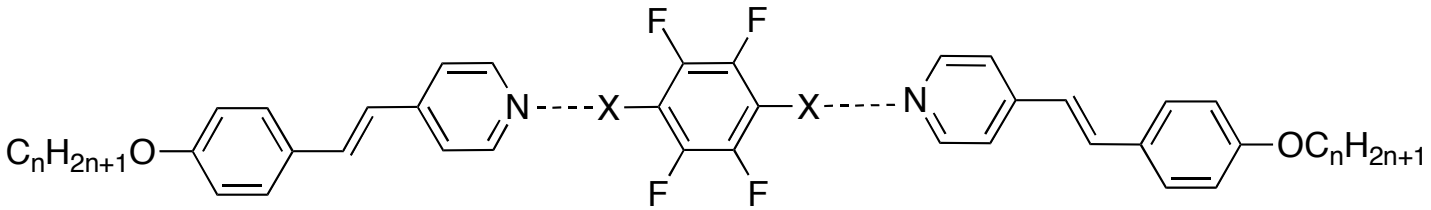
♦Mulliken atomic charge shows that iodine is affected by oxygen in *para* position but is counterbalanced by fluorine atoms.

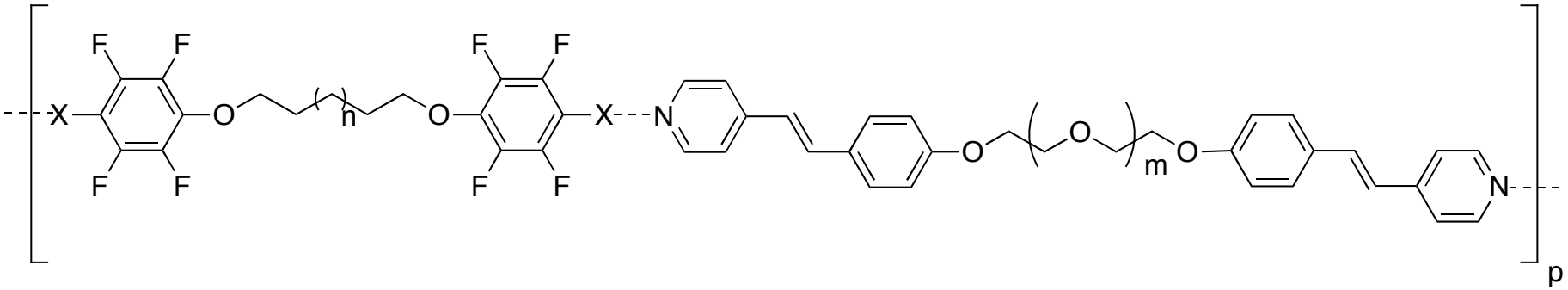
Xu, J.; Liu, X.; Lin, T.; Huang, J.; He, C. *Macromolecules* **2005**, *38*, 3554-3557.

Halogen Bonding in Liquid Crystals



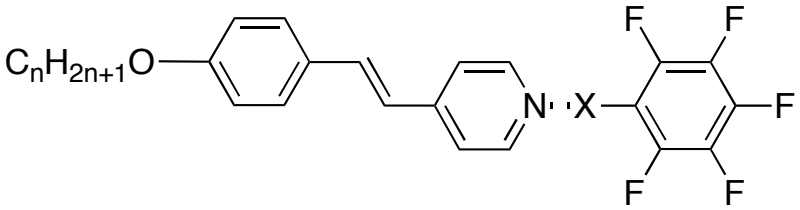
m = 4, 6, 8, 10
n = 4, 6, 8, 10, 12
X = I, Br





Metrangolo, P.; Meyer, F.; Pilati, T.; Resnati, G.; Terraneo, G. *Angew. Chem. Int. Ed.* **2008**, *47*, 6114-6127.

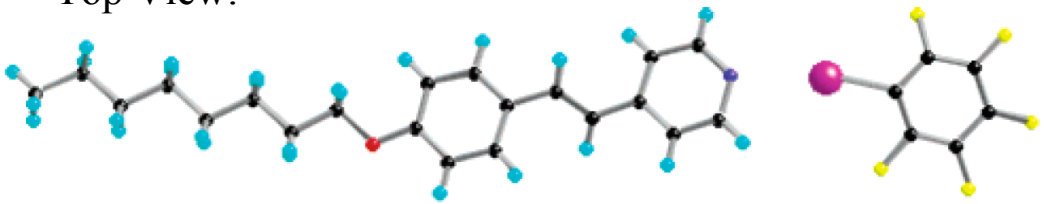
Coplanar Halogen Bonding in Liquid Crystals



1-[n] X = I, n = 4, 6, 8, 10, 12
2 X = Br, n = 12

1-[8]

Top View:



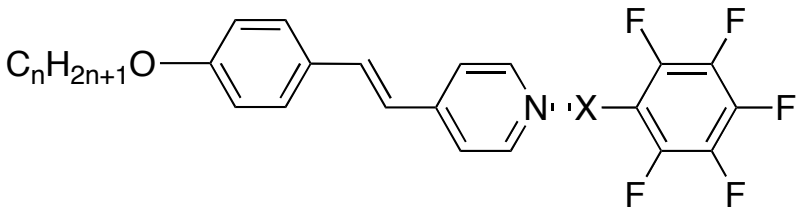
N-I distance = 2.812 Å

Side View:

N-X bond is coplanar where as X-X bond is non-coplanar.

Nguyen, H. L.; Horton, P. N.; Hursthouse, M. B.; Legon, A. C.; Bruce, D. W. *J. Am. Chem. Soc.* **2004**, *126*, 16-17.

Comparison of Hydrogen and Halogen Crystal Phases



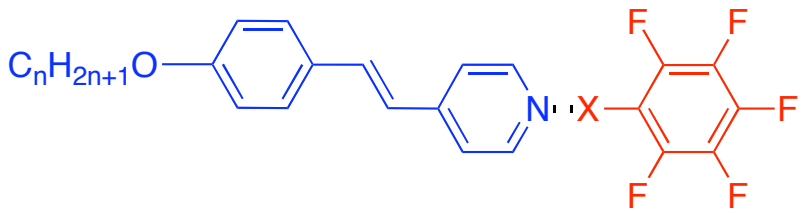
1 [n] X = I, n = 4, 6, 8, 10, 12
2 X = Br, n = 12
3 X = HO, n = 12
4 X = HOOC, n = 12

Temperature directly affects the liquid crystal phase.

Compound	Transition	T, °C
1 [10]	Crystalline - Smectic A	70
	SmecticA - Isotropic	82
1 [12]	Crystalline - Smectic A	81
	Smectic A - Isotropic	84
3	Crystalline - Isotropic	96
	Smectic A-Isotropic	94
4	Crystalline - Smectic A	104
	Smectic A - Isotropic	127

Nguyen, H. L.; Horton, P. N.; Hursthouse, M. B.; Legon, A. C.; Bruce, D. W. *J. Am. Chem. Soc.* **2004**, *126*, 16-17.

IR Shifts in Halogen Bonding



Blue-shifted

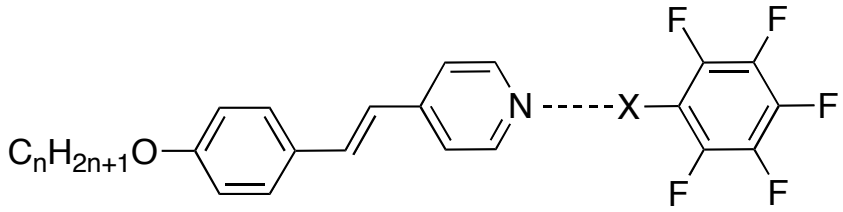
Stilbazole: 3022 cm^{-1}
Halogen/hydrogen bonded stilbazole: ~ 3028 cm^{-1}

Red-shifted

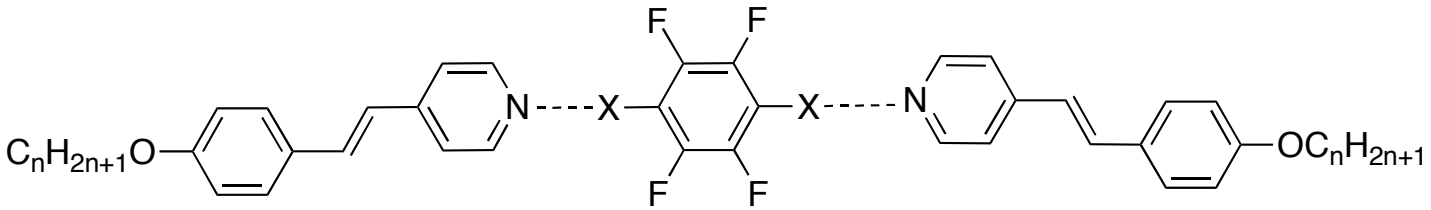
Fluorophenyl moiety: 1457, 940, 758 cm^{-1}
Halogen/hydrogen bonded fluorophenyl moiety: ~ 1450, 935, 754 cm^{-1}

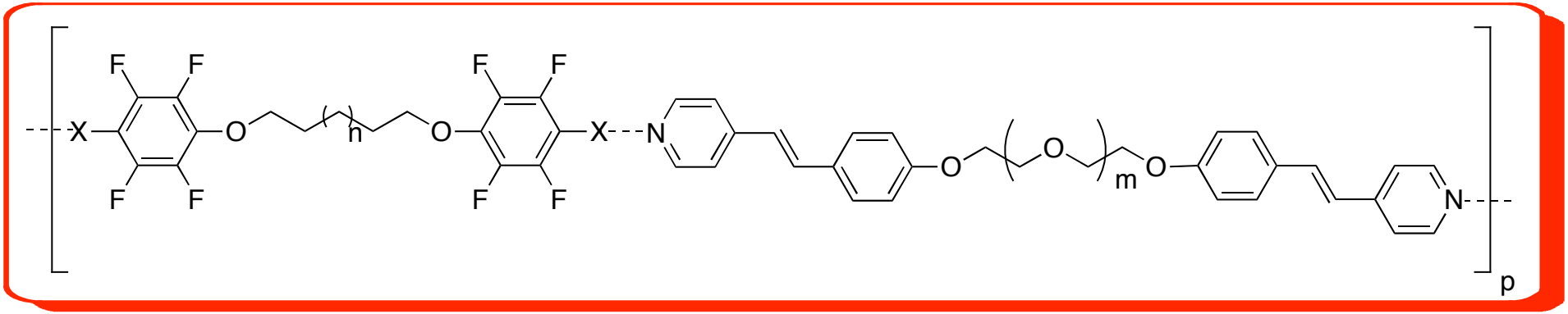
Bruce, D. W.; Metrangolo, P.; Meyer, F.; Präsang, C.; Resnati, G.; Terraneo, G.; Whitwood, A. C. *New J. Chem.* **2008**, *32*, 477-482.

Halogen Bonding in Liquid Crystals



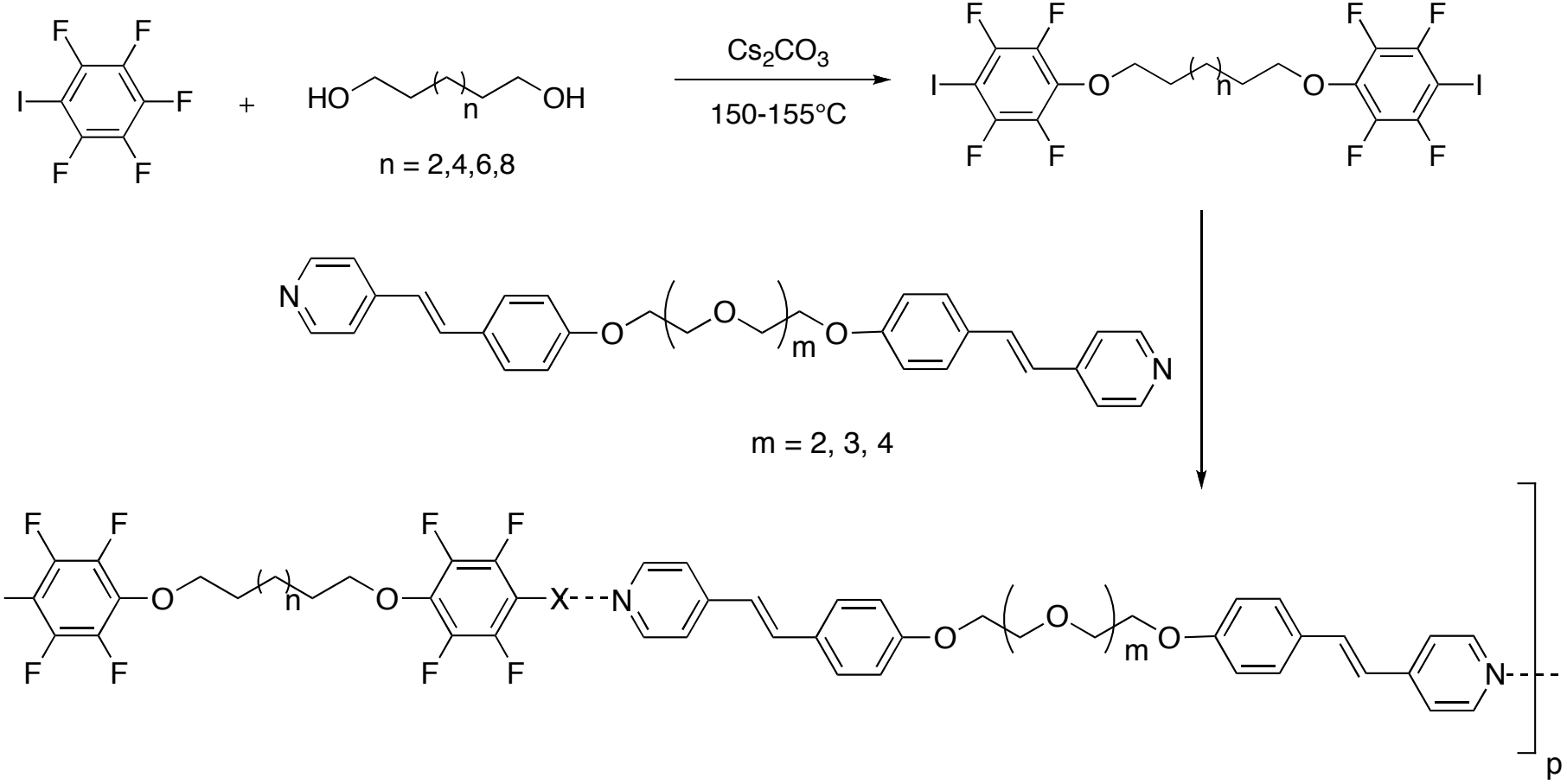
m = 4, 6, 8, 10
n = 4, 6, 8, 10, 12
X = I, Br





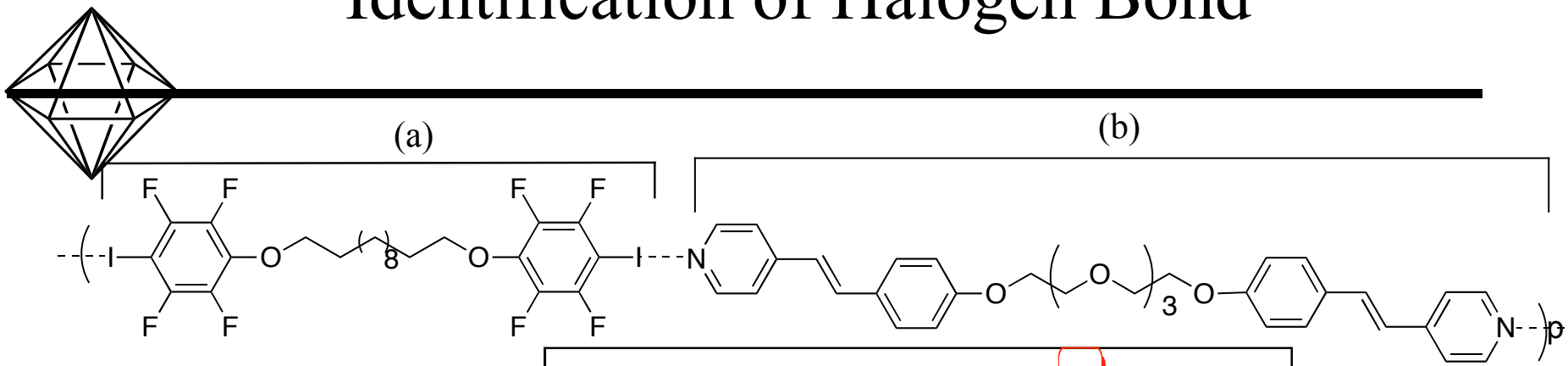
Metrangolo, P.; Meyer, F.; Pilati, T.; Resnati, G.; Terraneo, G. *Angew. Chem. Int. Ed.* **2008**, *47*, 6114-6127.

Synthesis of Liquid-Crystalline Polymer

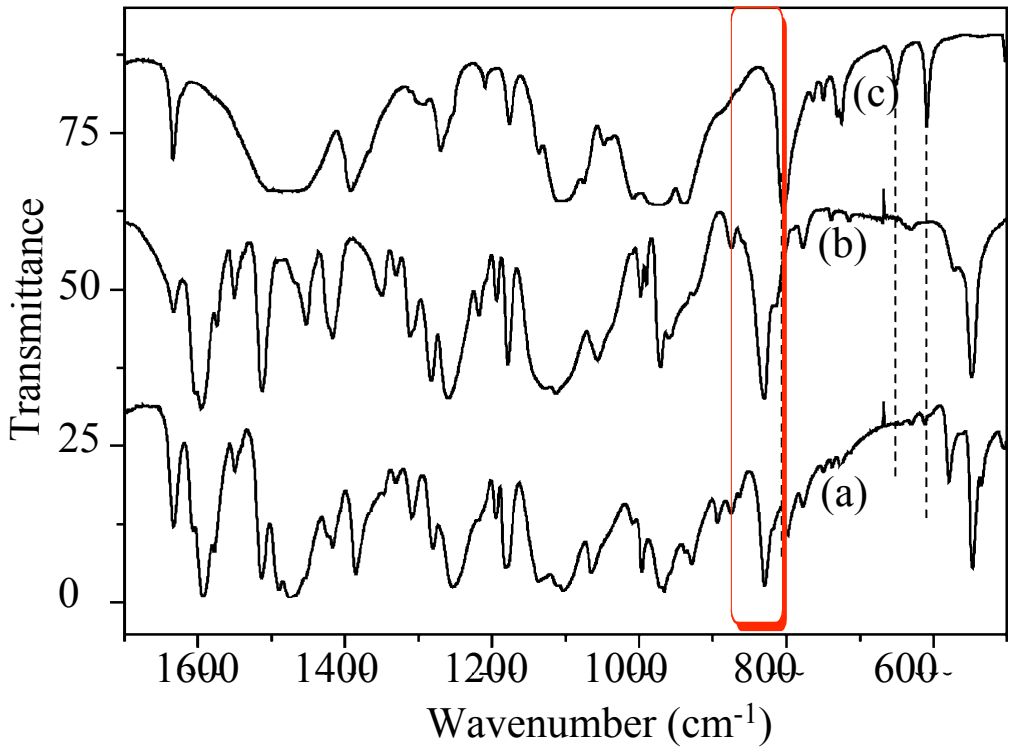


Xu, J.; Liu, X.; Lin, T.; Huang, J.; He, C. *Macromolecules* **2005**, *38*, 3554-3557.

Identification of Halogen Bond

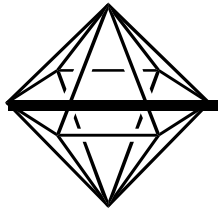


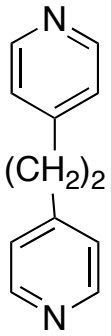
(c) Adduct of (a) + (b).



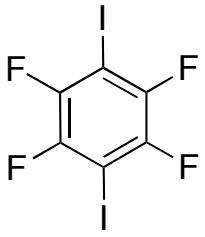
Xu, J.; Liu, X.; Lin, T.; Huang, J.; He, C. *Macromolecules* **2005**, *38*, 3554-3557.

Halogen *vs* Hydrogen Liquid Crystals

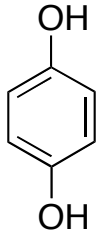




1a



2a



3a

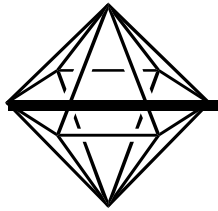
1a + 2a ⟶ **•••• 1a •••• 2a •••• 1a ••••2a ••••**

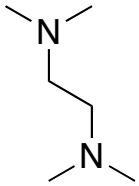
1a + 3a ⟶ **•••• 1a •••• 3a •••• 1a ••••3a ••••**

1a + 2a + 3a ⟶ **•••• 1a •••• 2a •••• 1a ••••2a ••••**

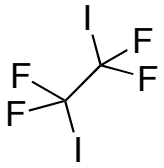
Corradi, E.; Meille, S. V.; Messina, M. T.; Metrangolo, P.; Resnati, G. *Angew. Chem* **2000**, *112*, 1852-1856.

Halogen *vs* Hydrogen Liquid Crystals

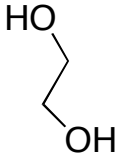




1b



2b



3b

1b + 2b ⟶ **•••• 1b •••• 2b •••• 1b ••••2b ••••**

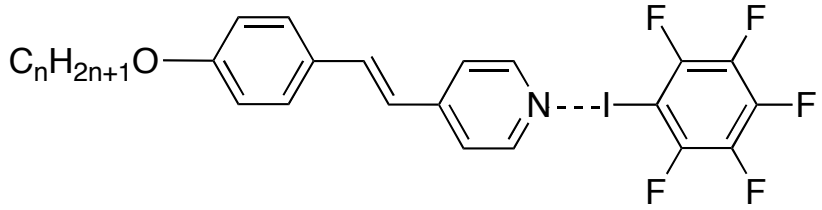
1b + 3b ⟶ **•••• 1b •••• 3b •••• 1b ••••3b ••••**

1b + 2b + 3b ⟶ **•••• 1b •••• 2b •••• 1b ••••2b ••••**

Corradi, E.; Meille, S. V.; Messina, M. T.; Metrangolo, P.; Resnati, G. *Angew. Chem* **2000**, *112*, 1852-1856.

Halogen Bonding Applied in Liquid Crystals

- Stilbazoles are good halogen bond acceptors in liquid crystal formation.



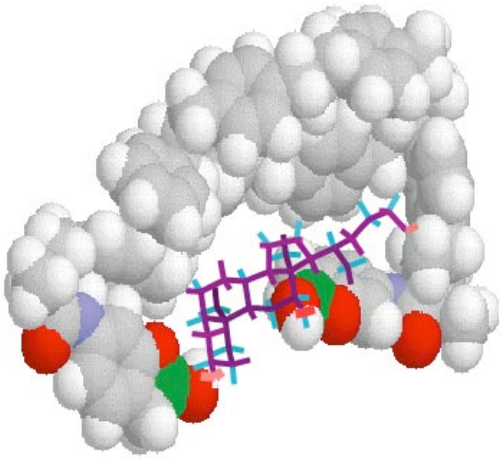
- Halogen bonding liquid crystal phases occur at a slightly lower temperature than those of hydrogen bonding.

Halogen Bonding	Smetic A	Isotropic	84
Hydrogen Bonding	Smetic A	Isotropic	94

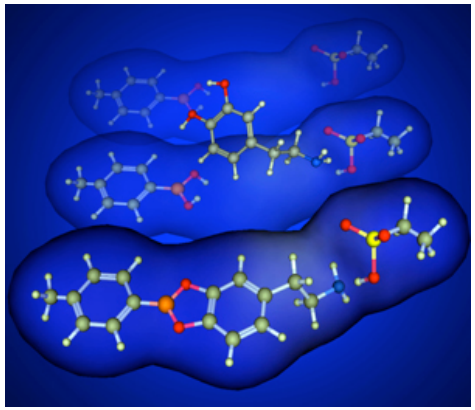
- Halogen bonding is capable of dominating over hydrogen bonding in a variety of liquid crystals. .

Applications of Molecular Imprinted Polymers (MIP)

MIP: a polymer that is formed in the presence of a molecule that is extracted afterwards, thus leaving a cavity behind.



Steroid imprint



MIP that binds to dopamine.

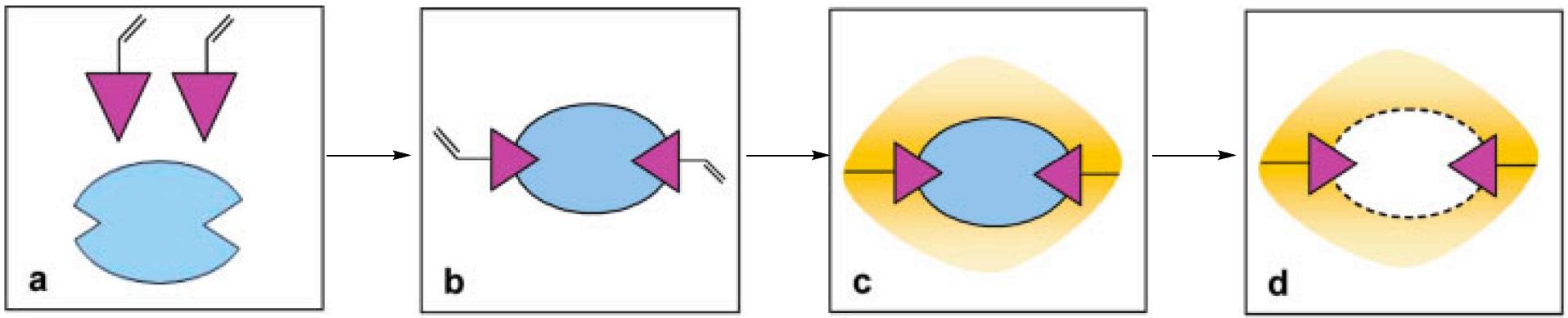
MIP can be related to a missing puzzle piece.

Also could be applied in:

1) drug delivery systems
2) extraction of toxic comounds
3) biosensors

Takeuchi, T.; Murase, N.; Maki, H.; Mukawa, T.; Shinmori, H. *Org. Biomol. Chem.* **2006,***4*, 565.
http://userweb.port.ac.uk/~alexandc/ResearchInterests.htm

Molecular Imprinted Polymers (MIP)



a)Monomer (violet) and imprinting agent (blue).

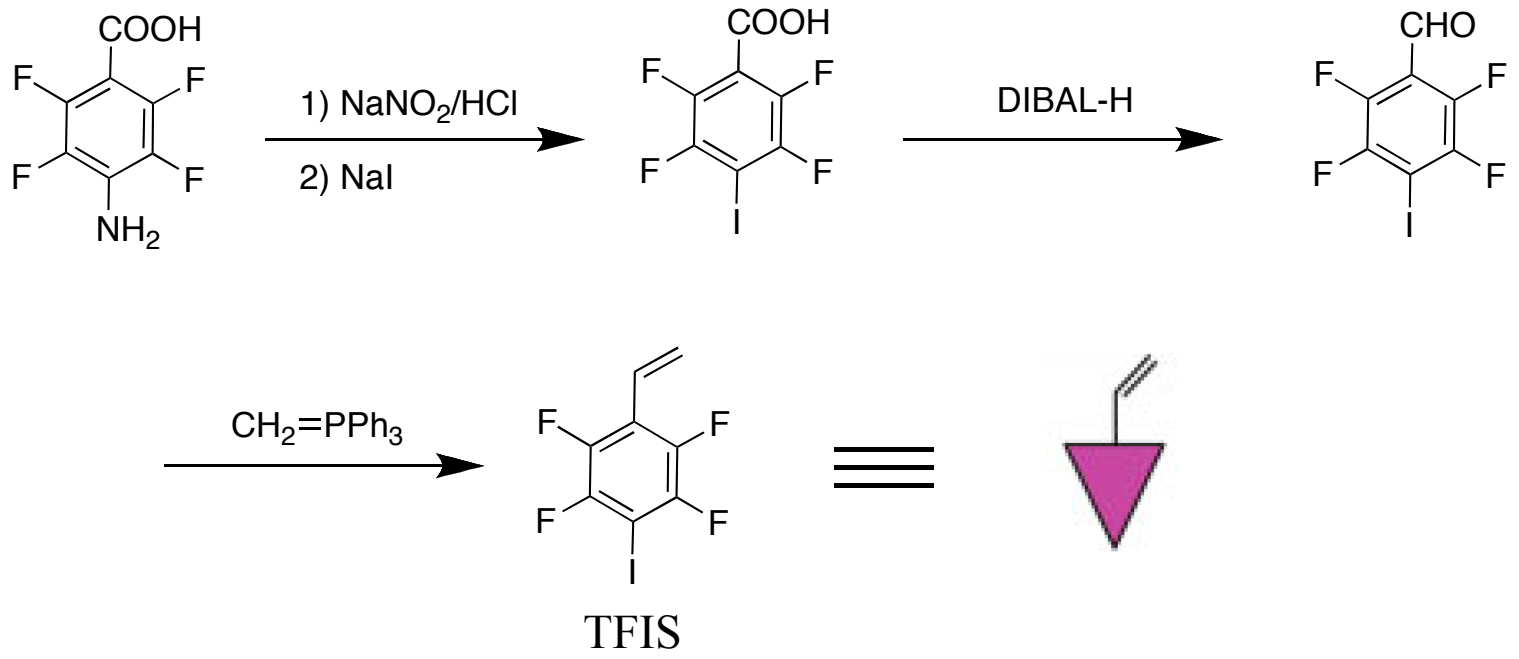
b) Self-assembly

c) Polymerization reaction.

d) Wash to remove imprinting agent.

Metrangolo P.; Resnati, G.; Pilati, T.; Liantonio, R.; Meyer, F. *J. Polym. Sci. Part A: Polym Chem.* **2007**, *45*, 1-15.

Synthesis of Functional Monomer

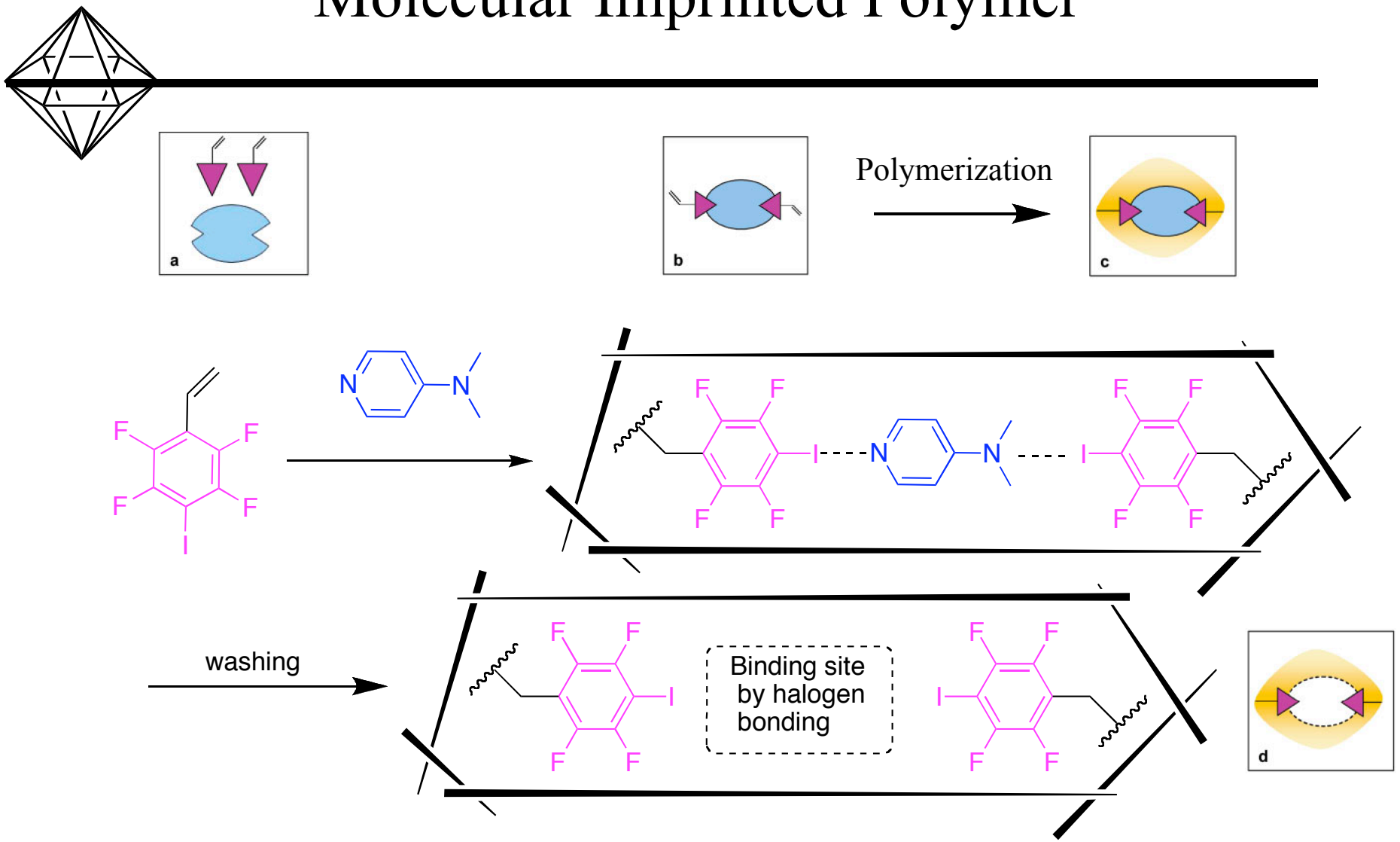


TFIS

2,3,5,6-Tetrafluoro-4-iodostyrene (TFIS)

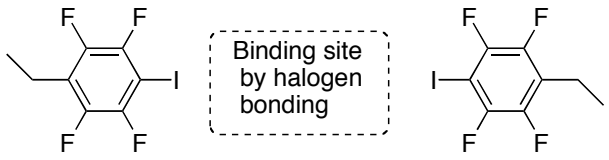
Metrangolo P.; Resnati, G.; Pilati, T.; Liantonio, R.; Meyer, F. *J. Polym. Sci. Part A: Polym Chem.* **2007**, *45*, 1-15.

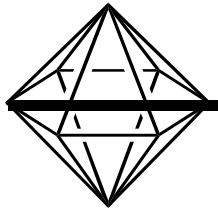
Molecular Imprinted Polymer

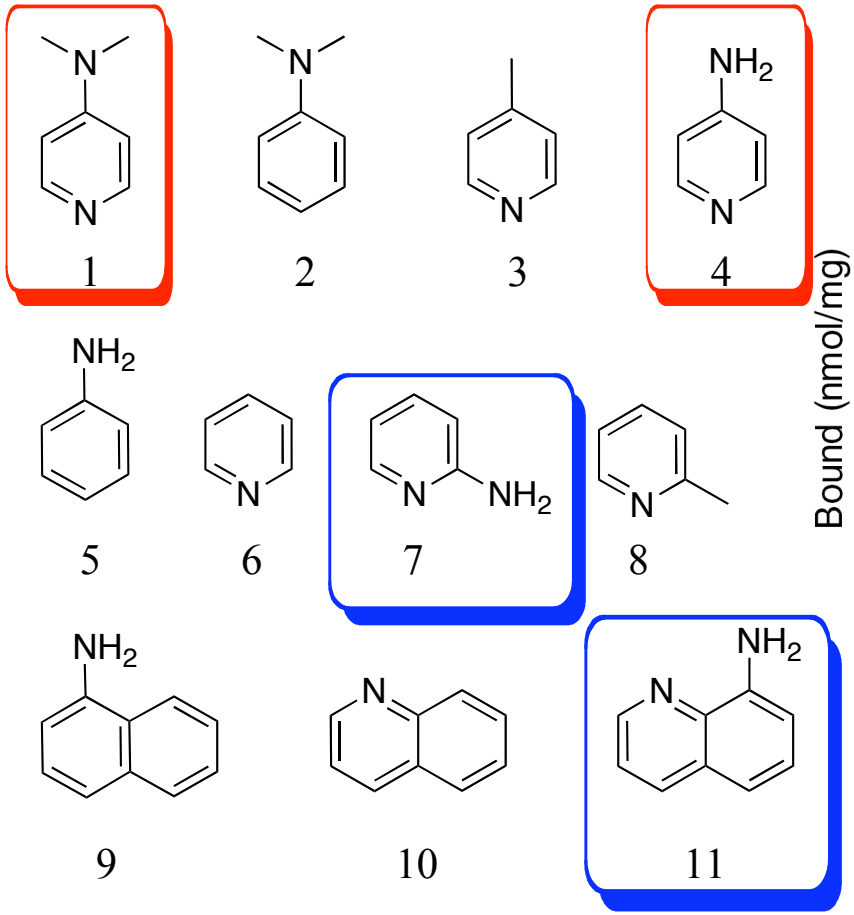


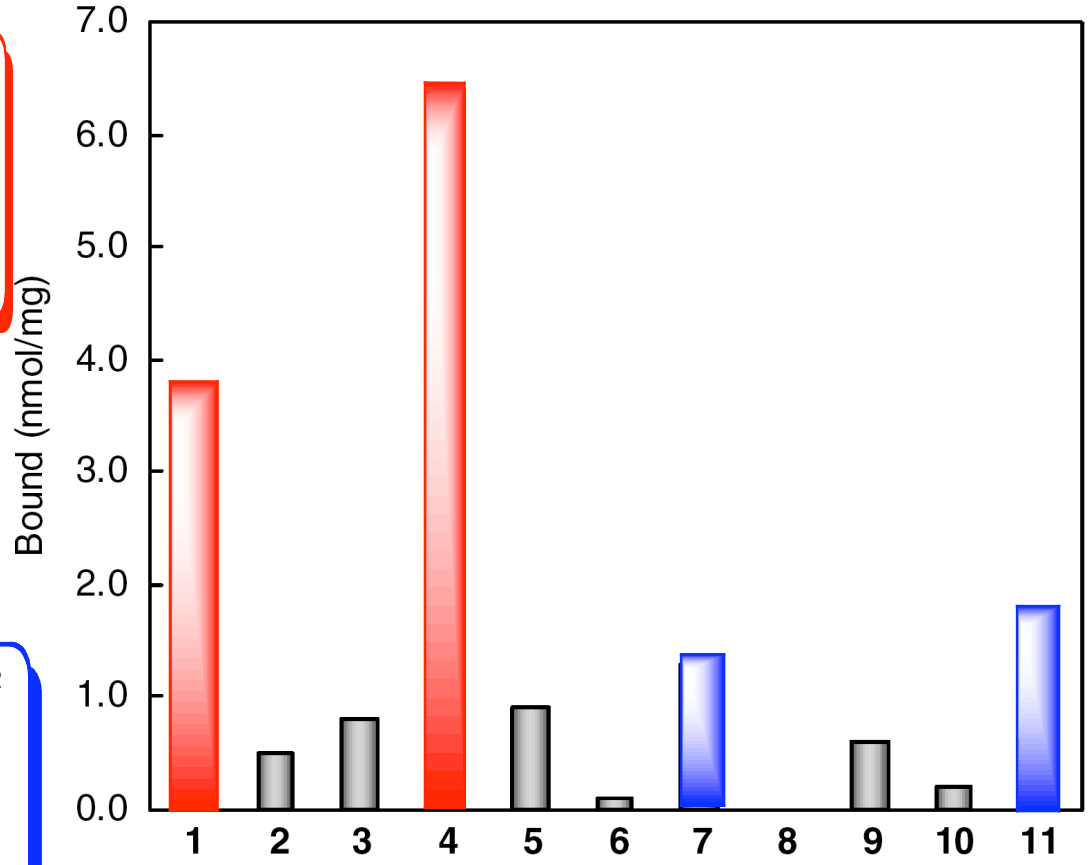
Metrangolo P.; Resnati, G.; Pilati, T.; Liantonio, R.; Meyer, F. *J. Polym. Sci. Part A: Polym Chem.* **2007**, *45*, 1-15.

Binding Abilities of the Imprinted Polymer



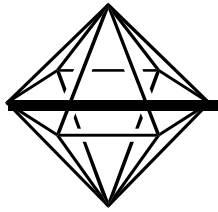






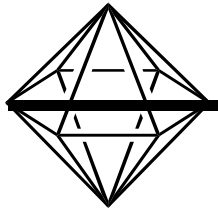
Metrangolo P.; Resnati, G.; Pilati, T.; Liantonio, R.; Meyer, F. *J. Polym. Sci. Part A: Polym Chem.* **2007**, *45*, 1-15.

Outline



- Discovery and types of halogen bonding (XB).
- Halogen bonding used in Liquid Crystals (LC), LC polymers and Molecular Imprinted Polymers (MIP).
- Use of halogen bonds in molecular conductors and formation of Borromean Rings (BR) .

Outline



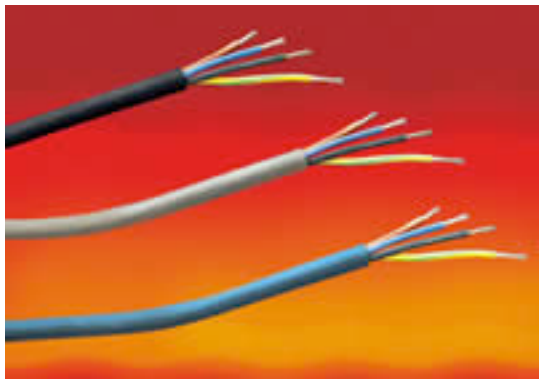
- Discovery and types of halogen bonding (XB).
- Halogen bonding used in Liquid Crystals (LC), LC polymers and Molecular Imprinted Polymers (MIP).
- Use of halogen bonds in molecular conductors and formation of Borromean Rings (BR) .

Semiconductor: Definition

Semiconductor: substance with electrical conductivity between a conductor and insulator.

Conductor

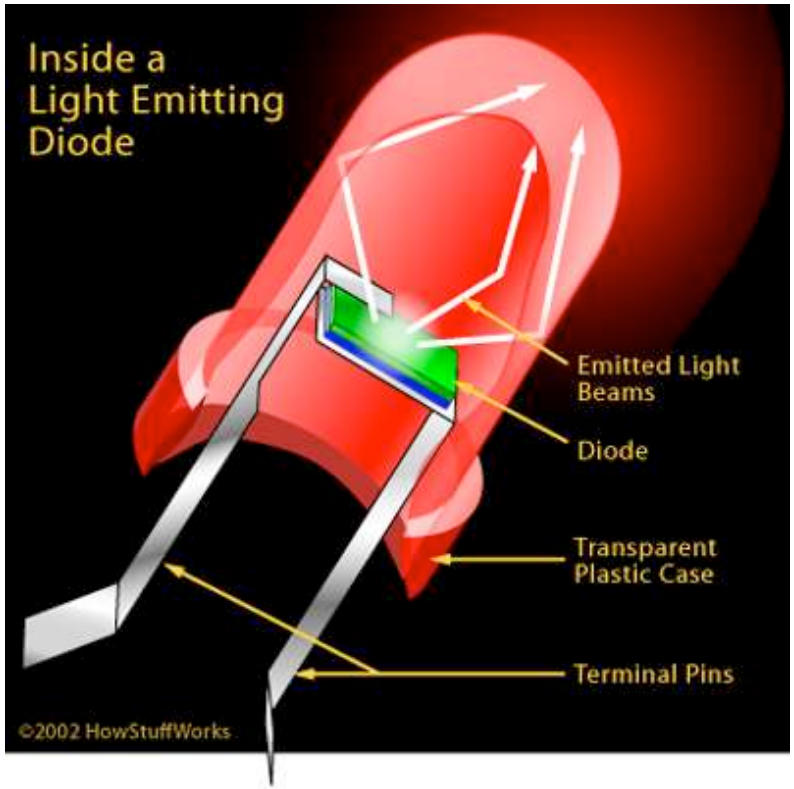
Semiconductor



Insulator

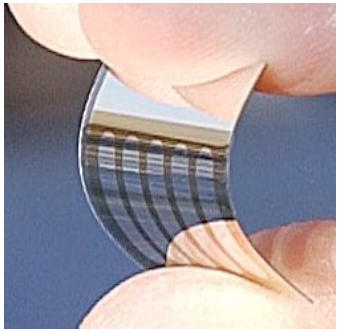
http://www.nasa.gov/vision/earth/technologies/electric_textiles.html
http://www.drillspot.com/products/46641/Bussmann_FWP-150A_Semiconductor_Fuse

Applications of Semiconductors

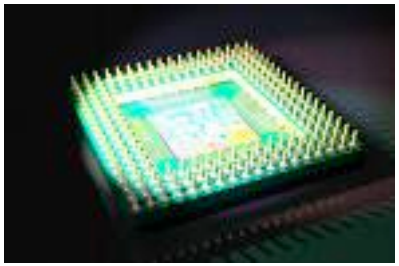


Light Emitting Diode (LED)

Photo cells



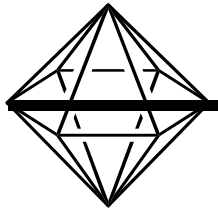
Organic solar cell



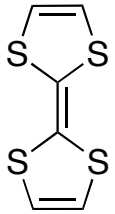
microprocessors

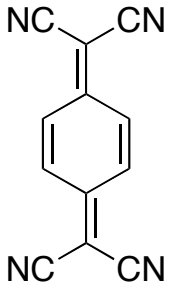
http://www.arrow-israel.co.il/Index.asp?CategoryID=126 http://www.livescience.com/technology/041224_solar_panels.html
http://www.eden-project.co.uk/latest_happenings47.htm

Thiofulvalene Skeleton of Semi-conductor Precursors

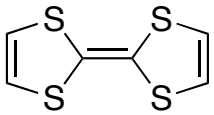


TTF-TCNQ:

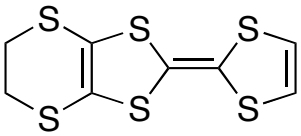




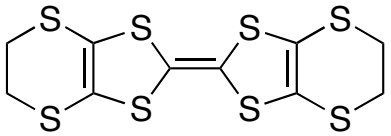
First organic metal discovered in 1972.



TTF



EDT-TTF

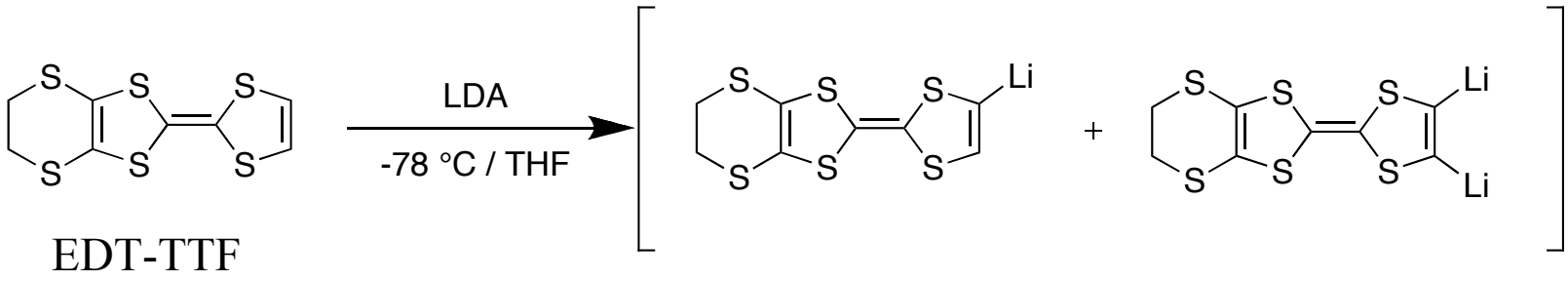


BEDT-TTF

BEDT: Bis(ethylenedithio) EDT: ethylenedithio TTF: tetrathiofulvalene

Imakubo, T. Sawa, H.; Kato, R. *Syn. Met.* **1995**, *73*, 117-122 .

Synthesis of Molecular Conductor Precursors



EDT-TTF

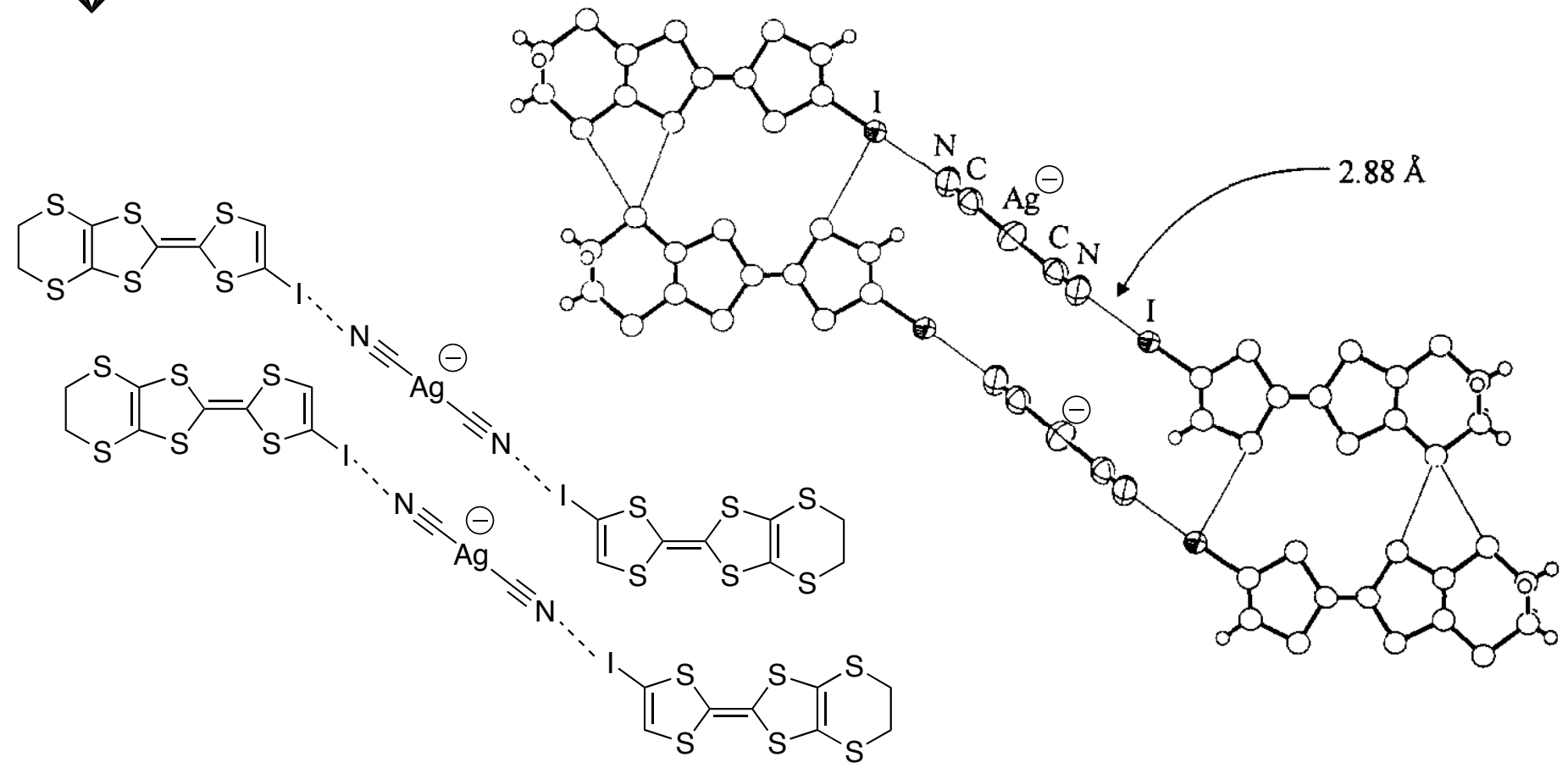
IEDT

DIET

IEDT: iodoethylenedithiofulvalene
DIET: diiodoethylenedithiothiofulvalene

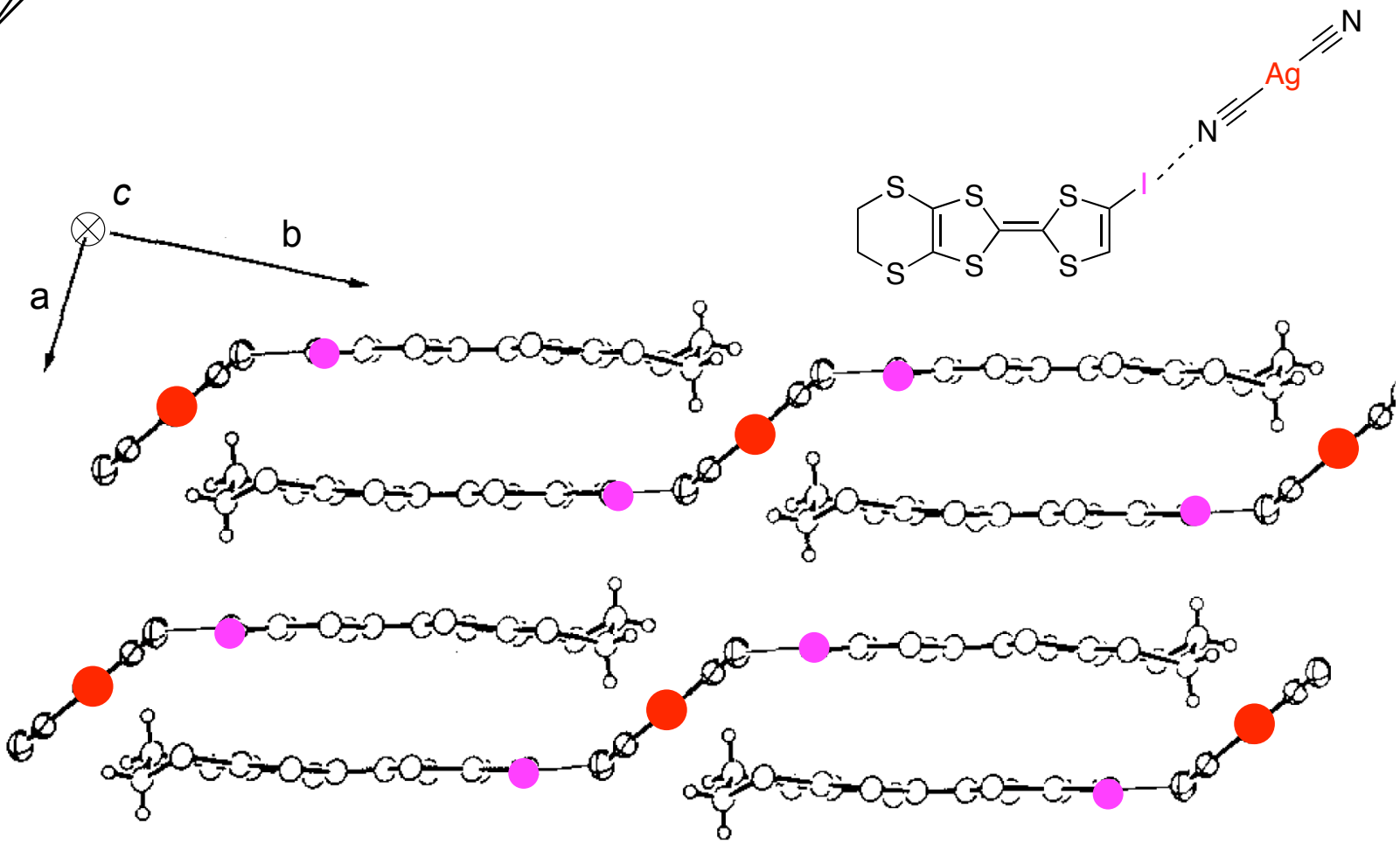
Imakubo, T. Sawa, H.; Kato, R. *Syn. Met.* **1995**, *73*, 117-122 .

IEDT Halogen Bonded to Dicyanosilver



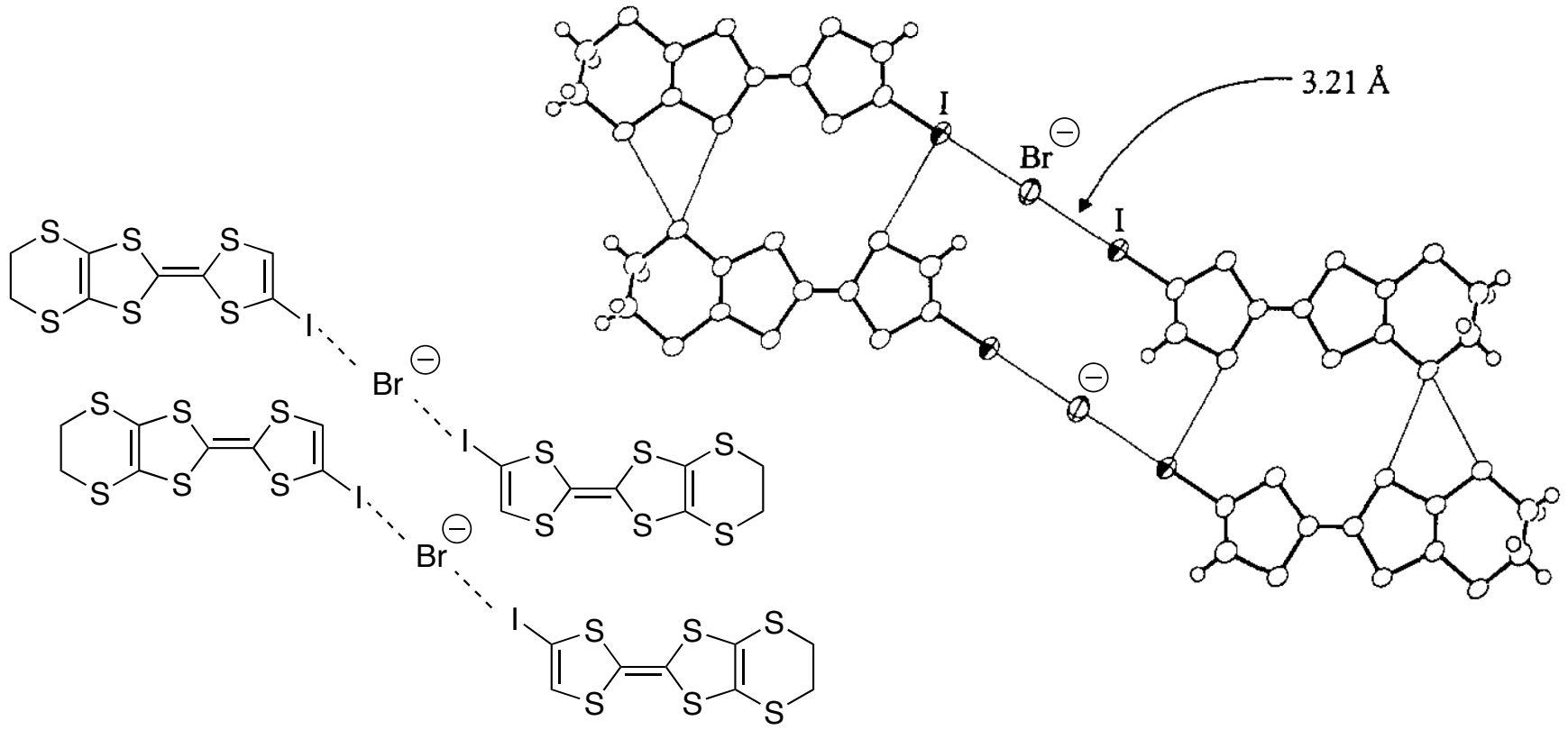
Imakubo, T. Sawa, H.; Kato, R. *Syn. Met.* **1995**, *73*, 117-122 .

Stacking Mode of IEDT and Dicyanosilver



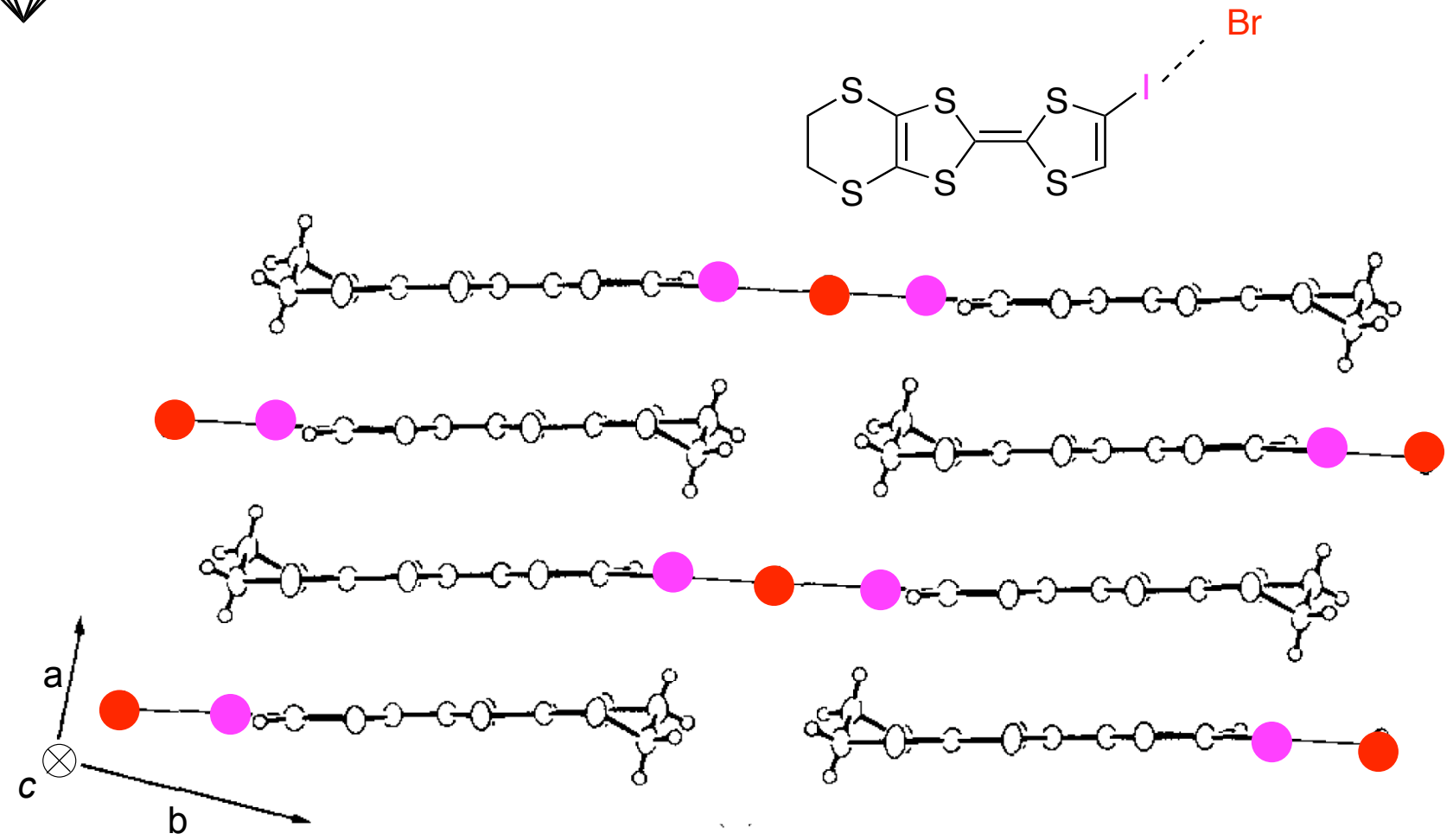
Imakubo, T. Sawa, H.; Kato, R. *Syn. Met.* **1995**, *73*, 117-122 .

EIDT Halogen Bonded to Bromine Anion



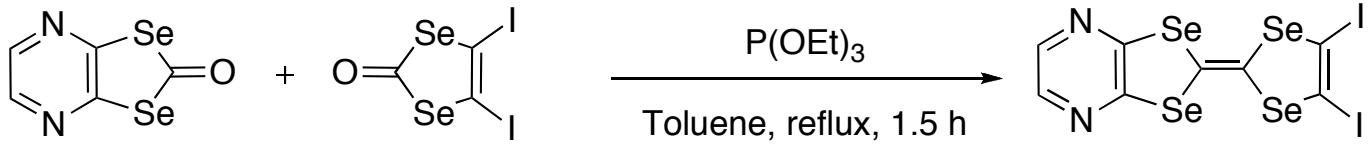
Imakubo, T. Sawa, H.; Kato, R. *Syn. Met.* **1995**, *73*, 117-122 .

Stacking Mode of EIDT and Bromine Anion

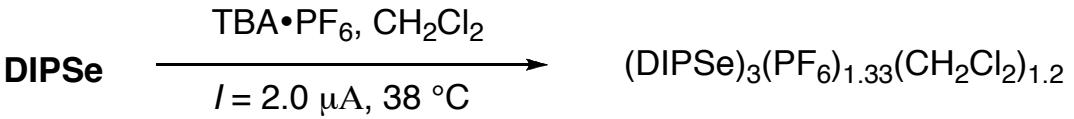


Imakubo, T. Sawa, H.; Kato, R. *Syn. Met.* **1995**, *73*, 117-122 .

Assembly of Supramolecular Conductor



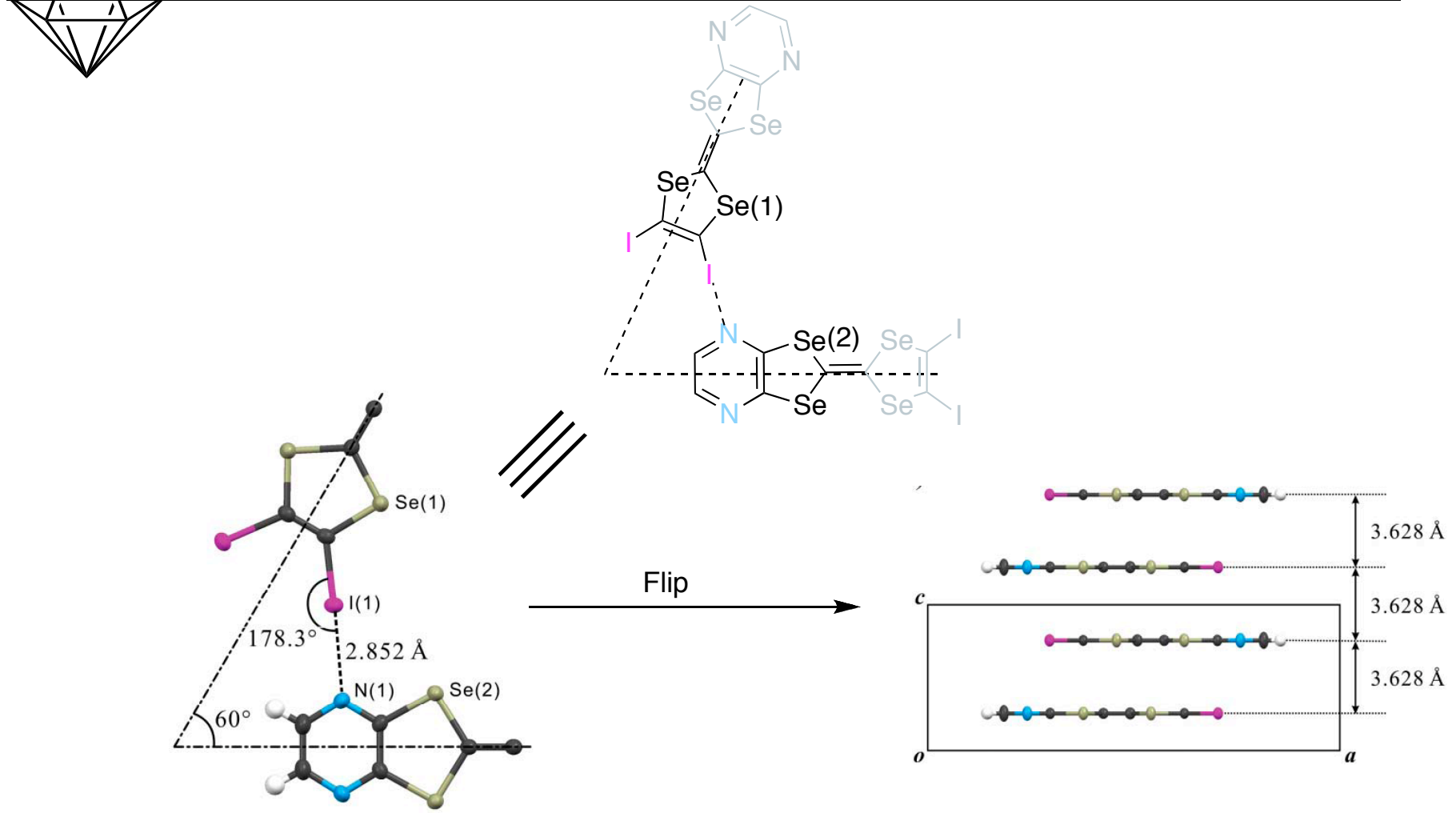
DIPSe



diiodo(pyrazino)tetraselenafulvalene (**DIPSe**)

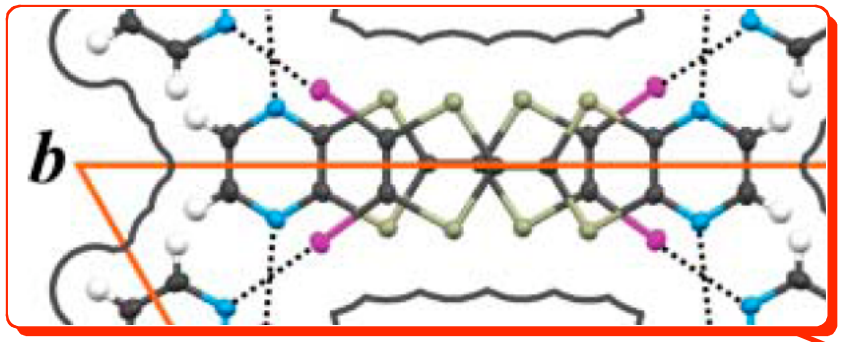
Imakubo, T.; Kibune, M.; Yoshino, H.; Shirahata, T.; Yoza, K. *J. Mater. Chem.* **2006**, *16*, 4110-4116.

Assembly of Supramolecular Conductor

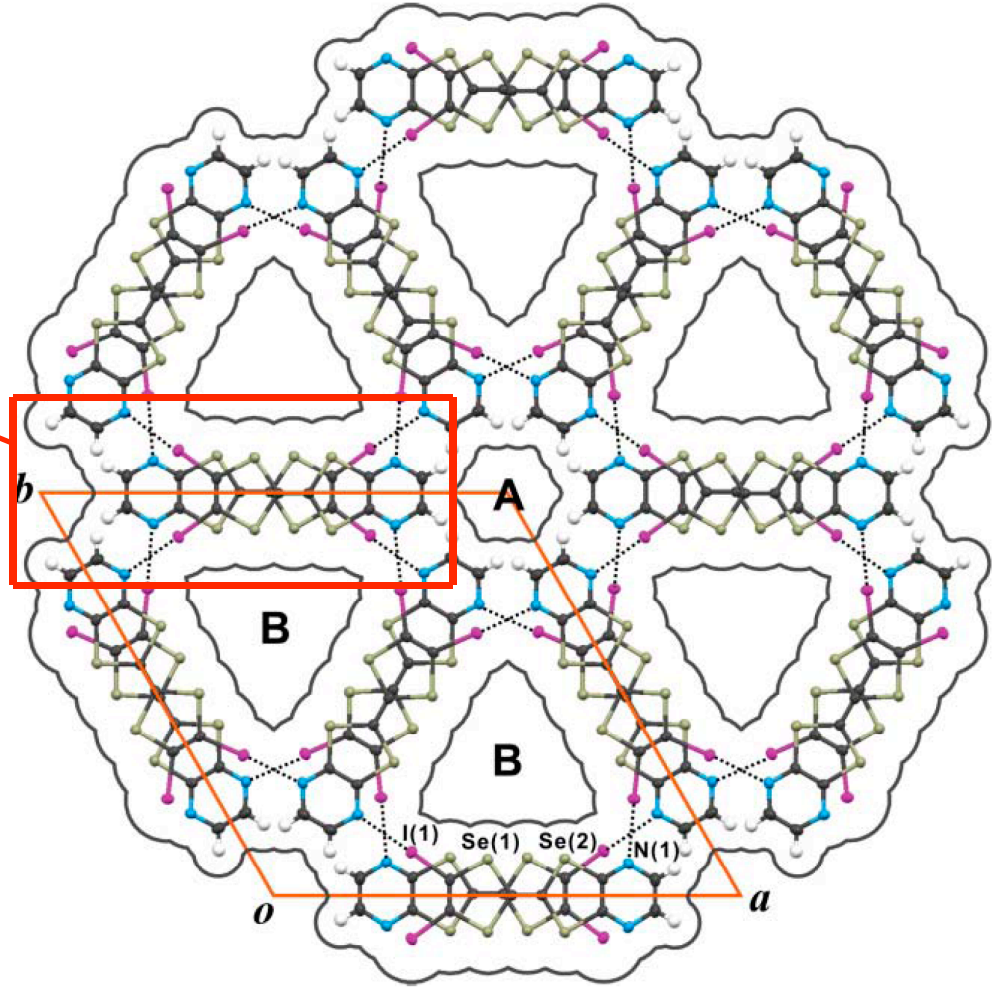


Imakubo, T.; Kibune, M.; Yoshino, H.; Shirahata, T.; Yoza, K. *J. Mater. Chem.* **2006**, *16*, 4110-4116.

Organic Conductor: Counter Anions



DIPSe $\xrightarrow[I = 2.0\ \mu A,\ 38\ ^\circ C]{TBA{\bullet}PF_6,\ CH_2Cl_2}$ $(DIPSe)_3(PF_6)_{1.33}(CH_2Cl_2)_{1.2}$



Cavity A houses 50 % of PF_6 anions.

Cavity B houses the Remaining 50 % of PF_6 anions and solvent (CH_2Cl_2).

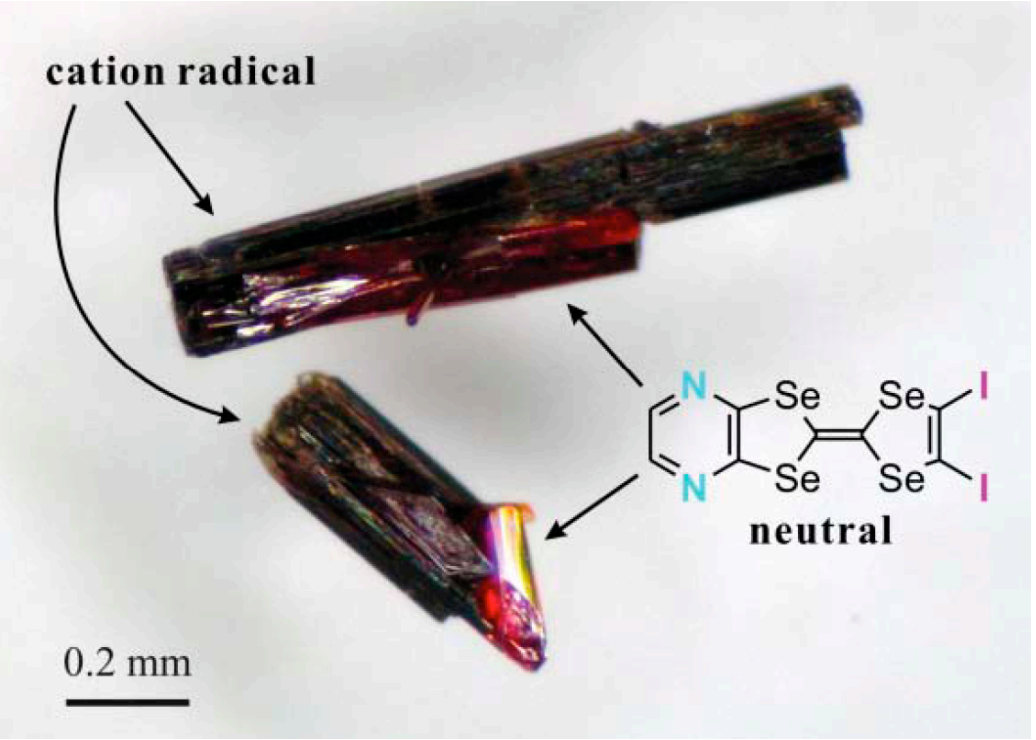
Imakubo, T.; Kibune, M.; Yoshino, H.; Shirahata, T.; Yoza, K. *J. Mater. Chem.* **2006**, *16*, 4110-4116.

Advantage of Halogen Bonded Supramolecular Conductor

Reversibility:

Reflux in variety of solvents frees the DIPSe crystals

$2DIPSe^{+\bullet} + H_2O \rightarrow$
$2\ DIPSe + 1/2\ O_2 + 2H^+$

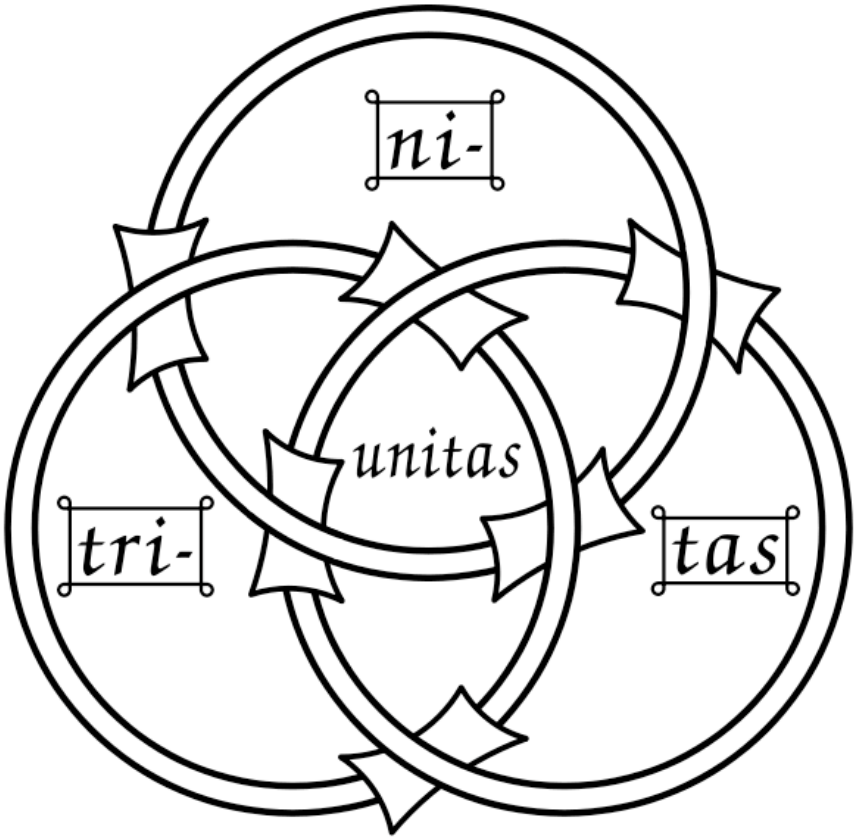


Imakubo, T.; Kibune, M.; Yoshino, H.; Shirahata, T.; Yoza, K. *J. Mater. Chem.* **2006**, *16*, 4110-4116.

The Borromean Ring

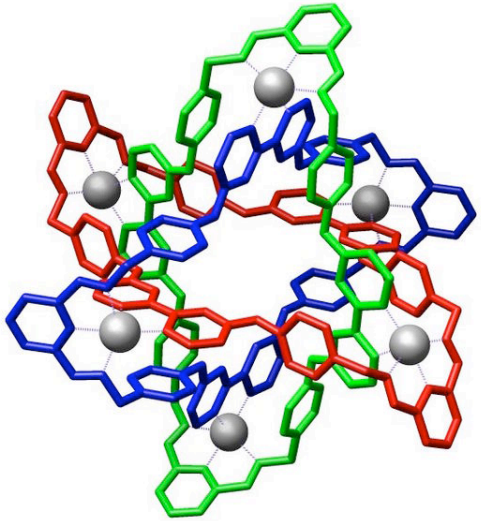
The borromean ring is often used in Christianity to represent the trinity:

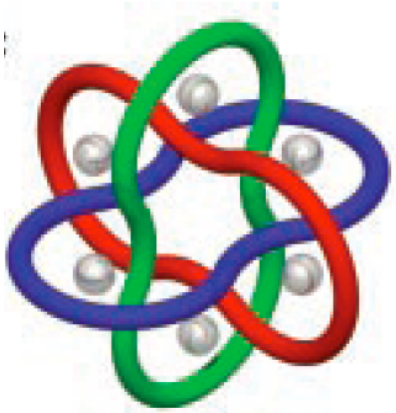
God existing as 3 persons
- God the Father
- God the Son
- God the Holy Spirit

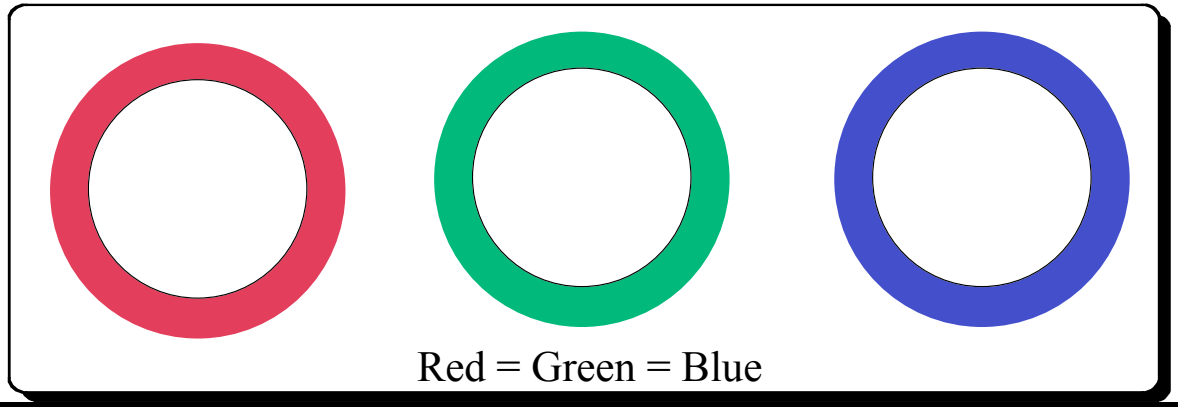


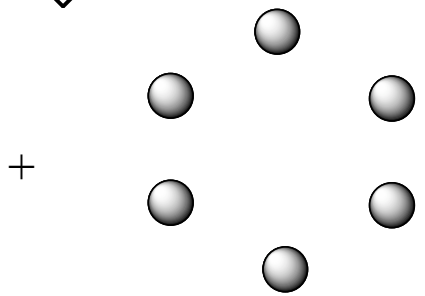
http://www.thercg.org/images/lit/ttigtio-trifoil_small.gif

Retrosynthetic disconnection of Borromean Ring









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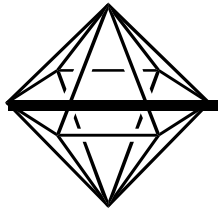
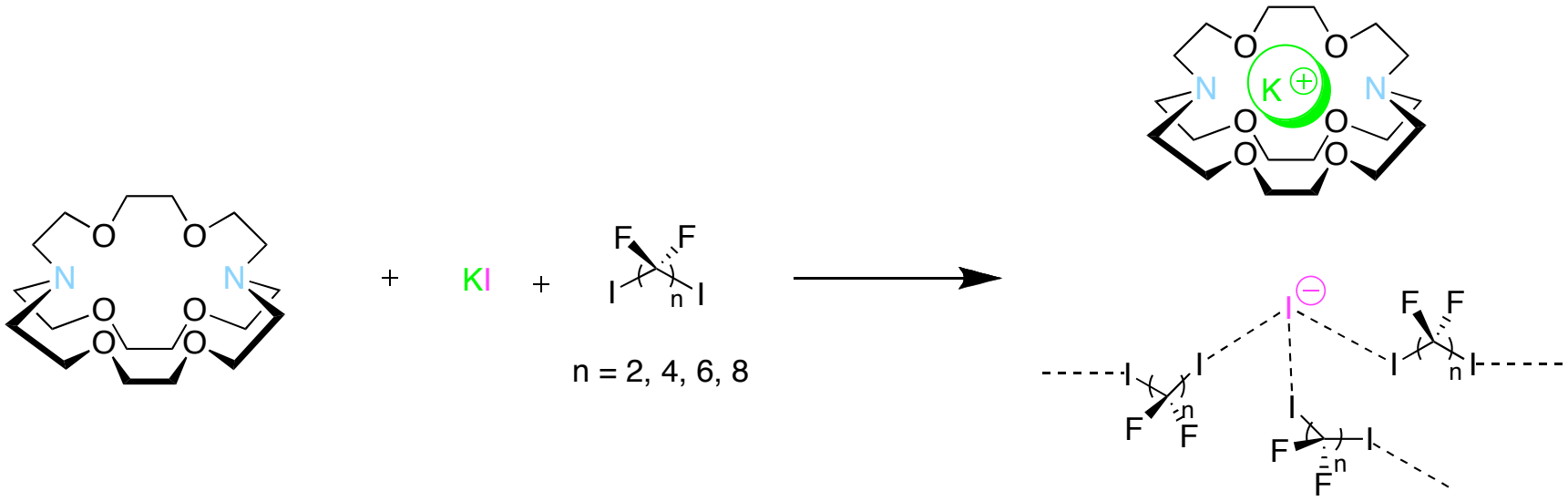
Iodide Ions Used as Tridentate X-Bond Acceptor



Metric Engineering: The prediction of the overall structural pattern of crystalline lattices.



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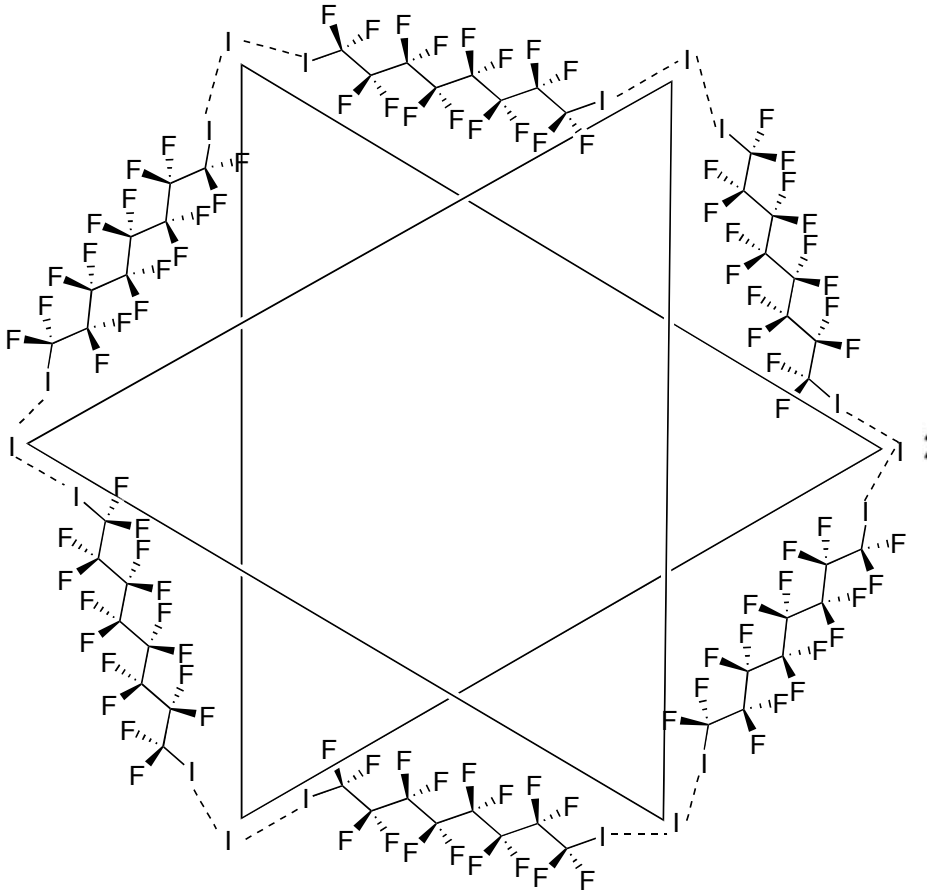
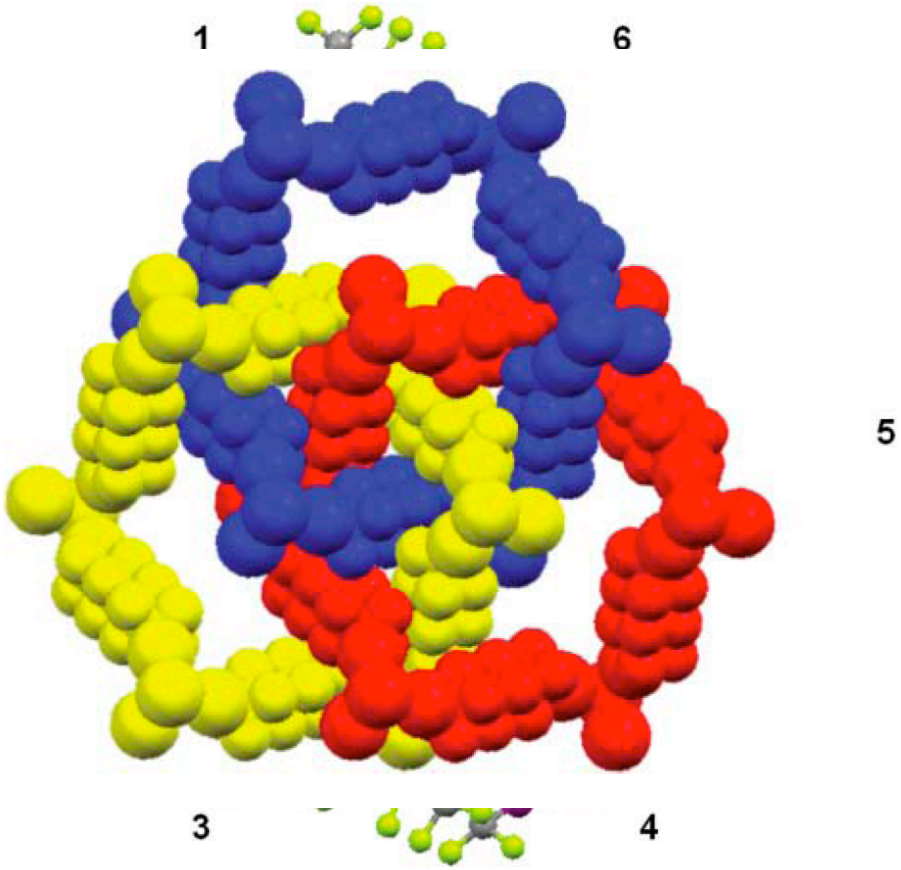
Borromean Ring





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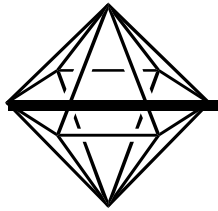
Conclusions



- Halogen bonding is very diverse: N, O, X, Anion.
- Halogen bonds induce directionality.
- Applications: liquid crystals, liquid crystals polymers, molecular imprinted polymers, conductors and Borromean rings.

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