Electronic Supplementary Material (ESI) for CrystEngComm.

# Supplementary material

# Halogen Bonding (HaB) in E-I···X-M systems: influence of the halogen donor in the HaB nature.

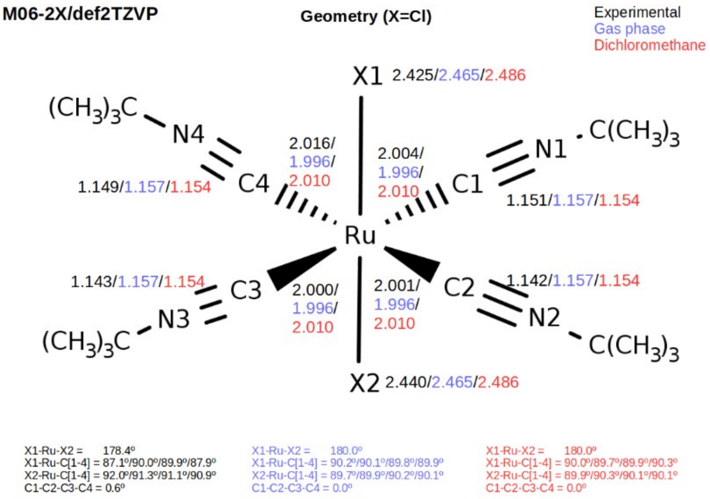
Silvia Dortéz,[a] Francisco Fernández-Palacio,[a] Jesús Damián,[a] Carlos Gaiteiro,[a] Javier Ramos,*,[b] Pilar Gómez-Sal *,[a] and Marta E. G. Mosquera*.

[a]*Departamento de Química Orgánica y Química Inorgánica, Instituto de Investigacion en Química "Andres M. del Río" (IQAR) Universidad de Alcalá, Campus Universitario, 28871-Alcala de Henares, Madrid. Spain. E-mail for M.E.G.M.:* *martaeg.mosquera@uah.es*

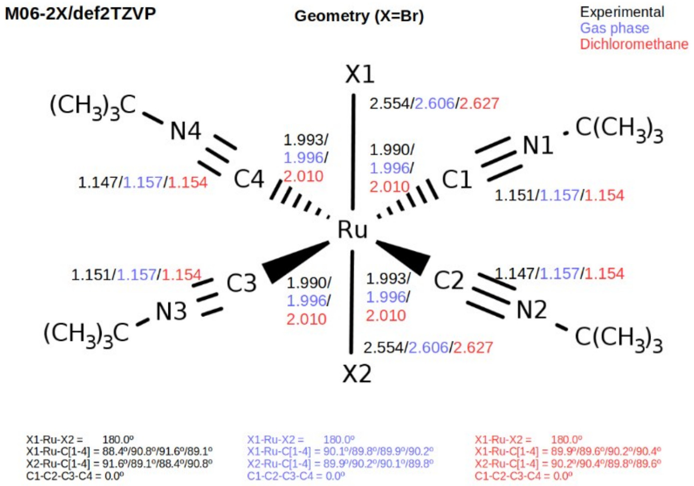
[b]*BIOPHYM, Department of Macromolecular Physics, Instituto de Estructura de la Materia, IEM-CSIC, C/ Serrano 113 bis, 28006 Madrid, Spain.*

# 1. GEOMETRICAL PARAMETERS

**1a**



**2a**



**3a**

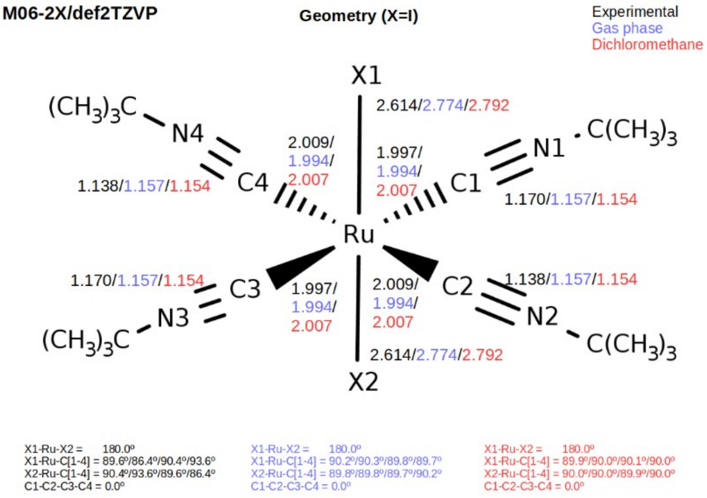


**Figure S.1:** Selected geometrical parameters for compounds **1a**, **2a** and **3a**. Experimental data from crystallographic information, optimized DFT in gas phase and optimized DFT in $CH_2Cl_2$ are given in black, blue and red, respectively. Bond lengths are shown in Angstrom and angles in degrees.

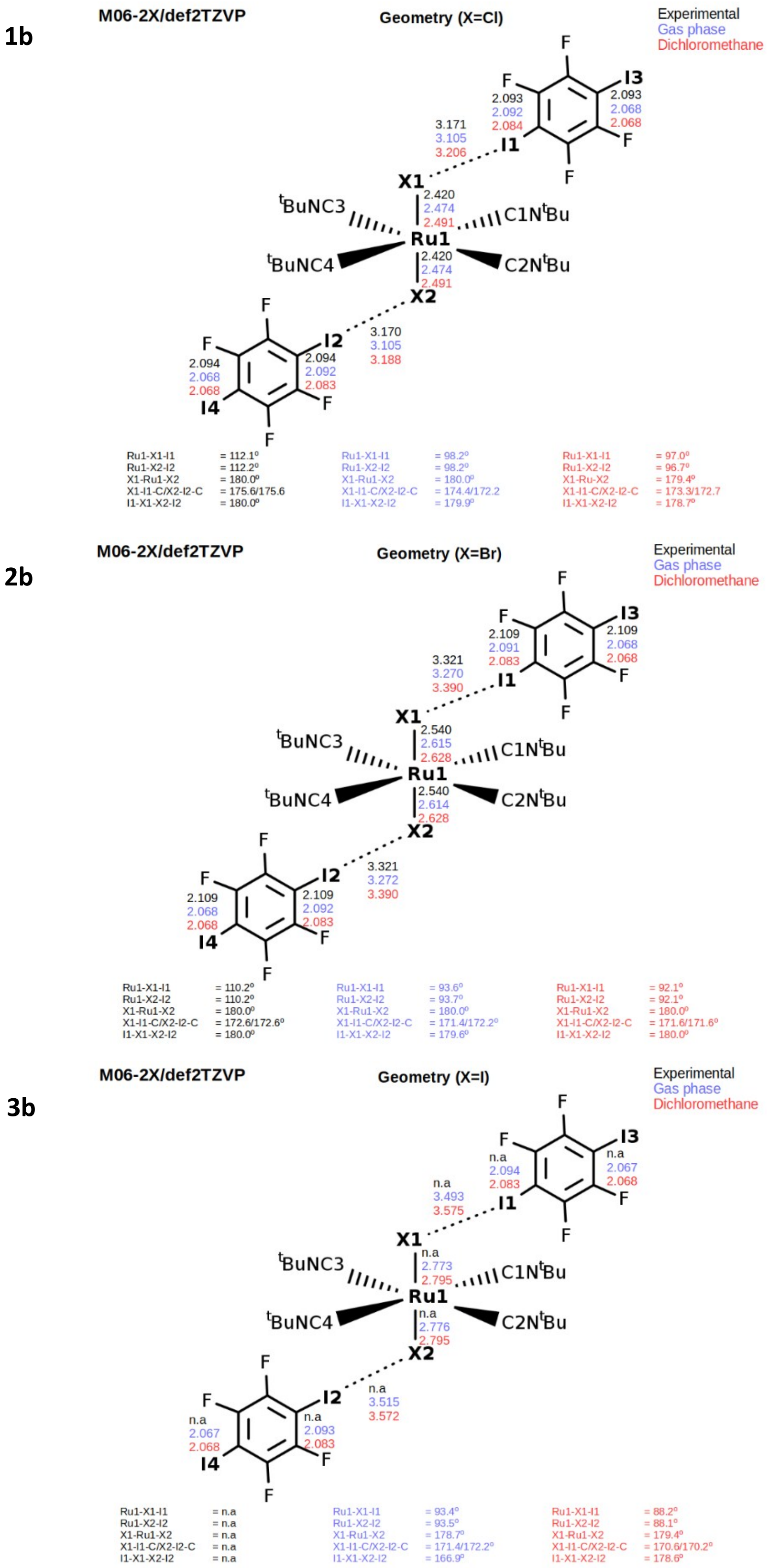
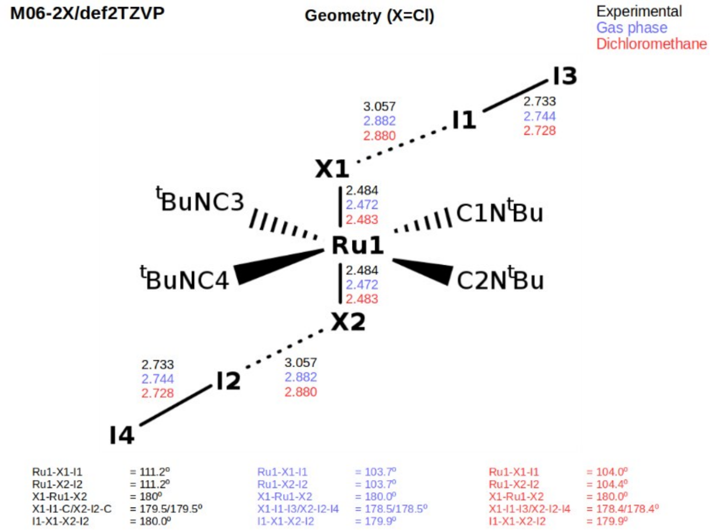
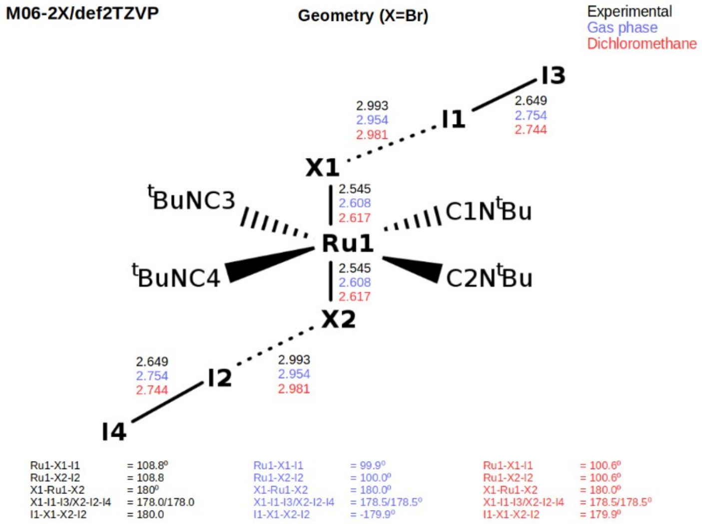


**Figure S.2:** Selected geometrical parameters for compounds **1b**, **2b** and **3b**. Experimental data from crystallographic information, optimized DFT in gas phase and optimized DFT in $CH_2Cl_2$ are given in black, blue and red, respectively. Bond lengths are shown in Angstrom and angles in degrees (n.a stands for not available)

**1c**



**2c**



**3c**

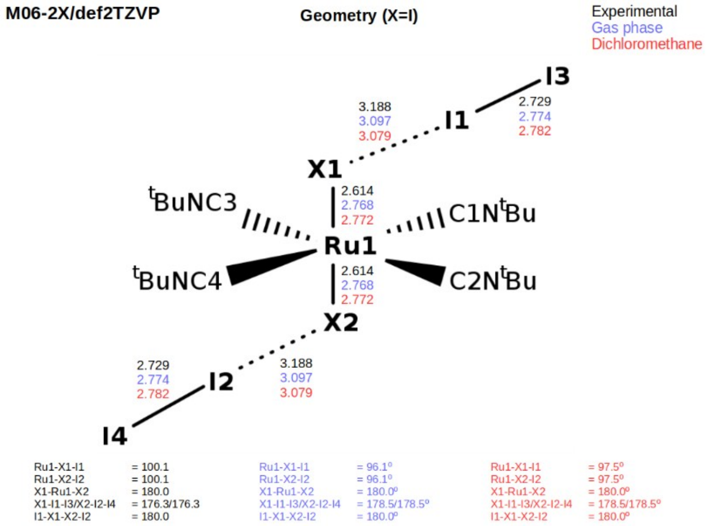
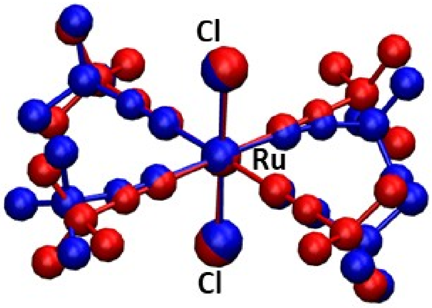
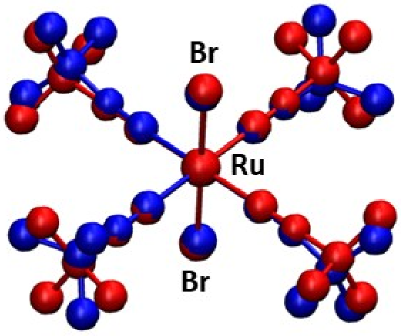


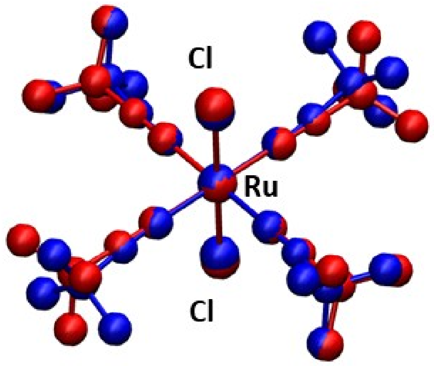
**Figure S.3:** Selected geometrical parameters for compounds **1c**, **2c** and **3c**. Experimental data from crystallographic information, optimized DFT in gas phase and optimized DFT in $CH_2Cl_2$ are given in black, blue and red, respectively. Bond lengths are shown in Angstrom and angles in degrees (n.a stands for not available)



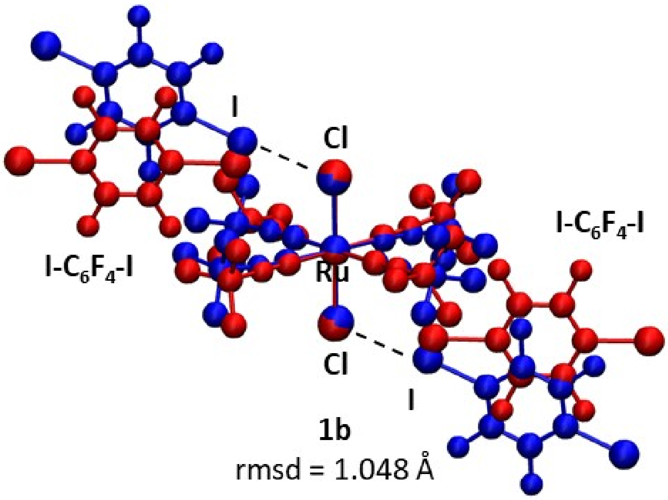
**1a**
rmsd = 0.674 Å



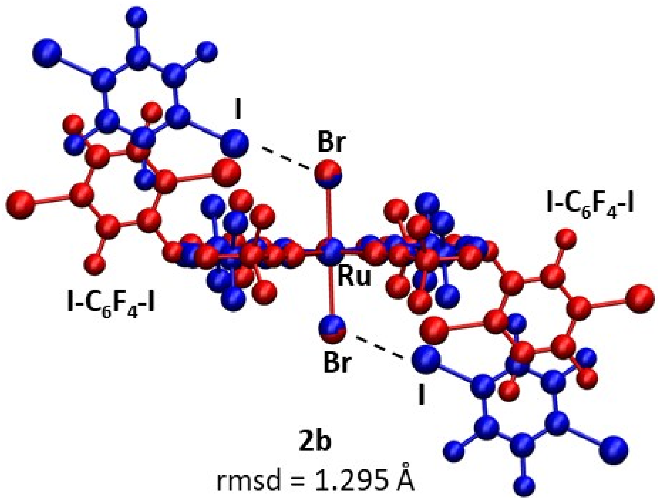
**2a**
rmsd = 0.683 Å



**3a**
rmsd = 0.759 Å



**1b**
rmsd = 1.048 Å



**2b**
rmsd = 1.295 Å

**Figure S.4:** Superimposition of optimized structures (red) and X-ray structures (blue) Root mean square deviation (rmsd)

**Table S.1:** Root mean square error (RMSE), mean square error (MAE) and Maximum in bond and bend angles differences between the optimized DFT and the experimental structures. The hydrogen atoms have not been considered in the error calculation.

| | **Distances (Å)** | | | **Bend angles (º)** | | |
|---|---|---|---|---|---|---|
| | **RMSE** | **MAE** | **Maximum** | **RMSE** | **MAE** | **Maximum** |
| **1a** | 0.039 | 0.025 | 0.144[1] | 3.6 | 2.6 | 11.0[2] |
| **2a** | 0.033 | 0.023 | 0.074 | 2.4 | 1.8 | 7.3[2] |
| **3a** | 0.052 | 0.032 | 0.162[3] | 3.4 | 2.4 | 11.0[2] |
| | | | | | | |
| **1b** | 0.022 | 0.016 | 0.071 | 2.8 | 1.5 | 15.3[4] |
| **2b** | 0.037 | 0.029 | 0.088 | 3.3 | 1.7 | 18.1[4] |
| **3b** | n.d | n.d | n.d | n.d | n.d | n.d |
| | | | | | | |
| **1c** | | | | | | |
| **2c** | | | | | | |
| **3c** | | | | | | |

[1] The maximum difference corresponds to an unreliable C-C bond in a $^{t}$Bu group of the X-Ray structure (Label 21 and 13).

[2] The C-N-C bend angles in the experimental structure are around 168º-172º instead of the expected 180º.

[3] The maximum difference corresponds to the Ru-I bond (Label 1 and 2).

[4] The Ru-X-I bend angles in the experimental structure are around 112º versus 97º in the DFT optimized. This might be due to the crystallographic packing.

n.d: not determined

RMSE stands for root mean square error defined as $RMSE = \sqrt[2]{\sum_{i=1}^{N} \left(x_{i,\,exp} - x_{i,\,DFT}\right)^2 / N}$ and MSE stands for mean square error $MSE = \sum_{i=1}^{N} \left(x_{i,\,exp} - x_{i,\,DFT}\right)^2 / N$

## 2. CRYSTAL PACKING

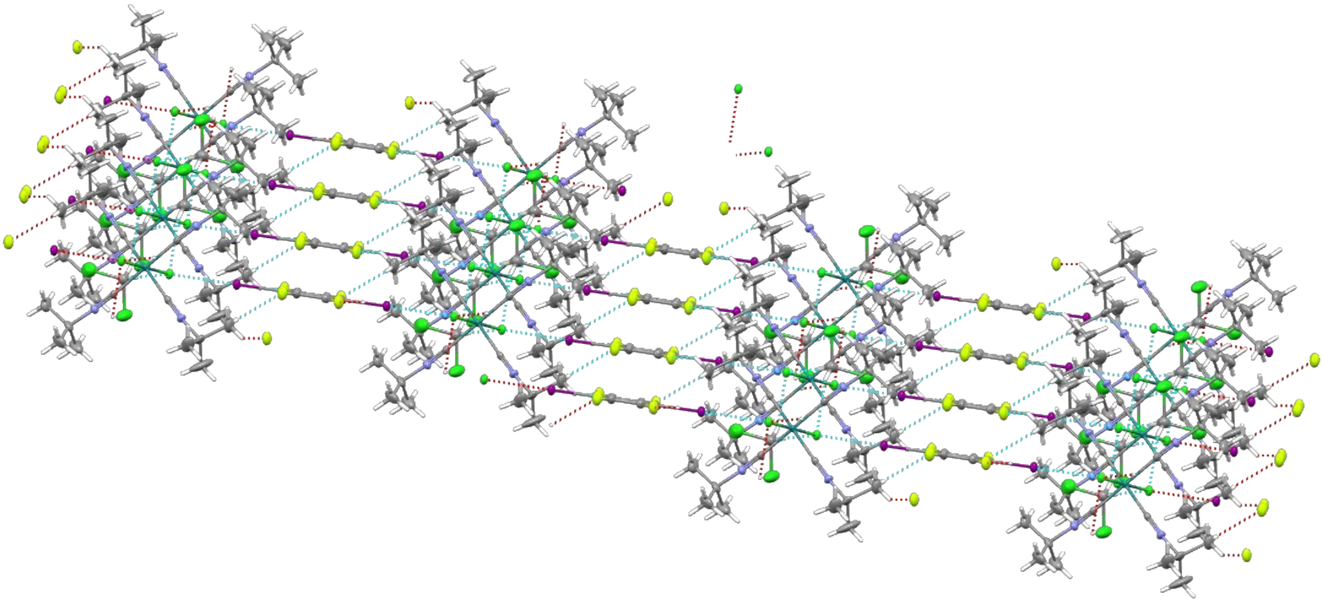


**Figure S.5:** Packing in the solid state for **1b**.

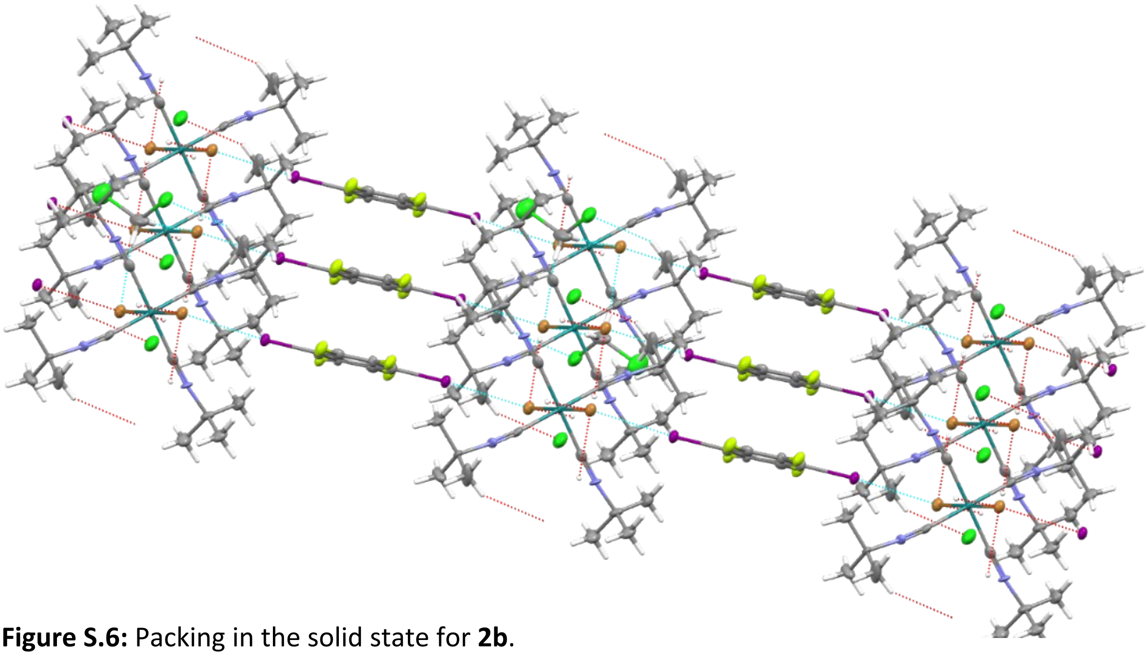


**Figure S.6:** Packing in the solid state for **2b**.