Supporting Information File

Halogen bond directionality translates tecton geometry into self-assembled architecture geometry

Marco Saccone,[a] Gabriella Cavallo,[a,b] Pierangelo Metrangolo,[a,b] Andrea Pace,[c] Ivana Pibiri,[c] Tullio Pilati,[a] Giuseppe Resnati[a,b]* and Giancarlo Terraneo[a,b]*

[a]NFMLAB-DCMIC "Giulio Natta", Politecnico di Milano, Via L. Mancinelli 7, 20131 Milan, Italy.
[b]Center for Nano Science and Technology@Polimi, Istituto Italiano di Tecnologia, Via Pascoli 70/3, 20133 Milan, Italy.
[b]Dipartimento di Scienze e Tecnologie Molecolari e Biomolecolari – Sez. Chimica Organica ''E. Paternò'' - Università degli Studi di Palermo, Viale delle Scienze Parco d'Orleans II, Ed. 17, 90128 - Palermo, Italy.

E-mail: pierangelo.metrangolo@polimi.it, giuseppe.resnati@polimi.it;
Fax: +39.02.2399.3180; Tel: +39.02.2399.3041 (P. M.), 3032 (G. R.).

S.1 Experimental

S.1.1 Materials and Methods

The starting materials were purchased from Sigma-Aldrich, Acros Organics, and Apollo Scientific, commercial HPLC-grade solvents were used without further purification. ^{1}H and ^{19}F NMR spectra were recorded at room temperature on a Bruker AV500 spectrometer, using $CDCl_3$ as solvent. ^{1}H NMR spectroscopy chemical shifts were referenced to tetramethylsilane (TMS) using the residual proton impurities of the deuterated solvents as standard reference, while ^{19}F NMR spectroscopy chemical shifts were referenced to an internal $CFCl_3$ standard. Melting points were determined on a Reichert instrument by observing the melting process through an optical microscope. ATR-FTIR spectra were obtained with a Nicolet Nexus FTIR spectrometer. The values, given in wave numbers, were rounded to 1 cm^{-1} using automatic peak assignment. The single crystal X-ray structure were determined on a Bruker Kappa Apex II diffractometer at 103 K using a fine-focus MoKα tube, λ=0.71073 Å. Data collection and reduction were performed by SMART[1] and SAINT[1] and absorption correction, based on multi-scan procedure, by SADABS[1]. The structures were solved by SIR92[2] and refined on all independent reflections by full-matrix least-squares based on F_o^2 by using SHELX-97[3]. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of **5** were assigned to idealized positions and were allowed to ride, while in **4**, their positional coordinates were allowed to refine.

S.1.2 Synthesis

3,5–Bis(pyridin–4–yl) –1,2,4–oxadiazole **1** was synthesized as previously reported[4] (m.p. 165–167 °C; lit[4] 165–167), ^{1}H NMR ($CDCl_3$) d 8.07 (m, 4H), 8.85 (d, J=5.7 Hz, 2H), 8.93 (d, J=5.5 Hz, 2H), FTIR νmax = 3045, 1603, 1579, 1543, 1520, 1487, 1414, 1365, 1338, 1313, 1289, 1209, 1142, 1092, 1062, 988, 980, 904, 863, 838, 752, 725, 714, 683 cm^{-1}.

S.1.3 Co-crystallization experiments

The 1,2,4-oxadiazole derivative **1** and the appropriate halogen bonding (XB) donor were separately dissolved in a CH_3OH-THF (1:9) solution at room temperature in a 1:1 stoichiometric ratio, under saturated conditions. The two saturated solutions containing the XB-donor and the XB-acceptor were then mixed in a clear borosilicate glass vial, which was left open in a closed cylindrical wide-mouth bottle containing paraffin oil. Solvents were allowed to slowly evaporate at room temperature for three days until the formation of good-quality single crystals occurred.

4: m.p. 172–174 °C, ^{1}H NMR ($CDCl_3$) d 8.07 (m, 4H), 8.85 (d, J=5.7 Hz, 2H), 8.93 (d, J=5.5 Hz, 2H), FTIR νmax = 3047, 1580, 1545, 1520, 1489, 1466, 1414, 1365, 1313, 1288, 1229, 1209, 1175, 1142, 1124, 1090, 1064, 1048, 989, 905, 863, 838, 816, 798, 753, 714, 692, 683, 631 cm^{-1}. Anal. Calcd for $C_{12}H_8N_4O{\cdot}C_4F_8I_2$: C, 28.34; H, 1.18; N, 8.26%. Found: C, 28.11; H, 1.31; N, 8.38%.

5: m.p. 175–176 °C, ^{1}H NMR ($CDCl_3$) d 8.07 (m, 4H), 8.85 (d, J=5.7 Hz, 2H), 8.93 (d, J=5.5 Hz, 2H), FTIR νmax = 3051, 1608, 1584, 1549, 1522, 1492, 1464, 1417, 1371, 1337, 1314, 1287, 1119, 1134, 1083, 1035, 995, 983, 933, 881, 862, 841, 804, 754, 718, 725, 685, 615 cm^{-1}. Anal. Calcd for $C_{12}H_8N_4O{\cdot}C_6F_{12}I_2$: C, 27.78; H, 1.04; N, 7.20%. Found: C, 27.95; H, 1.27; N, 7.31%.

S.1.4 NMR experiments

The experiments were carried out on diluted solutions (0.1 M in $CDCl_3$) of both complexes and starting materials. The ^{19}F data are given in Table **1**.

Table 1: ^{19}F chemical shift changes observed in solutions of **4** and **5**. $\Delta\delta = \delta_{\text{pure dioiodide}} - \delta_{\text{cocrystals}}$. For compound **2** we obtained $\delta_{(CF2CF2I)2}$ = -60.07, $\delta_{(CF2CF2I)2}$ = -113.39, for compound **3** we obtained $\delta_{(CF2CF2CF2I)2}$ = -60.24, $\delta_{(CF2CF2CF2I)2}$ = -114.27, $\delta_{(CF2CF2CF2I)2}$ = -122.13.

Compound	$\Delta\delta_{CF2I}$ (ppm)	$\Delta\delta_{CF2CF2I}$ (ppm)	$\Delta\delta_{CF2CF2CF2I}$ (ppm)
4	1.97	0.12	-
5	2.03	0.16	0.05

S.1.5 Crystallographic information

Crystallographic data and structure refinement parameters for co-crystals **4** and **5**

	4	**5**
Chemical Formula	$C_{16}H_8F_8I_2N_4O$	$C_{18}H_8F_{12}I_2N_4O$
Formula weight	678.06	778.08
Temperature K	103(2)	103(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
***a* (Å)**	8.0406(12)	13.1606(12)
***b* (Å)**	22.942(3)	5.5451(6)
***c* (Å)**	11.6153(15)	31.302(3)
α (°)	90.00	90.00
β (°)	108.400(12)	91.877(10)
γ (°)	90.00	90.00
Volume (Å^3)	2033.1(5)	2283.1(4)
Z	4	4
Crystal size	0.04 x 0.22 x 0.35	0.10 x 0.35 x 0.42
Crystal description and colour	Table, colourless	Prism, colourless
Density (g cm^{-3})	2.215	2.264
μ (mm^{-1})	3.182	2.873
***F* (000)**	1272	1464
ABS T_{min}, T_{max}	0.3687, 0.5233	0.4482, 0.7470
$\theta_{min,\ max}$ (°)	2.73, 34.74	2.45, 35.61
No. of reflections measured	29563	139794
No. of independent reflections	7828	9494
R_{int}	0.0281	0.0736
No of parameters	305	460
No of restraints	0	262
Final R_1 values ($I > 2\sigma(I)$),	0.0242	0.0327
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0532	0.0821
Final R_1 values (all data)	0.0340	0.0375
Final $wR(F^2)$ values (all data)	0.0573	0.0841
G.o.F	1.034	1.122
$\Delta\rho_{max,\ min}$ (eÅ^{-3})	1.00, -0.53	1.04, -1.49
CCDC No.	915396	915397

(1) *SMART*, *SAINT*, and *SADABS*, Bruker Analytical X-ray Systems; Bruker AXS Inc.: Madison, WI, 1999.

(2) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.

(3) Sheldrick, G. M. *SHELXL-97*, *Program for the Refinement of Crystal Structures*; University of Gottingen: Germany, 1997.

(4) I. Pibiri, A. Pace, S. Buscemi, V. Causin, F. Rastrelli, G. Saielli, *Phys. Chem. Chem. Phys.*, 2012, **14**, 14306−14314.

3,5–Bis(pyridin–4–yl)-1,2,4-oxadiazole / 1,4-Diiodoperfluorobutane (4).

checkCIF/PLATON (standard)

Structure factors have been supplied for datablock(s) ms050

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report

Datablock: ms050

Bond precision: C-C = 0.0029 A Wavelength=0.71073
Cell: a=8.0406(12) b=22.942(3) c=11.6153(15)
alpha=90 beta=108.400(12) gamma=90
Temperature: 103 K

	Calculated	Reported
Volume	2033.1(5)	2033.1(5)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C12 H8 N4 O, C4 F8 I2	C12 H8 N4 O, C4 F8 I2
Sum formula	C16 H8 F8 I2 N4 O	C16 H8 F8 I2 N4 O
Mr	678.06	678.06
Dx,g cm-3	2.215	2.215
Z	4	4
Mu (mm-1)	3.182	3.182
F000	1272.0	1272.0
F000'	1269.03	
h,k,lmax	12,36,18	12,36,18
Nref	8776	7828
Tmin,Tmax	0.436,0.880	0.369,0.523
Tmin'	0.325	

Correction method= MULTI-SCAN
Data completeness= 0.892 Theta(max)= 34.740
R(reflections)= 0.0242(6584) wR2(reflections)= 0.0573(7828)
S = 1.034 Npar= 305

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT431_ALERT_2_A Short Inter HL..A Contact I1 .. N3 .. 2.77 Ang.
PLAT431_ALERT_2_A Short Inter HL..A Contact I2 .. N4 .. 2.82 Ang.

Alert level G

PLAT128_ALERT_4_G Alternate Setting of Space-group P21/c P21/n
PLAT164_ALERT_4_G Nr. of Refined C-H H-Atoms in Heavy-Atom Struct. 8
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 6 Perc.

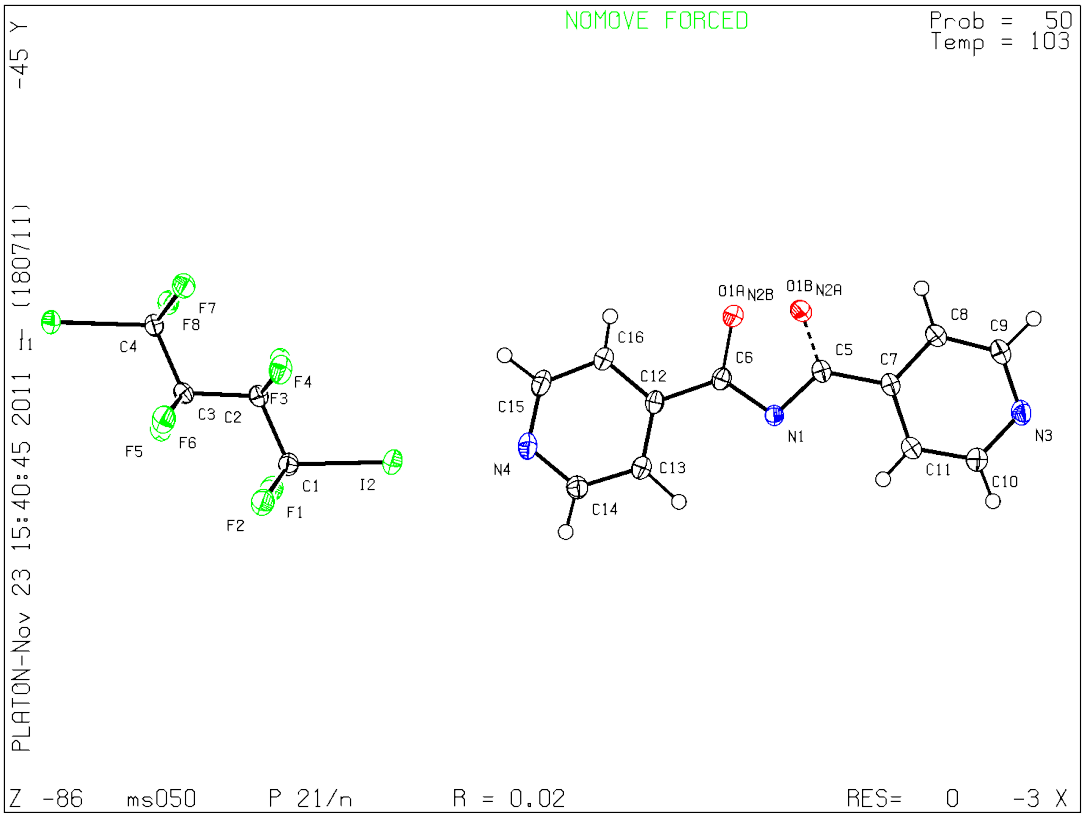
---

2 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
0 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
3 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

PLATON version of 18/07/2011; check.def file version of 04/07/2011

Datablock ms050 - ellipsoid plot



3,5–Bis(pyridin–4–yl)-1,2,4-oxadiazole / 1,6-Diiodoperfluorohexane (5).

checkCIF/PLATON (standard)

Structure factors have been supplied for datablock(s) ms051lt

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report

Datablock: ms051lt

Bond precision: C-C = 0.0030 A Wavelength=0.71073
Cell: a=13.1606(12) b=5.5451(6) c=31.302(3)
alpha=90 beta=91.877(10) gamma=90
Temperature: 103 K

	Calculated	Reported
Volume	2283.1(4)	2283.1(4)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C6 F12 I2, C12 H8 N4 O	C12 H8 N4 O, C6 F12 I2
Sum formula	C18 H8 F12 I2 N4 O	C18 H8 F12 I2 N4 O
Mr	778.08	778.08
Dx,g cm-3	2.264	2.264
Z	4	4
Mu (mm-1)	2.873	2.873
F000	1464.0	1464.0
F000'	1461.31	
h,k,lmax	21,9,51	21,8,51
Nref	10502	9494
Tmin,Tmax	0.311,0.750	0.448,0.747
Tmin'	0.288	

Correction method= MULTI-SCAN
Data completeness= 0.904 Theta(max)= 35.610
R(reflections)= 0.0327(8615) wR2(reflections)= 0.0841(9494)
S = 1.122 Npar= 460

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT220_ALERT_2_B Large Non-Solvent F Ueq(max)/Ueq(min) ... 4.1 Ratio

Alert level C

PLAT215_ALERT_3_C Disordered F12B has ADP max/min Ratio 3.4
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor 2.3

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 37
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites 24
PLAT022_ALERT_3_G Ratio Unique / Expected Reflections (too) Low .. 0.904
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ ?
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for C18B

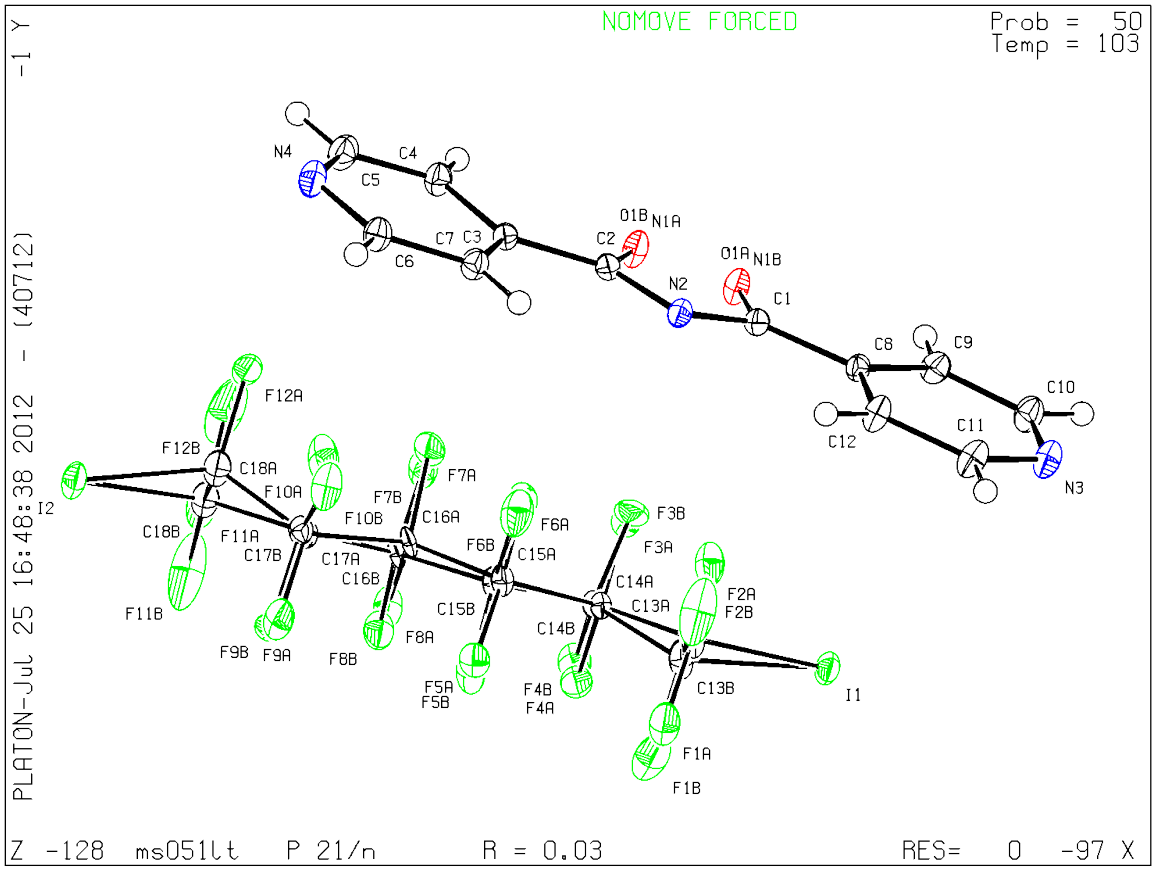
```
PLAT301_ALERT_3_G Note: Main Residue   Disorder ...................          54
Perc.
PLAT431_ALERT_2_G Short Inter HL..A  Contact   I1      ..   N3       .       2.86
Ang.
PLAT431_ALERT_2_G Short Inter HL..A  Contact   I2      ..   N4       .       2.88
Ang.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #           1
               C13B -I1   -C13A    1.555   1.555   1.555              9.70 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #           2
               C18B -I2   -C18A    1.555   1.555   1.555             12.59 Deg.
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms ....           !
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints .......        262
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   1 ALERT level B = A potentially serious problem, consider carefully
   2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  12 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   7 ALERT type 2 Indicator that the structure model may be wrong or deficient
   4 ALERT type 3 Indicator that the structure quality may be low
   2 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

PLATON version of 04/07/2012; check.def file version of 28/06/2012

Datablock ms051lt - ellipsoid plot



Electronic Supplementary Material (ESI) for CrystEngComm