

## Supporting Information

### Dissecting the packing forces in mixed perfluorocarbon/aromatic co-crystals

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## Materials and methods

The starting materials were purchased from Sigma-Aldrich, Acros Organics, Apollo Scientific and used as received. The synthesis of the bis(pyridil)-1,2,4-oxadiazole used for preparing the co-crystal **1** was performed according to literature procedures.<sup>1</sup> The melting point of **1** was determined on a Reichert instrument by observing the melting process through an optical microscope. The single crystal X-ray structure was determined on a Bruker Kappa Apex II diffractometer at 103K using a fine-focus MoK $\alpha$  tube,  $\lambda=0.71073$  Å. Data collection and reduction were performed by SMART<sup>2</sup> and SAINT<sup>2</sup> and absorption correction, based on multi-scan procedure, by SADABS.<sup>2</sup> The structure was solved by SIR92<sup>3</sup> and refined on all independent reflections by full-matrix least-squares based on  $F_o^2$  by using SHELX-97.<sup>4</sup> All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were allowed to ride. The structure was registered in the Cambridge Structural Database (CCDC number 2077920). Calculations were performed on a laptop equipped with an Intel® Core™ i7-8750H Processor, 32 GB RAM and the *CrystalExplorer* program. The model energies were calculated using the option “accurate”. A cluster of molecules within a radius of 4 Å (the default is 3.8 Å, but we recommend 4 Å for molecules including iodine) from the reference molecule was considered.

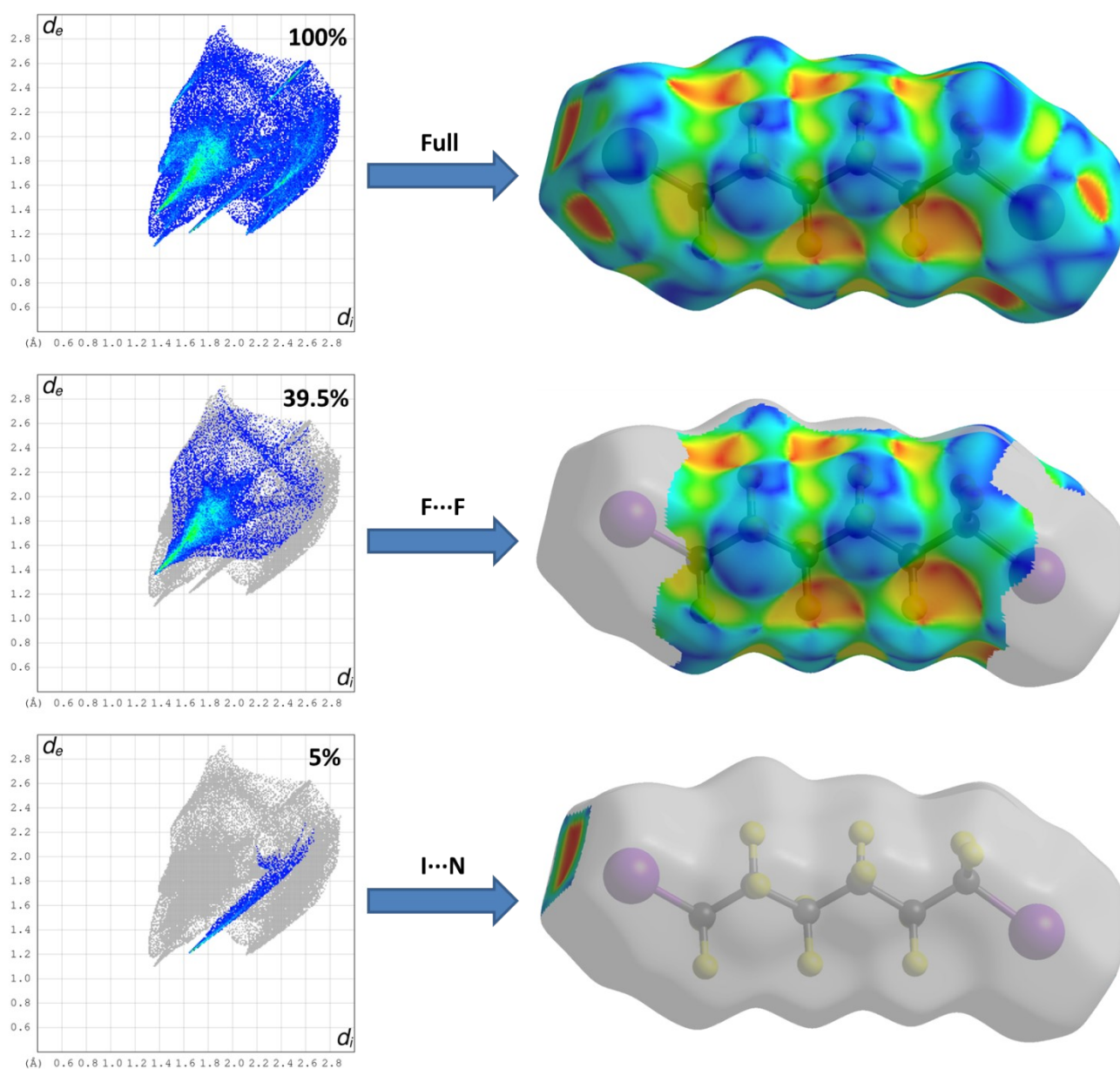
See [http://130.95.176.70/wiki/index.php/Intermolecular\\_Interaction\\_Energies](http://130.95.176.70/wiki/index.php/Intermolecular_Interaction_Energies) for further details.

## Co-crystallization experiments

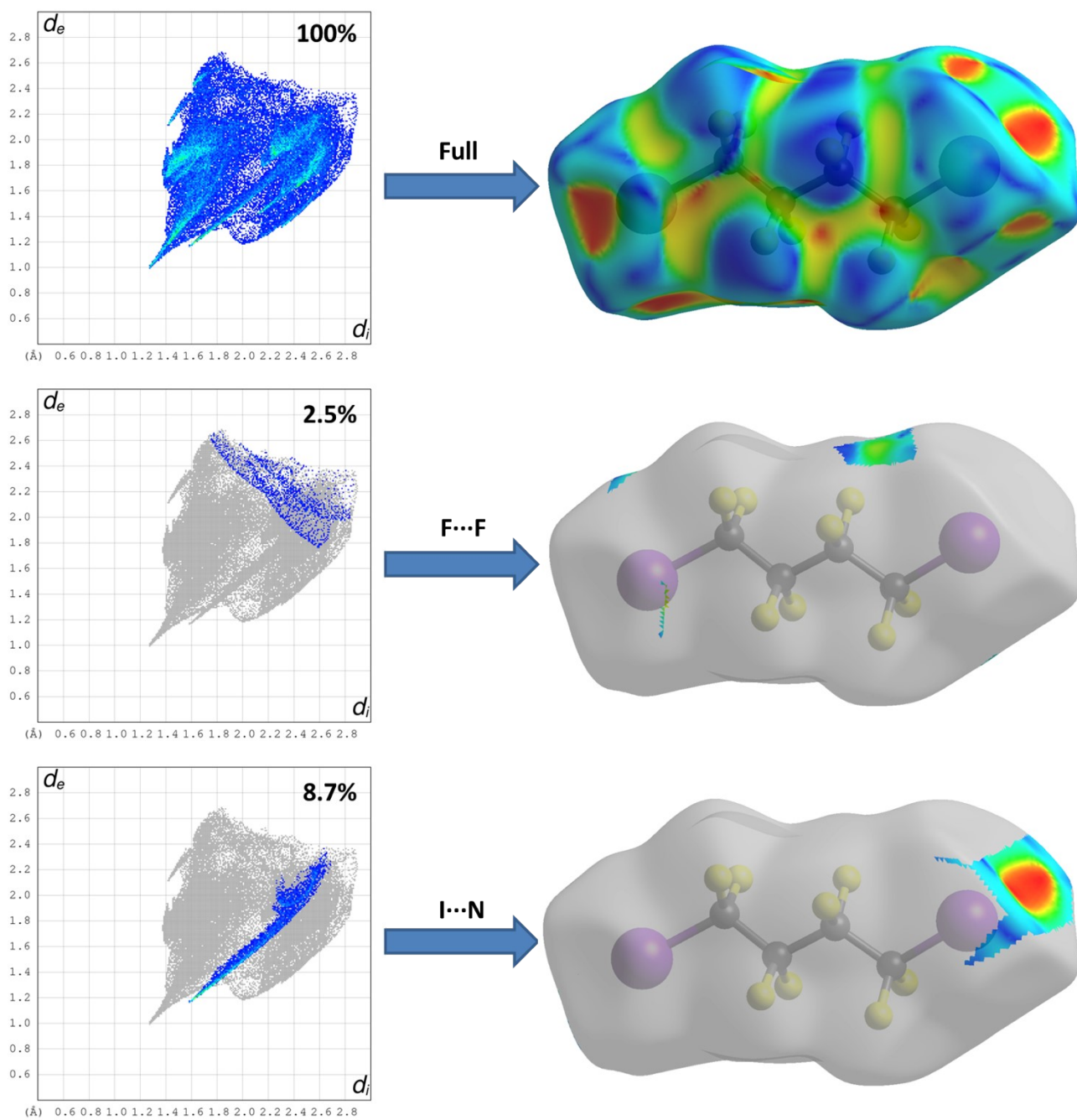
The 1,2,4-oxadiazole derivative and the 1-iodoperfluorodecane were separately dissolved in a CH<sub>3</sub>OH-THF (1:9) solution at room temperature in a 1:2 stoichiometric ratio, under saturated conditions. The two saturated solutions containing the halogen bonding donor and the halogen bonding acceptor 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 for two weeks at 4 °C (fridge) until the formation of good-quality single crystals occurred.

**1**: m.p. 178–180 °C, Anal. Calcd for C<sub>12</sub>H<sub>8</sub>N<sub>4</sub>O\*2(C<sub>10</sub>F<sub>21</sub>I): C, 25.35; H, 0.53; N, 3.70%. Found: C, 25.71; H, 0.58; N, 3.85%

## Hirshfeld surface analysis



**Figure S1:** Fingerprint plots of the  $\alpha,\omega$ -diiodoperfluorohexane, component of **2**, full and resolved into different interactions showing the percentages of contacts contributing to the total Hirshfeld surface area of the molecule. Surfaces in the right-hand columns highlight the relevant surface patches associated with the specific contacts in the total Hirshfeld surface area of the molecule.



**Figure S2:** Fingerprint plots of the  $\alpha,\omega$ -diiodoperfluorobutane, component of **3**, full and resolved into different interactions showing the percentages of contacts contributing to the total Hirshfeld surface area of the molecule. Surfaces in the right-hand columns highlight the relevant surface patches associated with the specific contacts in the total Hirshfeld surface area of the molecule.

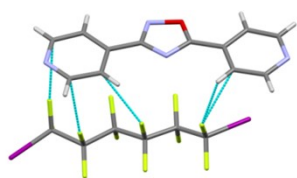
## Details on Structure Determinants

Below we give a chart which explains the information given in the Table 1, 2 and 3.

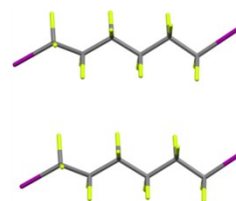
	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
1	2	3	4	5	6	7	8	9	10

- 1) Structure Determinant color, as provided in **Fig. 6-9**
- 2) The number of pairs, N, in the graphics window with that energy.
- 3) Symmetry operator joining the two molecules in the pair.
- 4) Distance between centers of mass of both molecules (Å).
- 5) Level of theory at which the electron density is computed: B3LYP/6-31G(d,p) here.
- 6) Electrostatic contribution (kJ/mol).
- 7) Polarization contribution (kJ/mol).
- 8) Dispersion contribution (kJ/mol).
- 9) Repulsion contribution (kJ/mol).
- 10) Total energy (kJ/mol): This is the *sum of scaled components* (using the scale factors appropriate to the model as given below), but the *separate components are not scaled*.

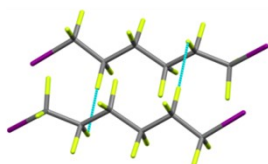
Energy Model	k_ele	k_pol	k_disp	k_rep
CE-B3LYP. . . B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618



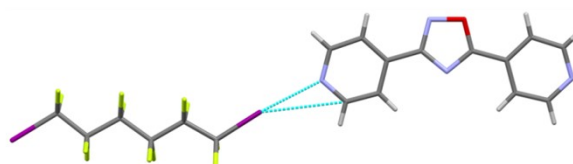
Structure Determinant 1: 35.3 kJ/mol



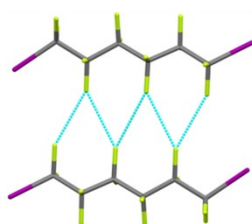
Structure Determinant 2: 21.5 kJ/mol



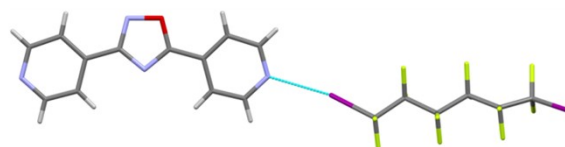
Structure Determinant 3: 20.6 kJ/mol



Structure Determinant 4: 19.1 kJ/mol

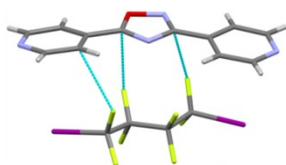


Structure Determinant 5: 16.9 kJ/mol

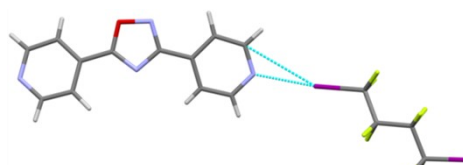


Structure Determinant 6: 16 kJ/mol

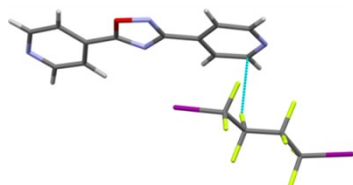
**Figure S3:** Supramolecular hierarchy of the six most stabilizing interactions in the co-crystals **2** as provided by *CrystalExplorer*. The diiodoperfluorohexane molecule is chosen as the reference. Blue lines represent short intermolecular contacts below the sum of the van der Waals radii of the respective atoms. Color chart: grey = C, white = H, red = O, blue = N, and yellow = F, and purple = I.



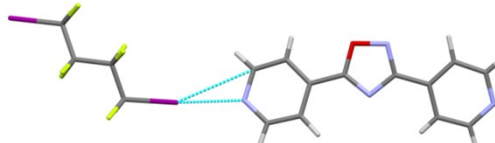
Structure Determinant 1: 33.9 kJ/mol



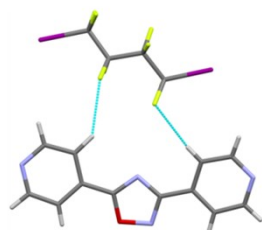
Structure Determinant 2: 18.7 kJ/mol



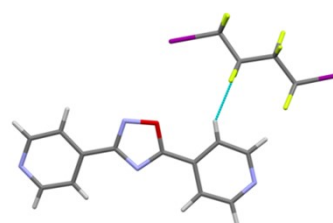
Structure Determinant 3: 16.9 kJ/mol



Structure Determinant 4: 16 kJ/mol

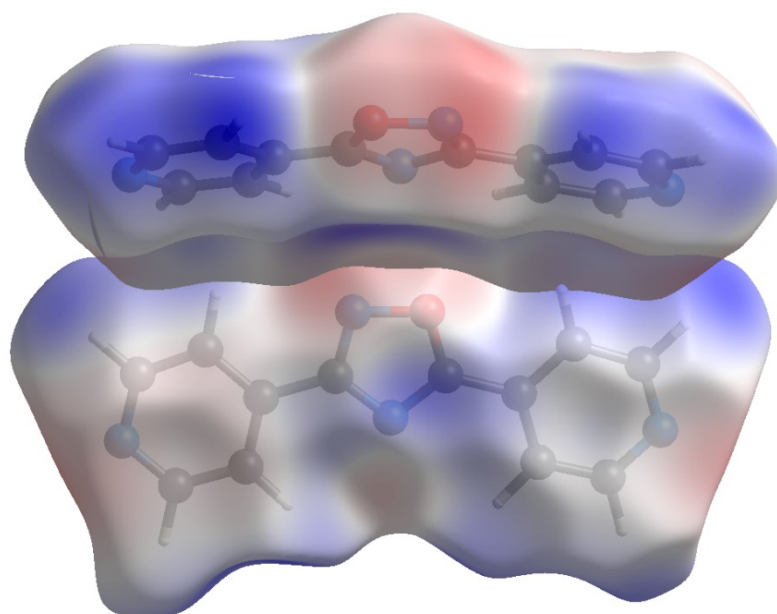


Structure Determinant 5: 15 kJ/mol

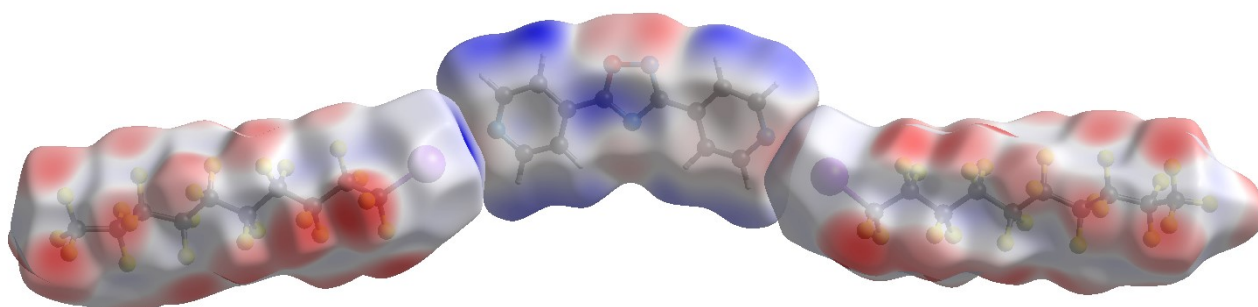


Structure Determinant 6: 14 kJ/mol

**Figure S4:** Supramolecular hierarchy of the six most stabilizing interactions in the co-crystals **2** as provided by *CrystalExplorer*. The diiodoperfluorobutane molecule is chosen as the reference. Blue lines represent short intermolecular contacts below the sum of the van der Waals radii of the respective atoms. Color chart: grey = C, white = H, red = O, blue = N, and yellow = F, and purple = I.



**Figure S5:** Molecular electrostatic potential mapped on the Hirshfeld surface for the Structure Determinant 1 of **1** (Blue more positive, red more negative).



**Figure S6:** Molecular electrostatic potential mapped on the Hirshfeld surface of **1** (Blue more positive, red more negative).

**ESI Table 1** Single-crystal X-ray data collections, structure solutions, and refinements of single crystals of **1**

	<b>1</b>
Chemical formula	C <sub>12</sub> H <sub>8</sub> N <sub>4</sub> O, 2(C <sub>10</sub> F <sub>21</sub> I)
<i>M</i> <sub>r</sub>	1516.22
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>
Temperature (K)	103
<i>a</i> , <i>b</i> , <i>c</i> (Å)	28.890(4), 5.5858(8), 28.523(3)
$\alpha$ , $\beta$ , $\gamma$ (°)	90, 104.40(2), 90
<i>V</i> (Å <sup>3</sup> )	4458.3(10)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	1.63
Crystal size (mm)	0.04 × 0.08 × 0.38
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.675, 0.779
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	35610, 11349, 7140
<i>R</i> <sub>int</sub>	0.051
(sin $\theta/\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.676
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.050, 0.111, 1.04
No. of reflections	11349
No. of parameters	1237
No. of restraints	4653
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.911, -1.01
CCDC number	2077920

Refinement details: The iodoperfluorodecane units in **1** show a severe degree of disorder and only one I-CF<sub>2</sub>-CF<sub>2</sub>- unit of one XB donor has been refined without applying any disorder model. The CF<sub>2</sub> and CF<sub>3</sub> moieties have been split over two positions and their populations have been refined. Restraints (SADI and SIMU) on bond lengths and angles as well as on displacement parameters



have been used. The adjacent O- and N-atom of the 1,2,4-oxadiazole ring show positional disorder order, during the refinement they have been treated accordingly.

## References

1. I. Pibiri, A. Pace, S. Buscemi, V. Causin, F. Rastrelli and G. Saielli, *Phys. Chem. Chem. Phys.*, 2012, **14**, 14306–14314.
2. SMART, SAINT, and SADABS, Bruker Analytical X-ray Systems; Bruker AXS Inc.: Madison, WI, 1999.
3. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.
4. Sheldrick, G. M. SHELXL-97, Program for the Refinement of Crystal Structures; University of Gottingen: Germany, 1997.