Supporting Information

Halogen bonding in Fluorine: Experimental charge density study on intermolecular F···F and F···S donor-acceptor contacts

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S-1: Experimental section

Crystallization: The synthesized sample was crystallized in a saturated solution of ethanol. Good quality single crystals were chosen using a polarizing microscope and affixed to a Hampton Research Cryoloop using Paratone-N oil.

Data collection and structure refinement details

A crystal of dimensions 0.5 X 0.2 X 0.2 mm, was cooled to 110 K with a liquid nitrogen stream using an Oxford Instruments Cryojet-HT nitrogen gas-stream cooling device. X-ray diffraction data was collected onan Oxford Xcalibur (Mova) diffractometer[1] equipped with an EOS CCD detector using *MoKα* radiation (λ= 0.71073 Å). The crystal to detector distance was fixed at 45 mm and the scan width ($\Delta\omega$) was 1° per frame during the data collection. The data collection strategy was chosen in such a way to yield a high resolution X-ray data set (d= 0.45 Å), with a high redundancy (~13) and completeness of 100%. Cell refinement, data integration and reduction were carried out using the program CrysAlisPro.[1] Face indexing was done to facilitate accurate numerical absorption correction. Sorting, scaling, and merging of the data sets were carried out using the program SORTAV.[2] The crystal structure was solved by direct method using SHELXS97and refined based on the spherical-atom approximation (based on F^2) using SHELXL97[3]included in the WinGX package suite.[4] The hydrogen atom was located on the difference Fourier map and its position and isotropic thermal parameters were allowed to refine in the spherical atom model.

Multipole Modeling. The charge density modeling and multipolar aspherical atom refinements were performed based on the Hansen and Coppens multipole formalism using XD2006.[5]The function, Σw2 was minimized for all reflections with I >3σ(I). Weights (w) were taken as $1/\sigma^2(F_o^2)$ and convergence criterion of the refinement was set to a maximal shift/esd $<10^{-10}$. Su-Coppens-Macchi wave functions[6, 7] were used for the core and valence scattering factors of all the atoms. The scale factor was refined against the whole resolution range of diffraction data in the first refinement step. The scatter plot of the variation of F_{obs} with F_{cal} is indicative of the quality of the data set after scaling. The positional and anisotropic displacement parameters of the non-hydrogen atoms were refined using reflection data with $\sin\theta/\lambda > 0.7$ Å^{-1}. In the next step of refinement, the position and displacement parameters of the non-hydrogen atoms were fixed to the refined values. The C—H bond length was constrained to the values obtained from neutron diffraction experiments reported in literature.[8] The isotropic displacement parameters of the H-atom was refined initially with reflection data $\sin\theta/\lambda <0.7$ Å^{-1}. Further, the converged model was used to calculate anisotropic displacement parameters of H-atom using the SHADE2 analysis.[9, 10] ADP value of the H-atom obtained from SHADE2 analysis was kept fixed during the subsequent multipole refinements.[11] Further scale, positional, and anisotropic displacement parameters, P_{val}, P_{lm}, κ and κ′on non-hydrogen atoms were refined in a stepwise manner, until the convergence criterion was reached. Separate κ and κ′ were used to define different non-H atom type based chemical environments with a separate value for the lone hydrogen atom. Local symmetry constraints were used in the multipole refinements on all atoms except sulfur. The multipole expansion was carried out upto hexadecapole level (l = 4) for only sulfur, where as for other non-hydrogen atoms it was truncated at the octupole level (l = 3). For the H atom, only monopole, bond directed dipole (d_z) and quadrupole (q_{3z^2-1}) components were refined during the multipole refinements. Towards the end a complete unrestricted refinement of the multipoles on all non-hydrogen atoms was done, which was taken as the final model. In addition the anharmonicity on sulfur atom was treated by refining the Gram-Charlier cumulative of 3rd order for only sulfur for high angle reflections ($\sin \theta/\lambda > 0.7$ Å^{-1}).[12] An isotropic, type I extinction correction with a Lorentzian mosaic distribution[13, 14] was included in the refinement to improve the scaling of reflections and improve the residuals. The quantitative analysis of the electron density topology and related properties was performed using the XDPROP and TOPXD[15] module of XD software suite.[5] Crystallographic refinement details of both spherical and multipolar model are summarized in Table 1.

Computational details. Positional parameters obtained from the experimental charge density model have been used for the single point periodic quantum mechanical calculations at TZVP level[16, 17] using CRYSTAL09 package.[18] The shrinking factors (IS1, IS2, and IS3) and the reciprocal lattice vectors were set to 4 (with 30 k-points in irreducible Brillouin zone). The bielectronic Coulomb and exchange series values for the truncation parameter were set as ITOL1_ITOL4 = 8 and ITOL5 = 17, respectively, for the calculations. The level shifter was set to 0.7 Hartree/cycle. An SCF convergence limit of the order of 10^{-6} Hartree was used.

In the static model, atomic thermal displacement parameters for all atoms were set to zero. Structure factors were calculated for a resolution of 1.08Å^{-1}, which were used for the theoretical multipolar model. Refinements and analysis for the theoretical charge density model were performed using the XD software package following the same methodology used for the experimental charge density modeling.

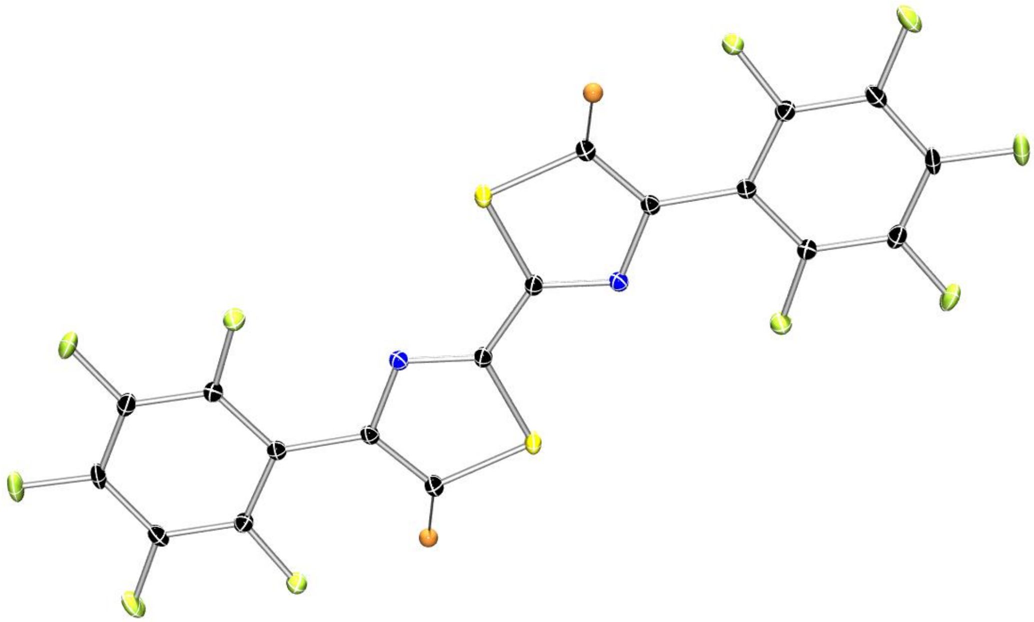


Figure 1: ORTEP diagram of the molecule

Table 2: Crystallographic table of the experimental structure

Compound	**1**
CCDC No.	936445
Molecular formula	$C_{18}H_2N_2F_{10}S_2$
Formula weight	500.36
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	4.9442(1)
b (Å)	9.9369(1)
c (Å)	16.7881(1)
α **(°)**	90
β **(°)**	90.584(1)
γ **(°)**	90
V **(Å^3)**	824.27(2)
Z	4
ρ_{calc} **(g/cm^3)**	2.016
F(000)	492
μ**. (mm^{-1})**	0.44
T (K)	110(2)
λ **(Å)**	0.71073
$(\sin\theta/\lambda)_{max}$ **(Å^{-1})**	1.08
Reflns. collected	111839
Unique reflns.	8687

Completeness (%)	99.9
Redundancy	12.9
R_{int}	0.042
Spherical atom refinement	
R_{obs}	0.041
$wR_2 (F^2)$	0.082
Goodness-of-fit	1.06
Multipole refinements	
Reflns. used [I> 3σ(I)]	7649
No of parameters	234
R (F)	0.019
$wR_2 (F)$	0.03
Goodness-of-fit	1.225
$\Delta\rho_{min, max}(eÅ^{-3})$	-0.24, 0.20

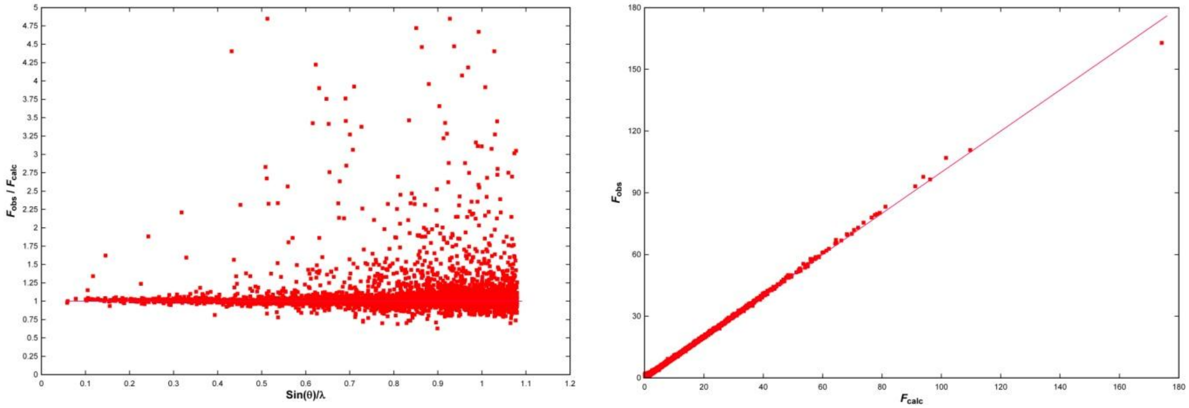


Figure 2: (a) Variation of F_{obs}/F_{cal} with (sinθ)/λ (b) Scatter plot depicting the variation of Fobs with Fcal for 1

Table 3: Topological parameters of intermolecular interactions

Interaction	R_{ij}(Å)	d_1 (Å)	d_2 (Å)	ρ ($eÅ^{-3}$)	$\nabla^2\rho$ ($eÅ^{-5}$)	ε	**G** ($kJmol^{-1}$ $bohr^{-3}$)	**V** ($kJmol^{-1}$ $bohr^{-3}$)	$\frac{\|V\|}{G}$
C9-F1···PPF3	2.6627	1.333	1.3297	0.06	1.3	0	26.86	-17.85	0.66
TZVP	*2.6627*	*1.3283*	*1.3344*	*0.06*	*1.3*	*0*	*26.86*	*-17.85*	*0.66*
C8-F2···F4	2.824	1.4146	1.4094	0.04	0.9	0.01	16.93	-10.65	0.63
TZVP	*2.824*	*1.4147*	*1.4093*	*0.04*	*0.9*	*0.01*	*16.93*	*-10.65*	*0.63*
C7-F3···PS1	3.2858	1.8291	1.4568	0.04	0.5	0.02	10.92	-7.21	0.66
TZVP	*3.2857*	*1.8336*	*1.4522*	*0.04*	*0.6*	*0.03*	*12.35*	*-8.36*	*0.68*
C6-F4···PPF5	2.9669	1.4884	1.4784	0.03	0.6	0.05	11.46	-6.94	0.61
TZVP	*2.967*	*1.4909*	*1.476*	*0.03*	*0.6*	*0.06*	*11.80*	*-7.25*	*0.61*
C2···C4	3.4817	1.7042	1.7775	0.04	0.5	0.75	9.82	-7.19	0.73

TZVP	*3.3658*	*1.7135*	*1.6524*	*0.03*	*0.3*	*0.36*	*6.35*	*-4.53*	*0.71*
C3···PC6	3.2944	1.6187	1.6757	0.05	0.5	0.08	11.76	-8.84	0.75
TZVP	*3.256*	*1.6548*	*1.6011*	*0.04*	*0.4*	*0.31*	*8.72*	*-6.55*	*0.75*
F3···C9	3.0927	1.4749	1.6178	0.04	0.6	0.54	12.75	-8.75	0.69
TZVP	*3.0863*	*1.508*	*1.5782*	*0.03*	*0.5*	*0.27*	*9.98*	*-6.34*	*0.64*

Table 4: Topological parameters of inter-molecular interactions from (a) Experiment and (b) Theory

(a)

	R_{ij}(Å)	**d_1 (Å)**	**d_2 (Å)**	**ρ (eÅ^{-3})**	**$\nabla^2\rho$ (eÅ^{-5})**	**λ_1**	**λ_2**	**λ_3**	**ε**
S1-C1	1.7079	0.9074	0.8006	1.44	-6.0	-8.7	-7.3	10.0	0.19
S1-C2	1.7264	0.8786	0.8478	1.38	-4.5	-8.1	-5.9	9.5	0.38
F1-C9	1.3316	0.8276	0.504	1.98	-17.6	-16.3	-14.4	13.1	0.13
F2-C8	1.3346	0.8208	0.5138	1.98	-18.4	-16.1	-15.5	13.1	0.04
F3-C7	1.3267	0.8432	0.4834	1.93	-14.8	-15.5	-14.0	14.7	0.10
F4-C6	1.3292	0.8341	0.4951	1.95	-16.8	-16.2	-14.6	14.0	0.11
F5-C5	1.3369	0.8458	0.4912	1.88	-15.0	-14.9	-13.7	13.5	0.09
N1-C2	1.3071	0.7608	0.5463	2.58	-28.5	-21.4	-18.0	10.9	0.19
N1-C3	1.3777	0.7804	0.5973	2.23	-18.8	-17.1	-14.9	13.2	0.15
C1-C3	1.3811	0.6931	0.6880	2.17	-19.8	-16.5	-12.5	9.1	0.32
C1-H1	1.0829	0.6833	0.3996	1.97	-21.7	-18.7	-17.0	14.0	0.10
C3-C4	1.4747	0.7140	0.7607	1.79	-13.3	-13.3	-10.8	10.8	0.24
C4-C5	1.4019	0.6707	0.7312	2.14	-19.2	-17.0	-13.0	10.8	0.30
C4-C9	1.4040	0.6788	0.7252	2.14	-19.3	-17.1	-13.0	10.8	0.32
C5-C6	1.3872	0.6931	0.6941	2.24	-22.0	-18.7	-13.3	10.1	0.40
C6-C7	1.3876	0.7161	0.6716	2.22	-22.6	-18.5	-13.4	9.4	0.39
C7-C8	1.3853	0.6725	0.7129	2.27	-23.7	-19.4	-13.6	9.3	0.42
C8-C9	1.3875	0.7102	0.6773	2.27	-23.3	-19.5	-13.7	9.9	0.43
C2-C2	1.4524	0.7262	0.7262	1.95	-17.4	-15.4	-12.2	10.3	0.26

(b)

	R_{ij}(Å)	**d_1 (Å)**	**d_2 (Å)**	**ρ ($eÅ^{-3}$)**	**$\nabla^2\rho$ ($eÅ^{-5}$)**	**λ_1**	**λ_2**	**λ_3**	**ε**
S1-C1	1.7077	0.9054	1.42	-5.5	0.8023	-8.46	-7.01	9.93	0.21
S1-C2	1.726	0.9003	1.39	-5.6	0.8257	-8.44	-6.78	9.61	0.24
F1-C9	1.3317	0.8104	1.96	-15.4	0.5213	-15.76	-14.51	14.87	0.09
F2-C8	1.3346	0.8	1.91	-11.9	0.5346	-15.13	-13.4	16.66	0.13
F3-C7	1.3267	0.8054	1.96	-13.6	0.5213	-15.25	-14.09	15.73	0.08
F4-C6	1.3293	0.7985	1.99	-14.9	0.5308	-16.35	-14.88	16.29	0.1
F5-C5	1.3369	0.8111	1.91	-13.4	0.5258	-14.51	-14.18	15.3	0.02
N1-C2	1.3068	0.7343	2.55	-24.7	0.5726	-21.11	-18.27	14.7	0.16
N1-C3	1.3777	0.7688	2.11	-16.3	0.6089	-16.24	-14.66	14.65	0.11
C1-C3	1.3816	0.6939	2.17	-19.0	0.6877	-16.79	-12.94	10.74	0.3
C1-H1	1.0828	0.6773	1.92	-21.4	0.4055	-18.46	-16.91	14.01	0.09
C3-C4	1.4747	0.748	1.81	-13.1	0.7267	-13.36	-11.17	11.43	0.2
C4-C5	1.4019	0.6686	2.07	-16.4	0.7333	-15.74	-12.36	11.69	0.27
C4-C9	1.4042	0.6698	2.05	-16.9	0.7343	-15.84	-12.44	11.42	0.27
C5-C6	1.3873	0.687	2.18	-19.9	0.7003	-18.36	-13.22	11.67	0.39
C6-C7	1.3876	0.6937	2.19	-20.3	0.6939	-18.35	-13.66	11.75	0.34
C7-C8	1.3853	0.692	2.16	-18.2	0.6932	-17.83	-12.47	12.09	0.43
C8-C9	1.3875	0.6873	2.23	-21.0	0.7002	-18.84	-13.86	11.68	0.36
C2-C2	1.4524	0.7262	1.89	-14.4	0.7262	-15	-11.29	11.86	0.33

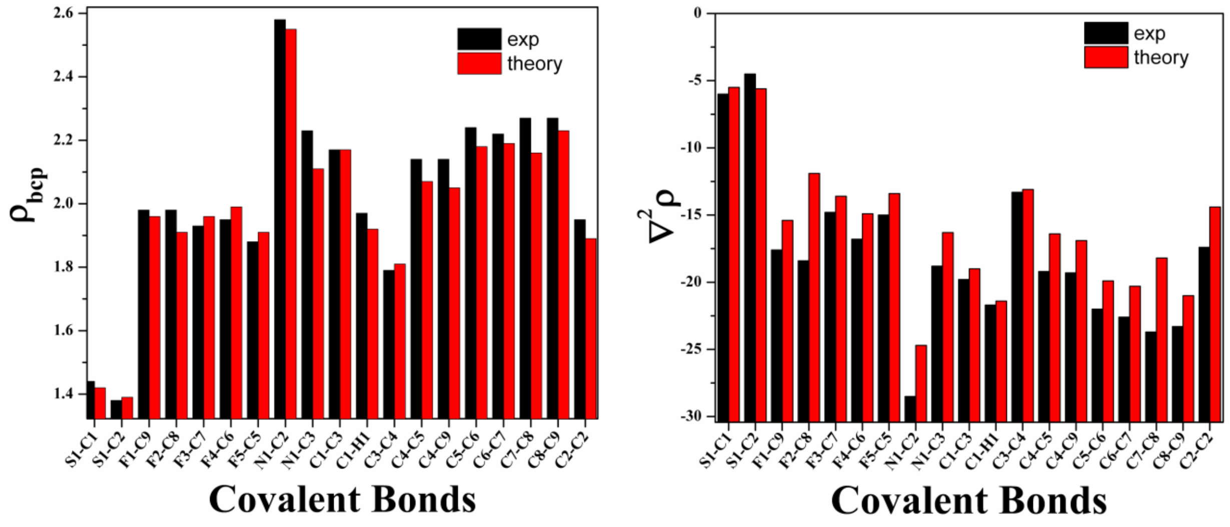


Figure 3: Comparison of intramolecular topological parameters

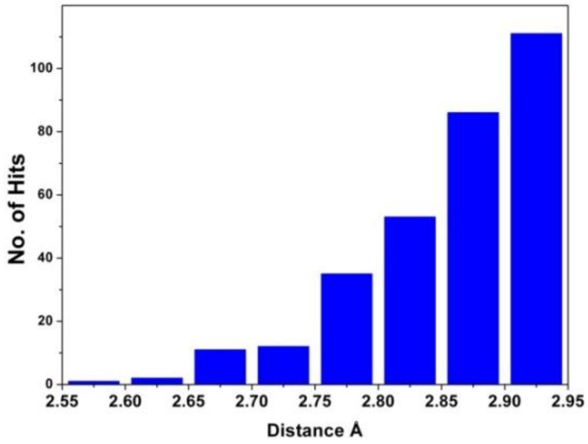


Figure 4: Histogram of all structures with F···F contacts devoid of X-H···F, C-H···O, C···C &C···F contacts

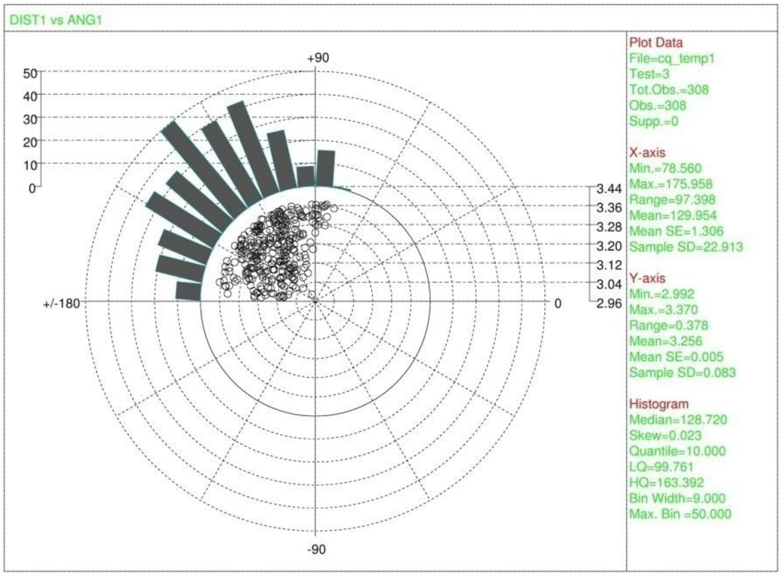
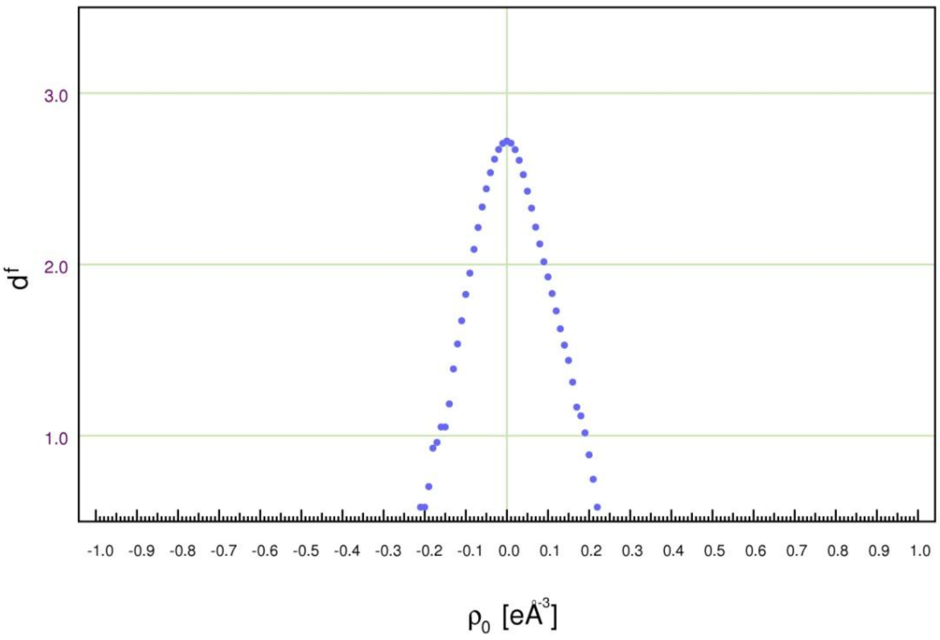
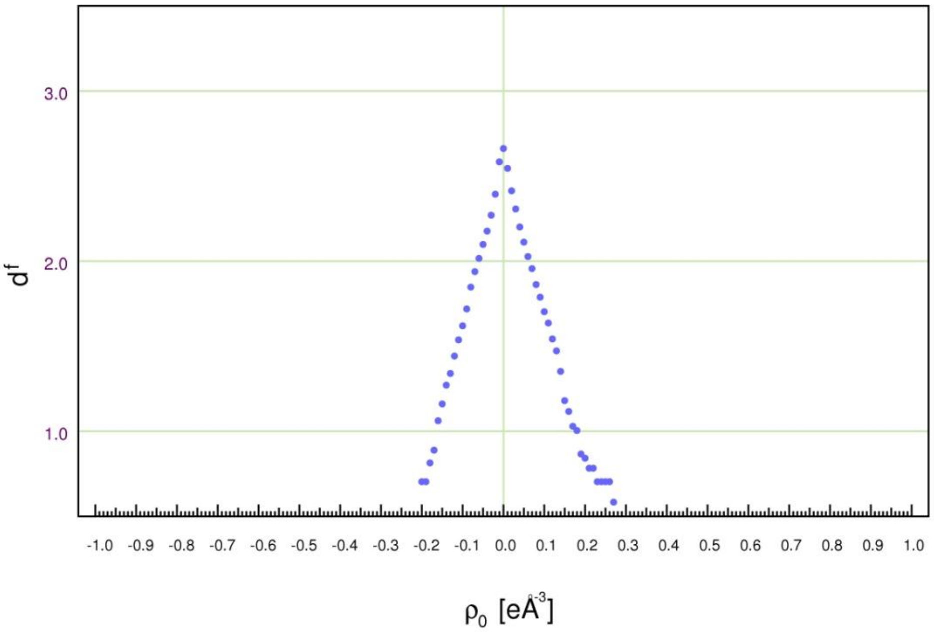


Figure 5: Polar histogram of C-F•••S interaction from CSD



(a)



(b)

Figure 6: Fractal dimension plot of (a) Experimental (b) Theoretical model

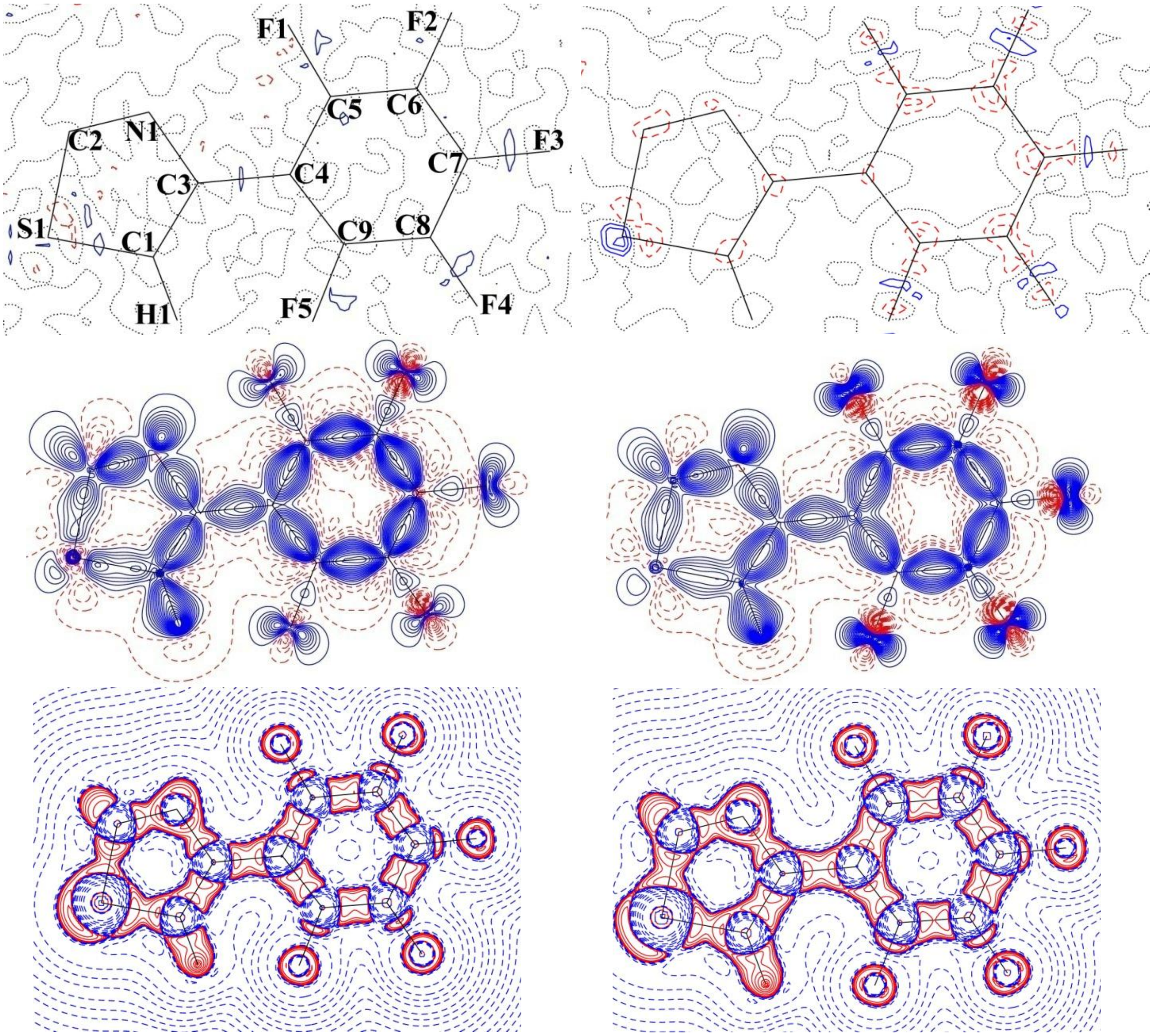


Figure 7: Experimental and Theoretical residual density, 2D deformation and Laplacian maps

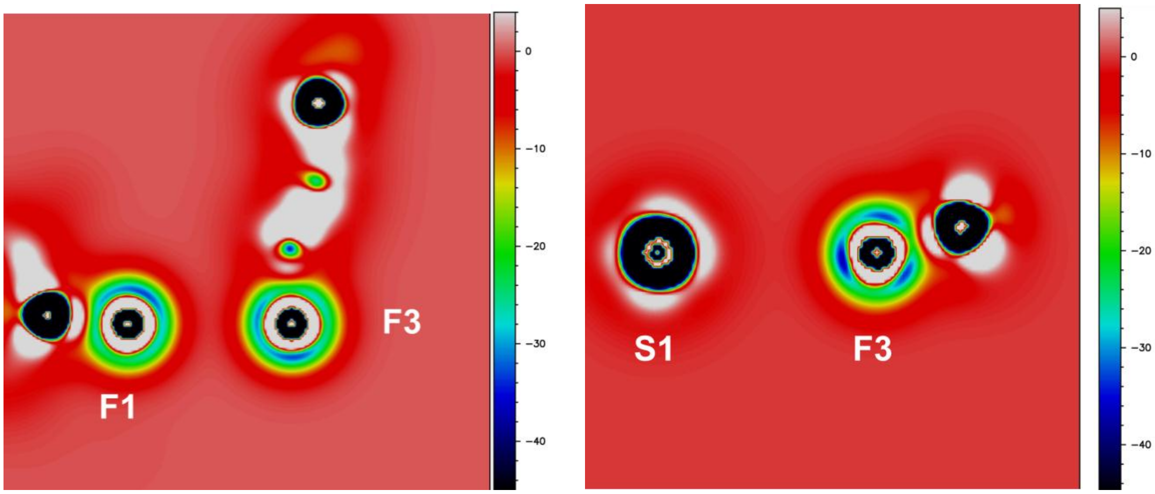


Figure 8: Laplacian plots for the F•••F and C-F•••S interaction region

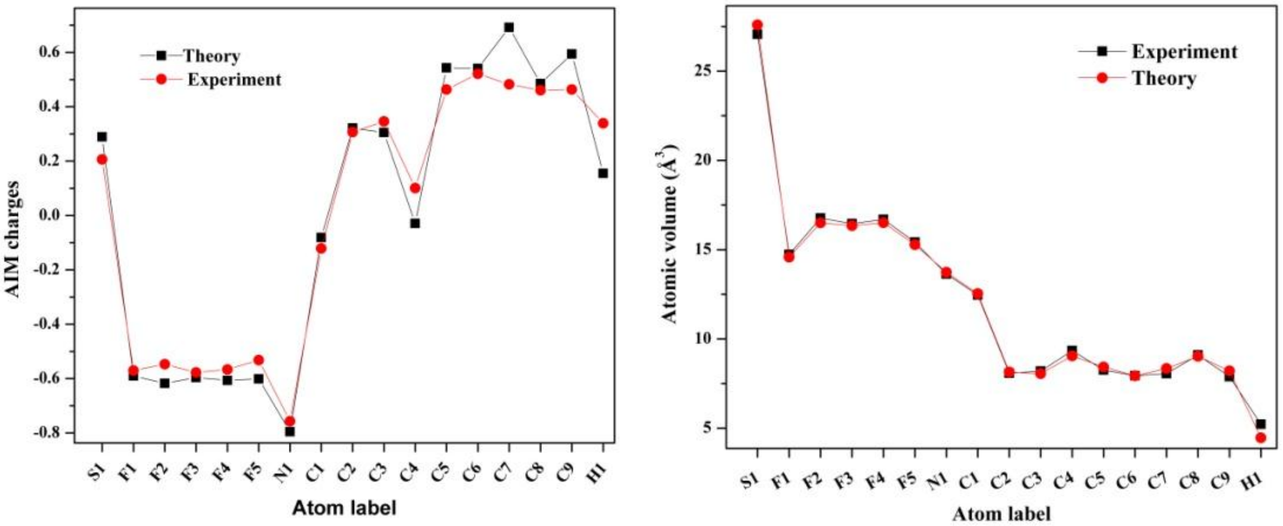
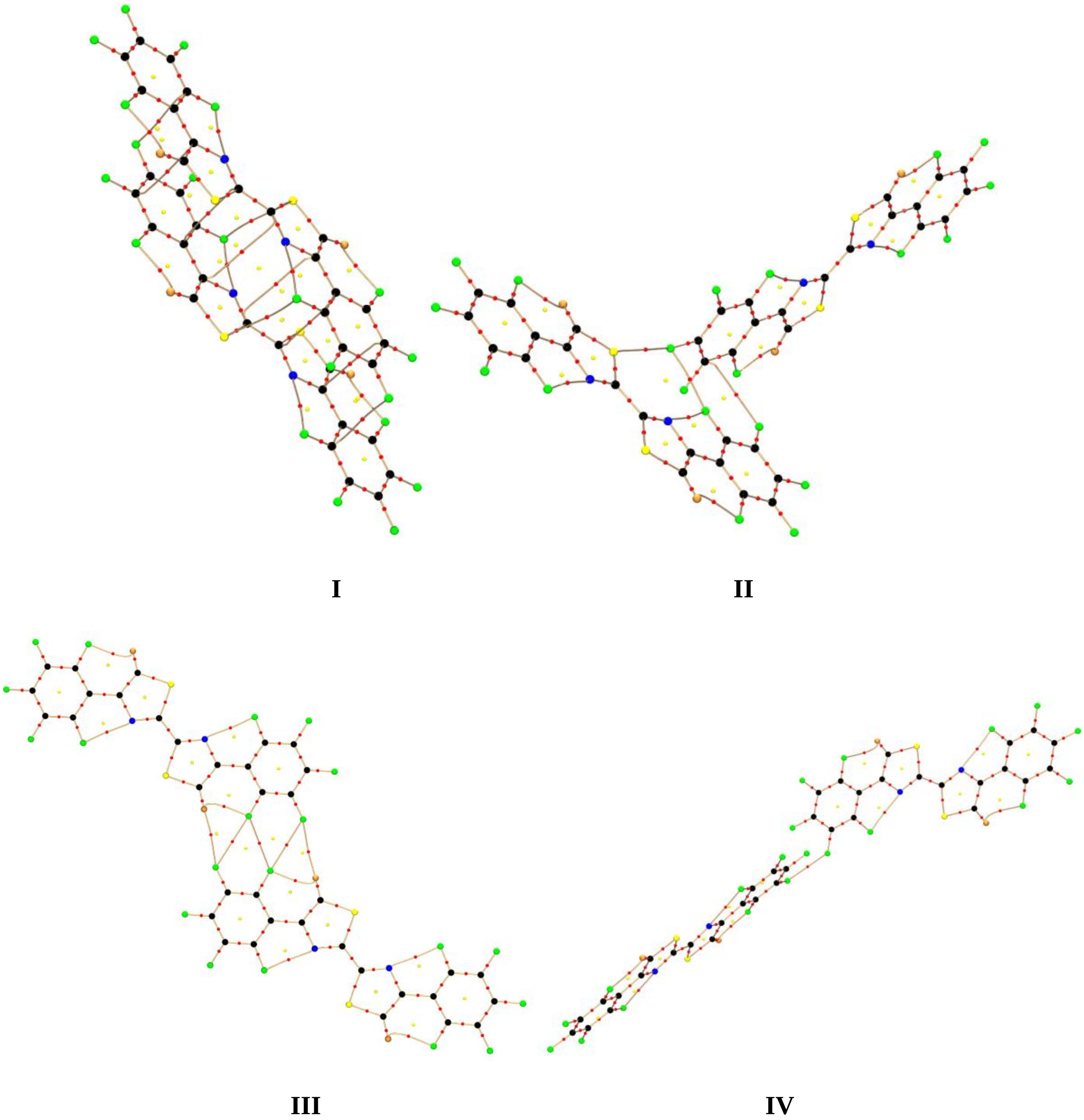


Figure 9: Comparison between experiment and theory AIM charges (q) and atomic volumes



I

II

III

IV

Figure 10: Molecular graphs of different dimers in the crystal structure

Table 5: Interaction energies calculated for the various molecular dimers in 1

Dimer (ESI)	Total Interaction energy(kJ/mol)		Electrostatic interaction energy(kJ/mol)	
	Exp	Theory	Exp	Theory
I	-89.63	-78.8	-51.75	-40.97
II	-12.7	-17.34	-7.9	-12.54
III	-5.01	-17.26	-2.55	-14.81
IV	-2.58	0.75	-1.27	2.06

References

1. AgilentTechnologies, *CrysAlis PRO*, (2011) Agilent Technologies Ltd., Yarnton,Oxfordshire, England.

2. R. Blessing, *J. Appl. Crystallogr.*, 1997, **30**, 421-426.

3. G. M. Sheldrick, *Acta Crystallogr. Sect. A: Found. Crystallogr.*, 2007, **64**, 112-122.

4. L. Farrugia, *J. Appl. Crystallogr.*, 2012, **45**, 849-854.

5. A. Volkov, P. Macchi, L. J. Farrugia, C. Gatti, P. R. Mallinson, T. Richter and T. S. Koritsanszky, *XD2006*, (2006) University at Buffalo, State University of New York, NY, USA, New York.

6. P. Macchi and P. Coppens, *Acta Crystallogr. Sect. A: Found. Crystallogr*, 2001, **57**, 656-662.

7. Z. Su and P. Coppens, *Acta Crystallogr. Sect. A: Found. Crystallogr*, 1998, **54**, 357.

8. F. H. Allen and I. J. Bruno, *Acta Crystallogr. Sect. B*, 2010, **66**, 380-386.

9. A. Madsen, *J. Appl. Crystallogr.*, 2006, **39**, 757-758.

10. P. Munshi, A. O. Madsen, M. A. Spackman, S. Larsen and R. Destro, *Acta Crystallogr. Sect. A: Found. Crystallogr*, 2008, **64**, 465-475.

11. N. K. Hansen and P. Coppens, *Acta Crystallogr. Sect. A: Found. Crystallogr*, 1978, **34**, 909-921.

12. H. O. Sorensen, R. F. Stewart, G. J. McIntyre and S. Larsen, *Acta Crystallographica Section A*, 2003, **59**, 540-550.

13. P. J. Becker and P. Coppens, *Acta Crystallographica Section A*, 1974, **30**, 129-147.

14. P. J. Becker and P. Coppens, *Acta Crystallographica Section A*, 1974, **30**, 148-153.

15. A. Volkov, C. Gatti, Y. Abramov and P. Coppens, *Acta Crystallogr.*, *Sect. A: Found. Crystallogr.*, 2000, **56**, 252-258.

16. A. Schafer, H. Horn and R. Ahlrichs, *The Journal of Chemical Physics*, 1992, **97**, 2571-2577.

17. M. F. Peintinger, D. V. Oliveira and T. Bredow, *J. Comput. Chem.*, 2012, n/a-n/a.

18. R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, P. D’Arco and M. Llunell, *CRYSTAL09 User's Manual*, (2009) University of Torino, Torino.