Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Experimental evidence for ‘carbon bonding’ in the solid state from charge density analysis

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S-1: Experimental section

Crystallization: Fenobam (**I**) was crystallized from a saturated solution of ethanol at room temperature, while dimethylamine hydroxybenozate (**II**) was crystallized from a solution of ethanol: water at 65°C. 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

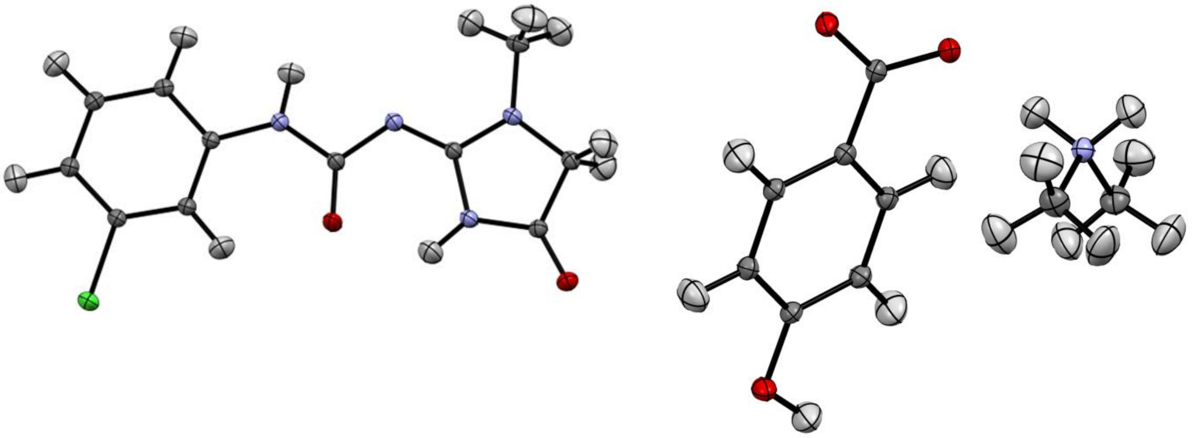
The crystals were cooled to 100 K with a liquid nitrogen stream using an Oxford Cryostream nitrogen gas-stream cooling device. X-ray diffraction data was collected on an Oxford Xcalibur (Mova) diffractometer equipped with an EOS CCD detector using MoKα radiation (λ= 0.71073 Å). The crystal to detector 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 high redundancy and completeness of 100%. Cell refinement, data integration and reduction were carried out using the program CrysAlisPro.[1] Face indexing was done for the 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 SHELXS2012 and refined based on the spherical-atom approximation (based on F) using SHELXL2012 included in the WinGX suite.[3,4] The hydrogen atoms were located on the difference Fourier map and the 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, $\Sigma w\{|F_o|^2-K|F_c|^2\}^2$ was minimized for all reflections with I >2σ(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. Scale factors for each individual resolution shell were chosen (10 scale factors) and refined against the entire 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}. Since the space group of fenobam was *C*c, the origin was fixed on the Chlorine atom. In the next step of refinement, the position and displacement parameters of the non-hydrogen atoms were fixed to the refined values. The X—H bond lengths was constrained to the values reported by neutron diffraction experiments 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 SHADE2.1 server.[9,10] ADP value of the H-atom obtained from SHADE2.1 server was kept fixed during the subsequent multipole refinements.[11] Then the 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, while for the hydrogen atoms the value was fixed at 1.2. Local symmetry constraints were used in the multipole refinements in both the cases barring a few atoms in both **I** and **II** (the atoms involved in the carbon bonded geometry were refined with an unrestricted multipole model).

The multipole expansion was truncated upto hexadecapole level (l = 4) for only chlorine in **I**, where as for other non-hydrogen atoms it was truncated at the octupole level (l = 3) in both cases. For the H atoms, only monopole, bond directed dipole (d_z) and quadrupole (q_{3z^2-1}) components were refined during the multipole refinements. In addition the anharmonicity on chlorine atom was treated by refining the Gram-Charlier cumulative of 3rd order for high angle reflections ($\sin\theta/\lambda > 0.7$ Å^{-1}).[12] The quantitative analysis of the electron density topology and related properties was performed using the XDPROP and TOPXD[13] 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[14,15] using CRYSTAL09 package.[16] 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 to 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.

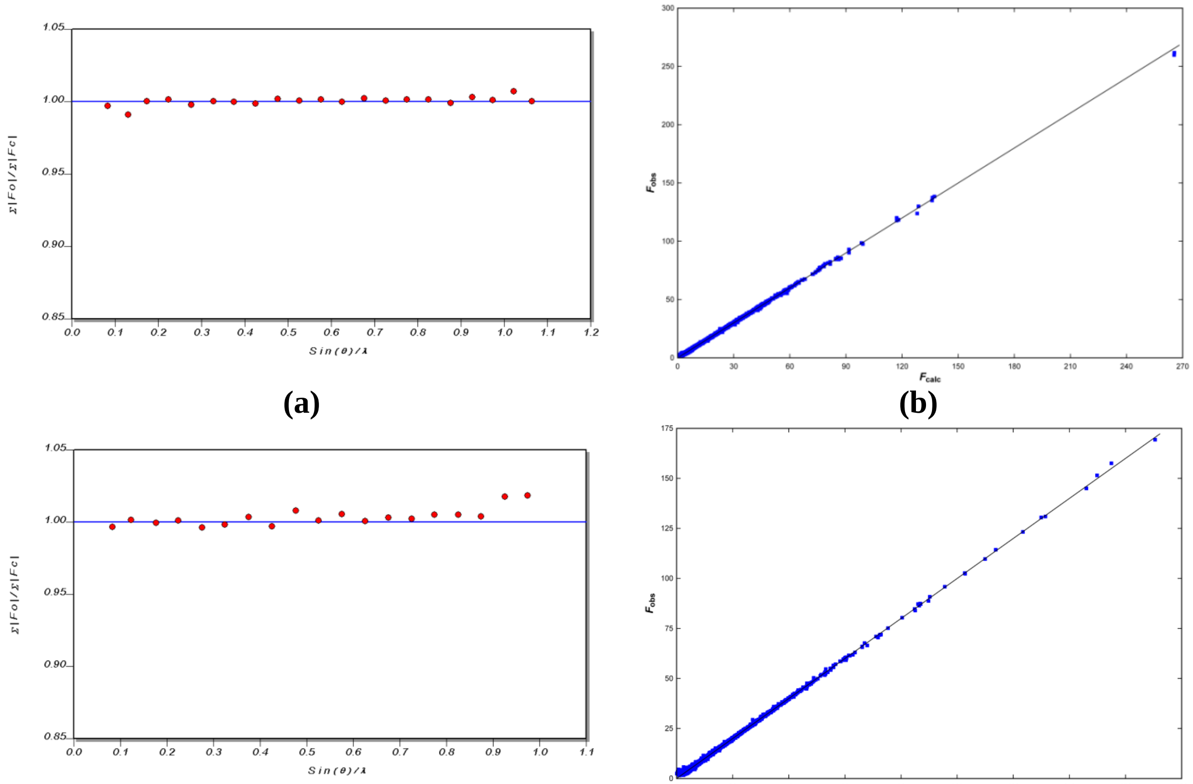


(a) (b)

Figure 1: ORTEP diagram of (a)Fenobam (b) Dimethylamine 4-hydroxybenzoate

Table 1: Crystallographic details of the experimental charge density analysis

Compounds	Fenobam	DMHYSALT
CCDC No.	962724	962725
Formula	$C_{11}H_{11}ClN_4O_2$	$C_9H_{13}NO_3$
Formula weight	266.69	183.2
Crystal system	Monoclinic	Orthorhombic
Space group	*Cc*	*P*bca
a **(Å)**	12.8504(2)	10.2123(2)
b **(Å)**	7.6927(1)	9.9415(2)
c **(Å)**	11.9619(2)	19.0947(4)
α **(°)**	90	90
β **(°)**	101.321(1)	90
γ **(°)**	90	90
Volume (Å^3), ***Z***	1159.48(3), 4	1938.60(7), 16
ρ_{calc} ***(g/cm^3)***	1.528	1.255
F(000)	552	784
μ ***(mm^{-1})***	0.33	0.09
T (K)	100(2)	100(2)
λ (Å)	0.71073	0.71073
$(\mathrm{Sin}\theta/\lambda)_{max}$ **(Å^{-1})**	1.08	1.00
Total reflections	180449	89238
Unique reflections	12156	10267
Redundancy and completeness (%)	14.8, 99.35	8.7, 99.9%
R_{int}	0.0635	0.0545
Spherical atom refinement		
R_{obs}	0.039	0.042
$wR_2\,(F^2)$	0.100	0.121
Goodness-of-fit	1.020	1.023
Flack parameter	0.00(2)	–
Multipole refinement		
Reflns. used **[*I*> 2σ(*I*)]**	10048	7048
No of parameters	276	190
Goodness-of-fit	0.971	1.027
$R(F^2)$, $wR(F^2)$	0.025, 0.044	0.027, 0.055
$\Delta\rho_{min}$, $\Delta\rho_{max}$ **(eÅ^{-3})**	–0.130, 0.144	–0.168, 0.181



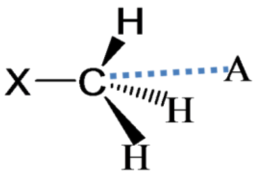
(a) (b)

(c) (d)

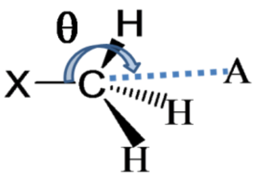
Figure 2: (i) (a) and (c) Variation of F_{obs}/F_{cal} with $(\sin\theta)/\lambda$ in **I** and **II** (ii) (b) and (d) Scatter plot depicting the variation of Fobs with Fcal for **I** and **II** respectively.

S-2: CSD Analysis

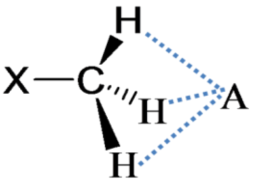
A Cambridge Structural Database (CSD v5.34 February 2013) analysis was carried out to investigate the propensity of carbon bonding in the solid state. Separate searches were carried out for the possible carbon boned motif with various acceptor atoms such as N, P, O, S, F and Cl. The analysis was carried out with the following search criteria; (I) the distance between the carbon atom in the $–CH_3$ group and the nucleophile / carbon bond acceptor atom A (where A= O, N, S, Cl etc.) is within the sum of their van der Waal radii, and (II) X–C···O angle is within the range of 140°-180° (considering $n \rightarrow \sigma^*$ nature of this interaction). (III) the distances from the O atom to the $–CH_3$ protons are ***not*** within the sum of their van der Waal radii (fig.1). Structures with any kind of errors and/or disorder were omitted from the search results.



I



II

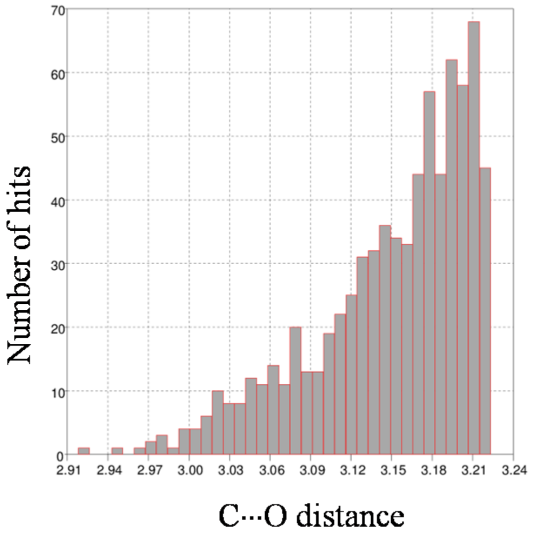


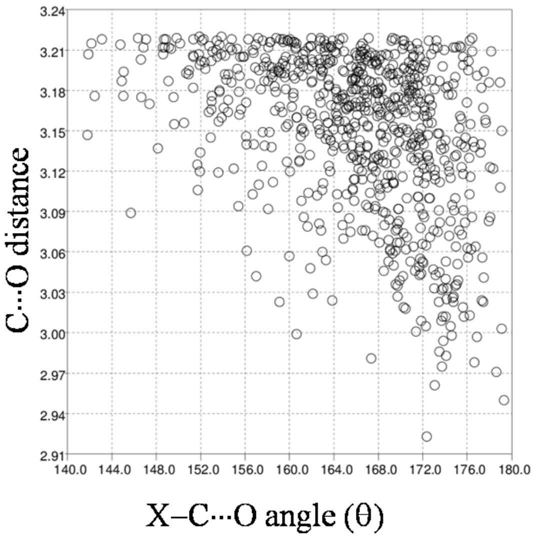
III

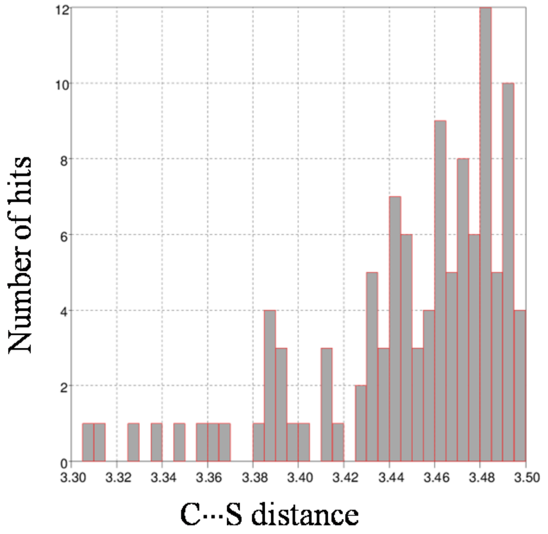
Table 2: Summary of CSD Analysis

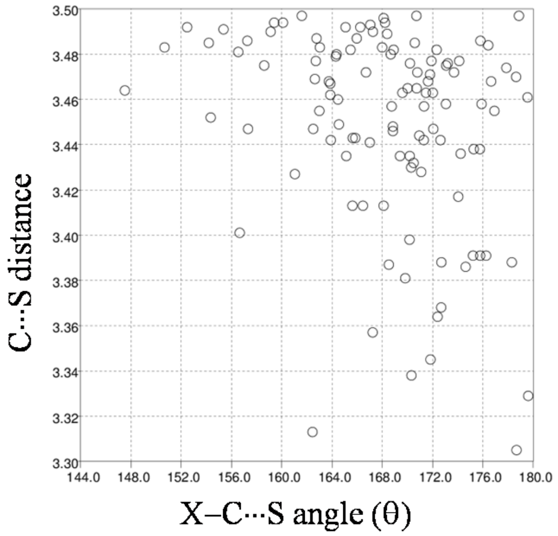
Carbon bond acceptor atom (A)	Number of entries	Mean C···A distance (Å)	Mean X–C···A angle, θ (°)
N	189	3.19	168.26
P	2	3.37	175.88
O	716	3.15	169.95
S	110	3.45	168.20
F	143	3.11	166.93
Cl	157	3.40	167.13

The distribution of X–C···O angle is indicative of n→σ* nature of carbon bonding. This is in agreement with the reported red shifts in the X–C bonds upon carbon bond formation (reference 6 in the main manuscript). The figures 1-5 represent the distribution of C···A distances (Å) and X–C···A angle, θ (°).









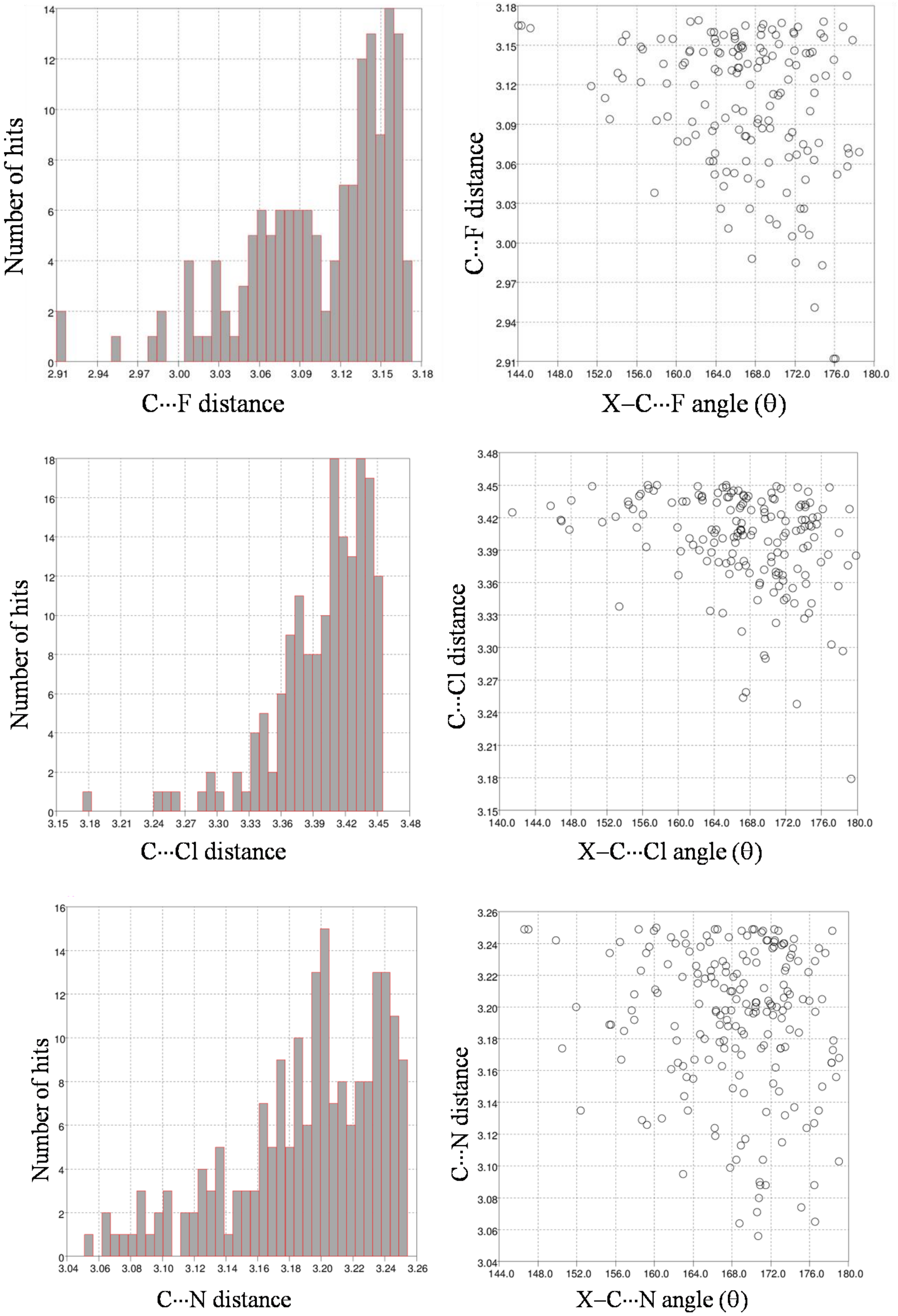
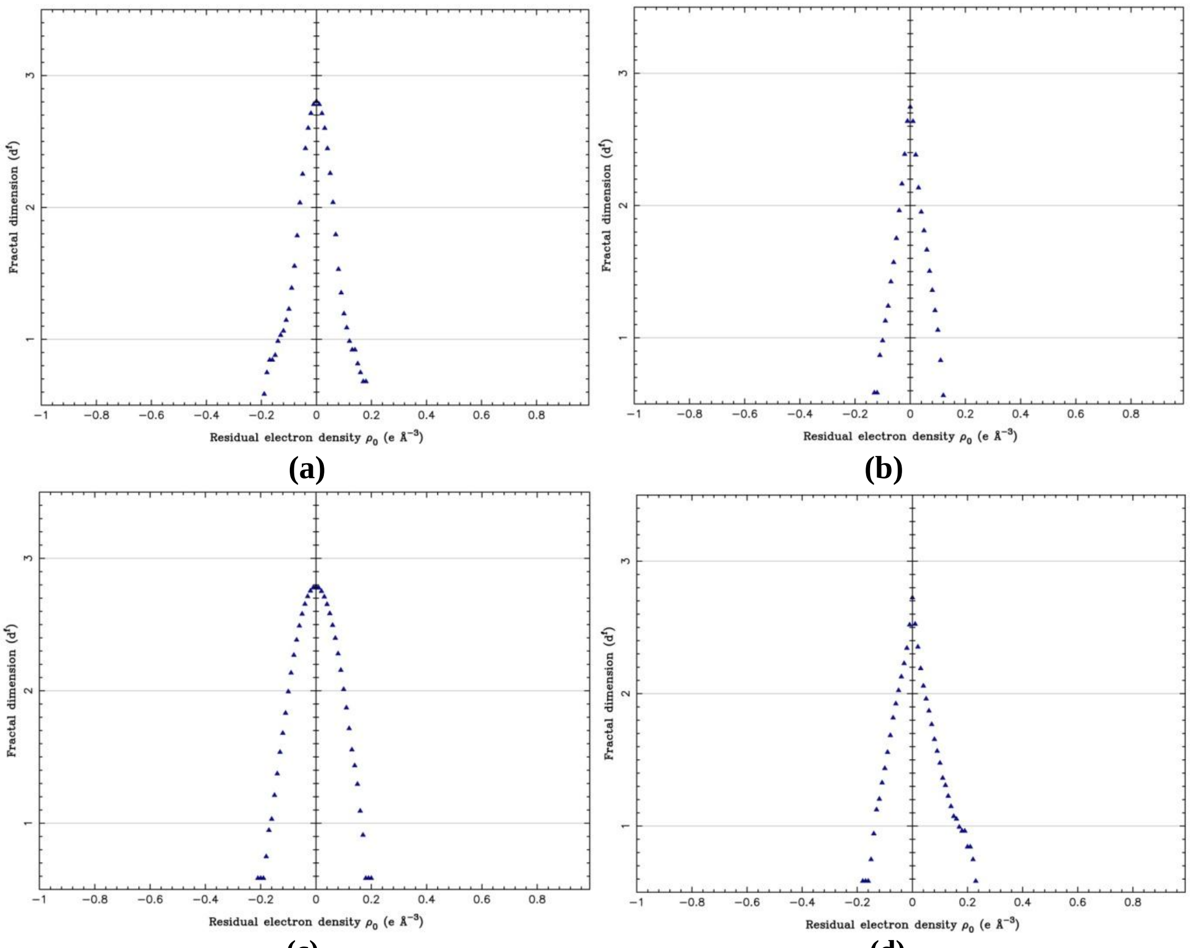


Figure 3: Histograms depicting various C···A distance distribution along with corresponding scatter plots showing the C···A distance vs X–C···A angle.



(a) (b)

(c) (d)

Figure 4: Fractal dimension plot of experimental and theoretical model (a)&(b) **I** (c)&(d) **II**

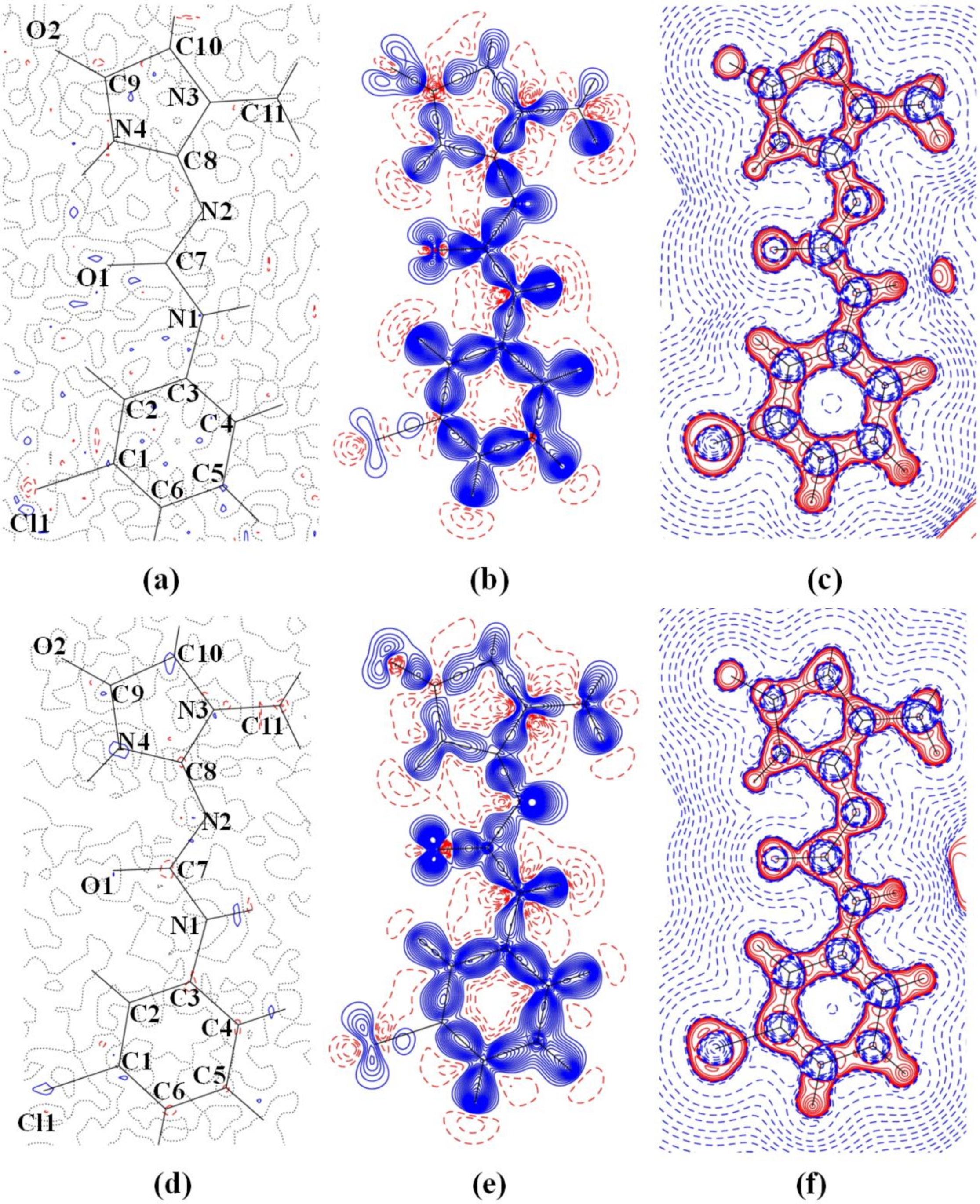
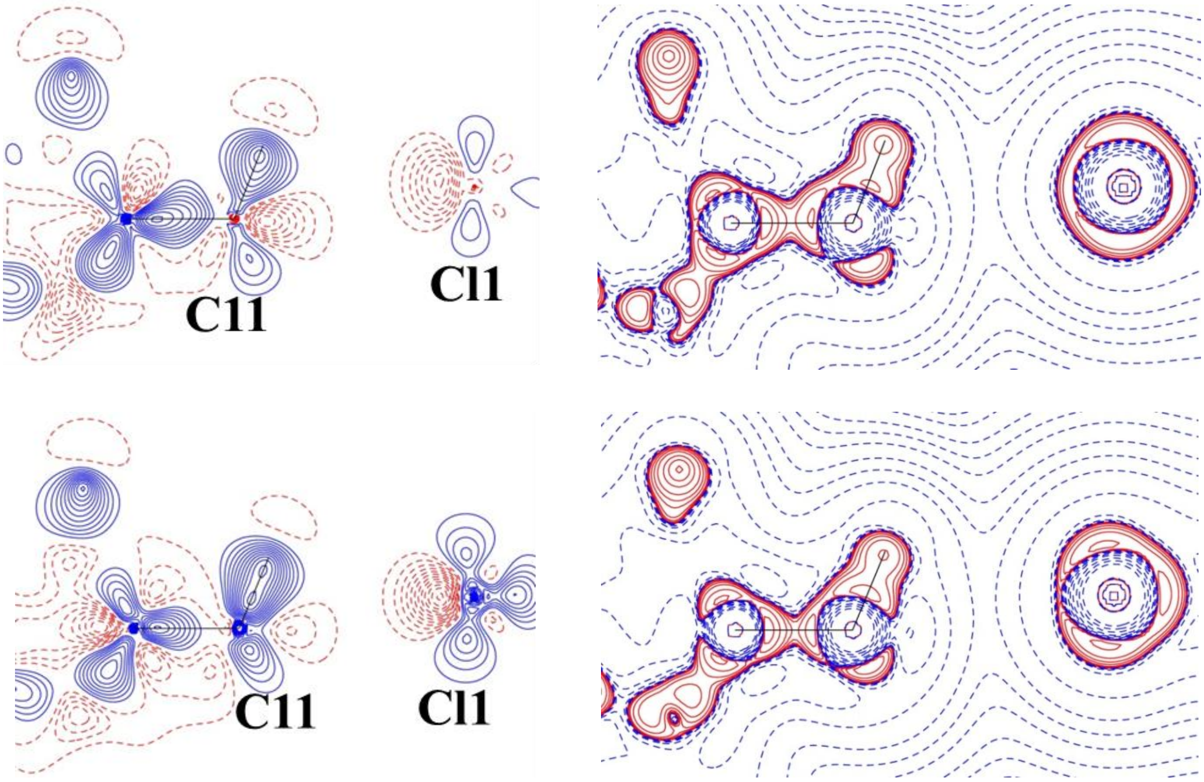


Figure 5: (a) Residual (b) deformation and (c) Laplacian of density maps obtained after multipolar refinement of the experimental and (d) (e) (f) theoretical (CRYSTAL09 B3LYP/TZVP periodic calculations) charge density data of **I**. Contours are drawn at the intervals of ±0.05 e Å^{-3} in case of Residual and deformation. Laplacian is drawn in logarithmic contours



(a) **(b)**

Figure 6: (a) Deformation and (b) Laplacian of density maps obtained after multipolar refinement of the experimental and theoretical model in C···Cl region (CRYSTAL09 B3LYP/TZVP periodic calculations)

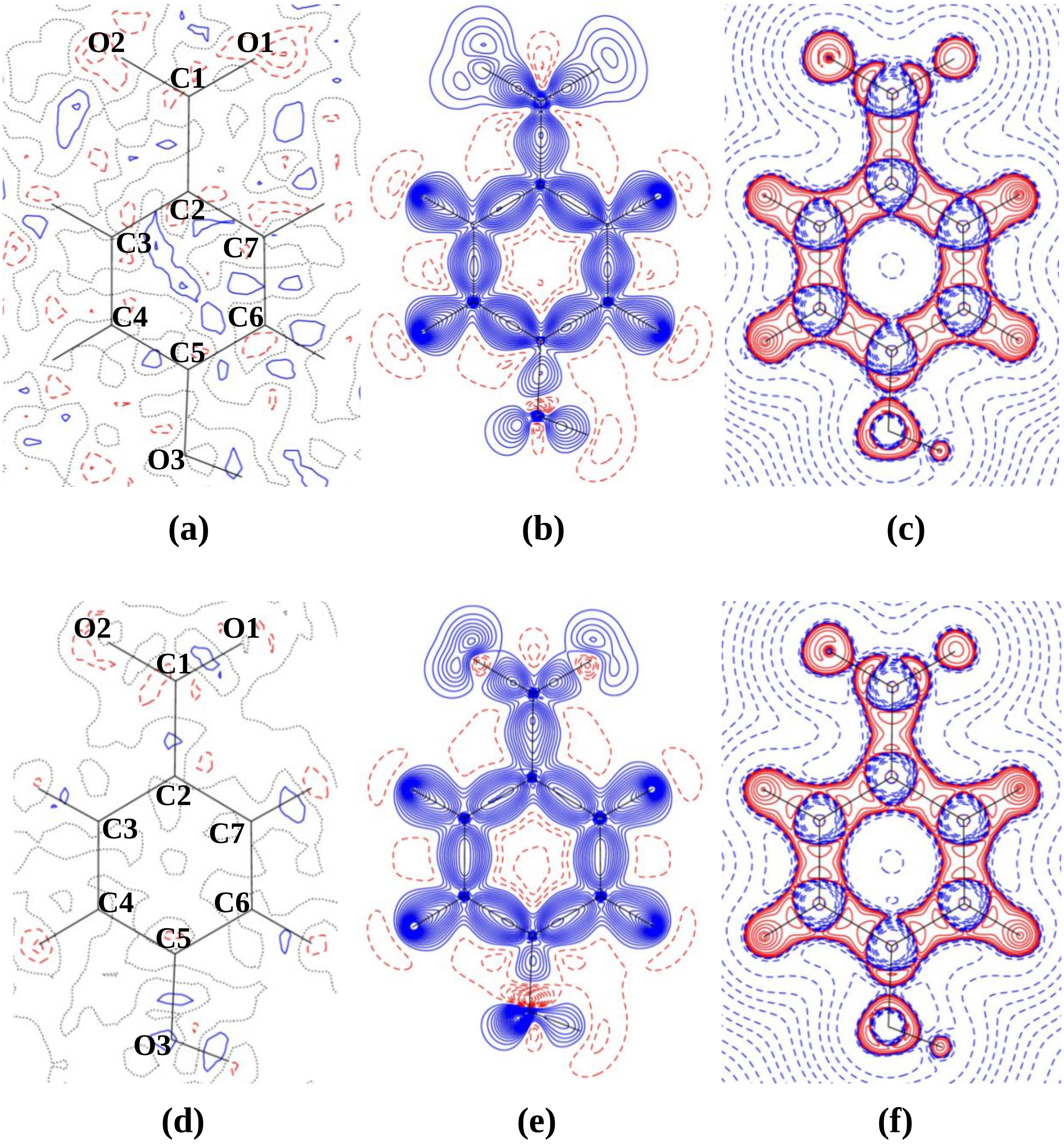
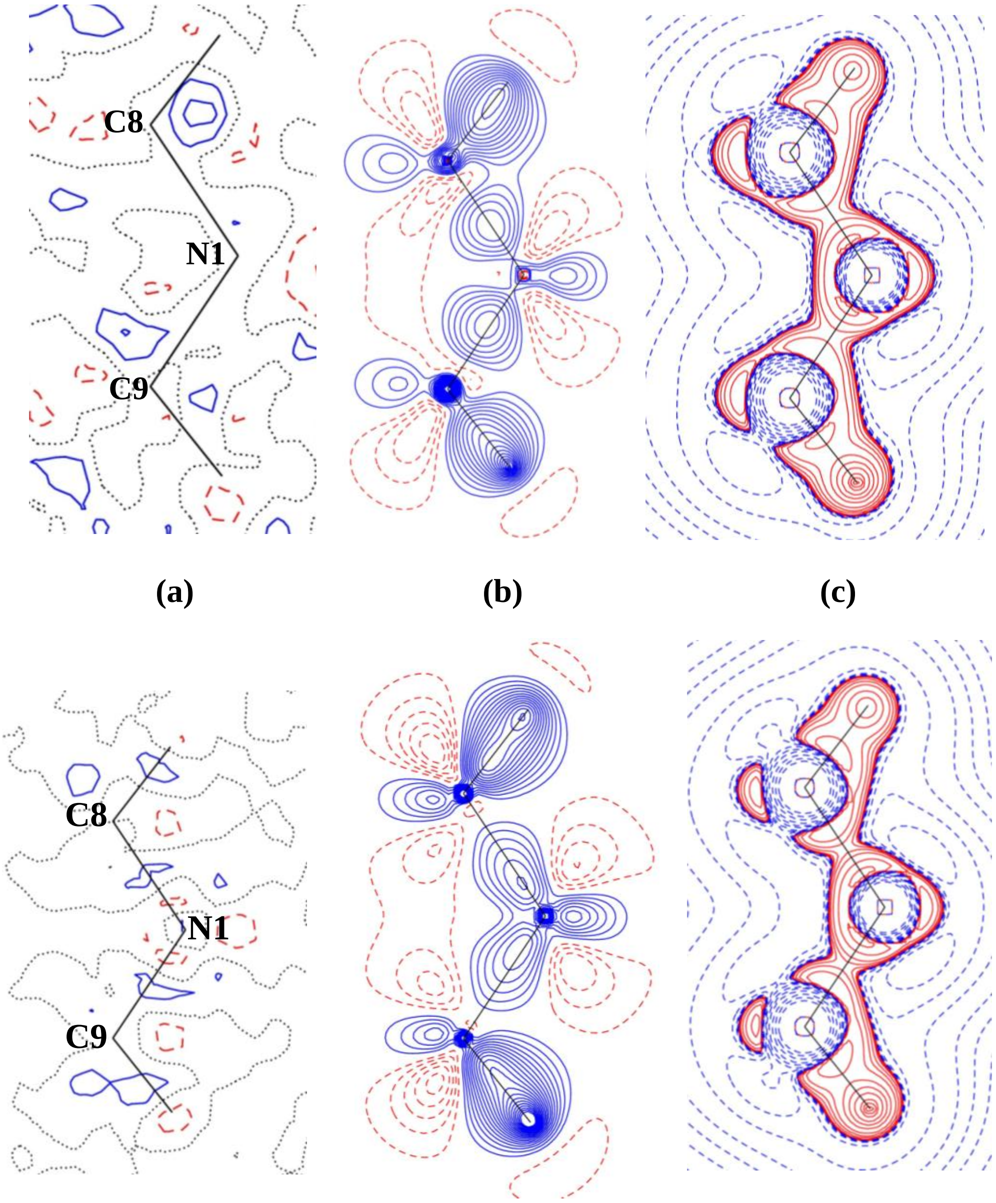


Figure 7: (a) Residual (b) deformation and (c) Laplacian of density maps obtained after multipolar refinement of the experimental and (d) (e) (f) theoretical (CRYSTAL09 B3LYP/TZVP periodic calculations) charge density data of 4-hydroxybenzoate in **II**. Contours are drawn at the intervals of ±0.05 e Å^{-3} in case of Residual and deformation. Laplacian is drawn in logarithmic contours



(a) (b) (c)

(d) (e) (f)

Figure 8: (a) Residual (b) deformation and (c) Laplacian of density maps obtained after multipolar refinement of the experimental and (d) (e) (f) theoretical (CRYSTAL09 B3LYP/TZVP periodic calculations) charge density data of dimethyl amine in **II**. Contours are drawn at the intervals of ±0.05 e Å^{-3} in case of Residual and deformation. Laplacian is drawn in logarithmic contours

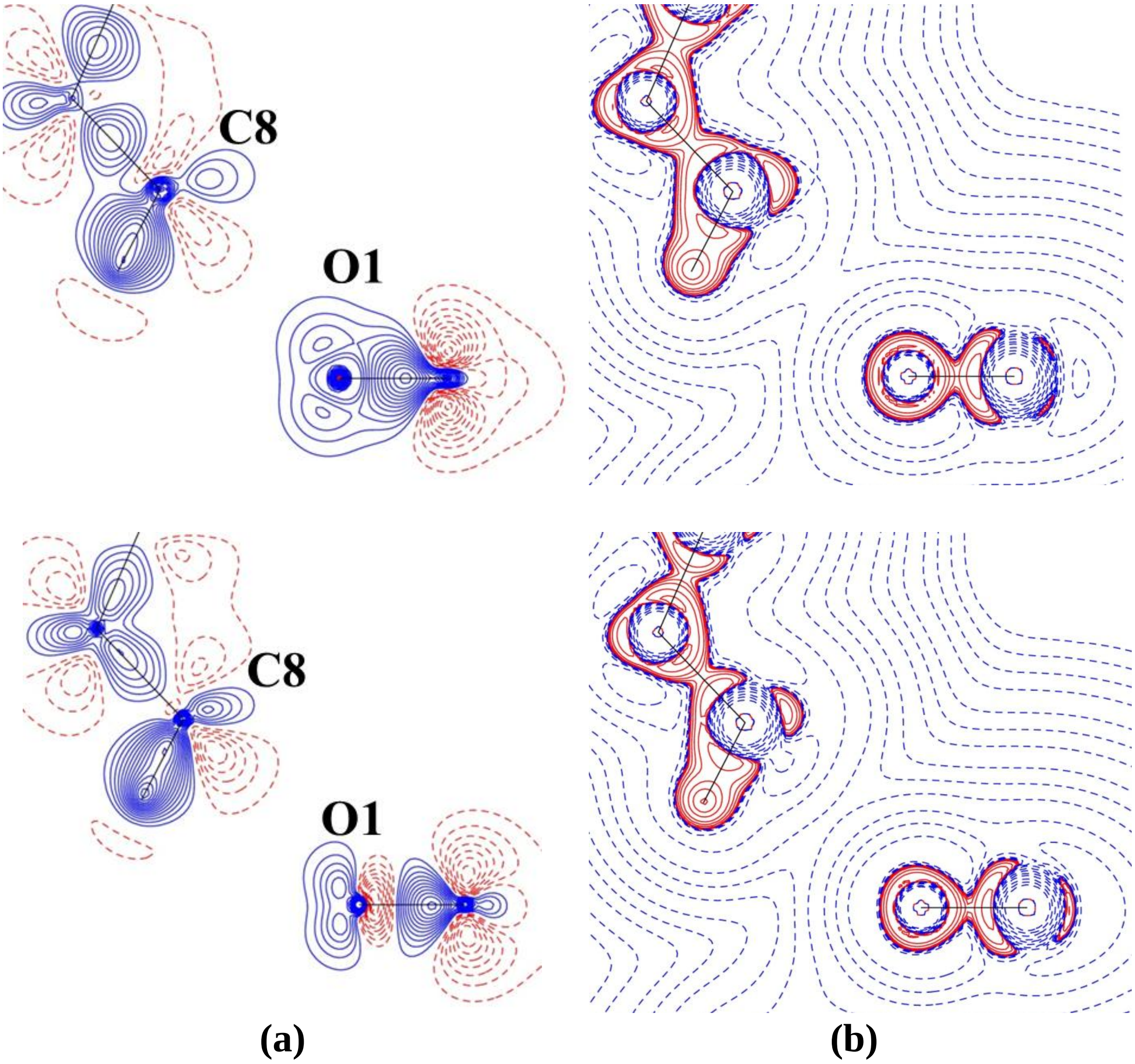


Figure 9: (a) Deformation and (b) Laplacian of density maps obtained after multipolar refinement of the experimental and theoretical model in C···O region (CRYSTAL09 B3LYP/TZVP periodic calculations)

Table 3: Topological parameters of inter-molecular interactions from Experiment and Theory (italics) in **I**

Interaction	**R_{ij}(Å)**	**ρ (eÅ^{-3})**	**$\nabla^2\rho$ (eÅ^{-5})**	**ε**	**G (kJmol^{-1} bohr^{-3})**	**V (kJmol^{-1} bohr^{-3})**	**$\frac{\lvert V \rvert}{G}$**
N4–H4N··· O1	2.064	0.15	2.7	0.29	62.5	-52.0	0.83
	2.037	*0.16*	*2.6*	*0.05*	*61.8*	*-52.3*	*0.85*
C2–H2···O1	2.352	0.09	1.7	0.97	36.6	-26.3	0.72
	2.237	*0.11*	*1.7*	*0.04*	*39.9*	*-32.1*	*0.81*
N1–H1N···O2	1.928	0.15	1.7	0.04	44.5	-42.3	0.95
	1.938	*0.10*	*3.0*	*0.10*	*62.0*	*-41.6*	*0.67*
C4–H4···O2	2.485	0.04	0.7	0.51	13.9	-8.8	0.63
	2.529	*0.05*	*0.8*	*0.19*	*16.2*	*-10.8*	*0.66*

C10–H10A···O1	2.703	0.03	0.4	0.16	8.2	-5.1	0.63
	2.694	*0.03*	*0.5*	*0.08*	*9.6*	*-5.8*	*0.60*

Table 4: Topological parameters of inter-molecular interactions from Experiment and Theory (italics) in **II**

Interaction	**R_{ij}(Å)**	ρ **(eÅ^{-3})**	**$\nabla^2\rho$ (eÅ^{-5})**	**ε**	**G (kJmol^{-1} bohr^{-3})**	**V (kJmol^{-1} bohr^{-3})**	**$\frac{\lvert V\rvert}{G}$**
N1–H1N···O1	1.725	0.29	3.2	0.05	96.6	-106.7	1.10
	1.725	*0.31*	*3.0*	*0.03*	*98.8*	*-115.8*	*1.17*
O3–H3O···O2	1.627	0.34	4.0	0.01	125.7	-141.8	1.13
	1.627	*0.35*	*4.3*	*0.02*	*132.3*	*-147.4*	*1.11*
N1–H2N···O2	1.677	0.38	2.5	0.02	107.2	-145.2	1.35
	1.677	*0.35*	*3.6*	*0.01*	*119.6*	*-141.1*	*1.18*
C4–H4···C7	2.765	0.04	0.6	1.12	11.2	-7.4	0.66
	2.799	*0.04*	*0.5*	*2.3*	*10.5*	*-7.5*	*0.71*
H9B···H3	2.710	0.05	0.6	0.97	12.4	-9.1	0.73
	2.658	*0.04*	*0.6*	*0.37*	*12.4*	*-8.4*	*0.68*

Table 5: Topological parameters of intramolecular bonds from Experiment and Theory (italics) in **I**

Bond	**ρ (eÅ^{-3})**	**$\nabla^2\rho$ (eÅ^{-5})**	**R_{ij}(Å)**	**d_1 (Å)**	**d_2 (Å)**	λ_1	λ_2	λ_3	ε
CL1–C1	1.32	–1.6	1.7398	0.9684	0.7714	–7.5	–6.8	12.7	0.11
CRYSTAL09	*1.26*	*0.3*	*1.7413*	*1.0166*	*0.7248*	*–6.9*	*–6.4*	*13.6*	*0.09*
O1–C7	2.86	–37.7	1.2425	0.7592	0.4833	–27.7	–23.7	13.6	0.17
CRYSTAL09	*2.68*	*–25.5*	*1.2421*	*0.8002*	*0.4419*	*–21.9*	*–21.0*	*17.4*	*0.05*
O2–C9	3.10	–43.7	1.2172	0.7603	0.4569	–31.6	–27.1	15.0	0.16
CRYSTAL09	*2.94*	*–33.4*	*1.2176*	*0.7652*	*0.4524*	*–27.1*	*–23.8*	*17.5*	*0.14*
N1–C3	2.05	–15.8	1.3973	0.7986	0.5987	–16.4	–13.8	14.5	0.19
CRYSTAL09	*1.97*	*–12.0*	*1.3980*	*0.7826*	*0.6154*	*–15.2*	*–13.0*	*16.1*	*0.17*
N1–C7	2.16	–18.7	1.3731	0.7844	0.5888	–18.2	–14.5	14.0	0.26
CRYSTAL09	*2.22*	*–17.6*	*1.3718*	*0.7740*	*0.5978*	*–17.1*	*–14.6*	*14.1*	*0.17*
N1–H1N	2.53	–37.1	1.0147	0.7199	0.2948	–32.8	–31.4	27.1	0.05
CRYSTAL09	*2.23*	*–24.0*	*1.0151*	*0.7329*	*0.2822*	*–28.3*	*–25.8*	*30.1*	*0.10*
N2–C7	2.27	–17.0	1.3819	0.7476	0.6343	–18.6	–16.4	18.0	0.13
CRYSTAL09	*2.06*	*–11.5*	*1.3812*	*0.7437*	*0.6375*	*–15.0*	*–13.2*	*16.7*	*0.13*
N2–C8	2.64	–26.1	1.3009	0.7068	0.5941	–23.0	–19.3	16.2	0.20
CRYSTAL09	*2.54*	*–22.8*	*1.3002*	*0.7136*	*0.5866*	*–19.7*	*–17.0*	*13.9*	*0.16*
N3–C8	2.30	–22.3	1.3447	0.7700	0.5747	–20.0	–15.6	13.3	0.29
CRYSTAL09	*1.98*	*–14.1*	*1.3936*	*0.8096*	*0.5839*	*–14.4*	*–12.8*	*13.0*	*0.13*
N3–C10	1.79	–7.7	1.4458	0.7987	0.6470	–12.6	–11.4	16.3	0.10
CRYSTAL09	*1.76*	*–8.1*	*1.4476*	*0.8066*	*0.6409*	*–12.8*	*–11.6*	*16.3*	*0.10*
N3–C11	1.81	–12.2	1.4482	0.8299	0.6183	–12.8	–12.7	13.2	0.01
CRYSTAL09	*1.61*	*–6.7*	*1.4461*	*0.8432*	*0.6029*	*–11.2*	*–9.9*	*14.5*	*0.13*

N4–C8	2.13	–17.6	1.3947	0.7791	0.6156	–17.9	–14.9	15.3	0.20
CRYSTAL09	*2.33*	*–20.8*	*1.3433*	*0.7578*	*0.5855*	*–18.4*	*–15.4*	*13.0*	*0.20*
N4–C9	2.27	–19.6	1.3713	0.7715	0.5997	–19.2	–15.9	15.5	0.21
CRYSTAL09	*2.07*	*–14.1*	*1.3718*	*0.7778*	*0.5940*	*–16.1*	*–13.6*	*15.5*	*0.19*
N4–H4N	2.30	–26.7	1.0142	0.7302	0.2840	–29.2	–27.7	30.2	0.05
CRYSTAL09	*2.11*	*–21.3*	*1.0150*	*0.7433*	*0.2718*	*–27.1*	*–25.2*	*31.0*	*0.08*
C1–C2	2.15	–18.3	1.3920	0.7257	0.6663	–16.3	–13.5	11.6	0.21
CRYSTAL09	*2.13*	*–18.2*	*1.3883*	*0.6983*	*0.6899*	*–15.7*	*–12.7*	*10.2*	*0.23*
C1–C6	2.19	–20.1	1.3889	0.7365	0.6524	–16.6	–14.2	10.7	0.17
CRYSTAL09	*2.09*	*–16.9*	*1.3917*	*0.7121*	*0.6796*	*–15.2*	*–12.3*	*10.6*	*0.23*
C2–C3	2.12	–17.8	1.4021	0.7017	0.7004	–16.5	–13.4	12.1	0.23
CRYSTAL09	*2.02*	*–15.6*	*1.3987*	*0.7468*	*0.6519*	*–14.3*	*–12.8*	*11.4*	*0.12*
C2–H2	2.10	–24.7	1.0822	0.6263	0.4559	–19.0	–18.2	12.5	0.05
CRYSTAL09	*1.91*	*–18.2*	*1.0833*	*0.6982*	*0.3850*	*–18.3*	*–16.6*	*16.7*	*0.11*
C3–C4	2.09	–17.5	1.4060	0.7495	0.6565	–16.0	–13.1	11.6	0.22
CRYSTAL09	*2.15*	*–17.3*	*1.3865*	*0.6807*	*0.7058*	*–15.8*	*–13.3*	*11.8*	*0.18*
C4–C5	2.09	–17.4	1.3890	0.7134	0.6757	–15.9	–13.5	12.0	0.17
CRYSTAL09	*2.05*	*–16.6*	*1.4060*	*0.6836*	*0.7223*	*–16.1*	*–12.9*	*12.3*	*0.25*
C4–H4	2.03	–22.0	1.0827	0.6480	0.4347	–18.3	–17.5	13.8	0.04
CRYSTAL09	*1.87*	*–17.0*	*1.0831*	*0.7218*	*0.3613*	*–18.5*	*–17.6*	*19.1*	*0.05*
C5–C6	2.13	–17.8	1.3990	0.6717	0.7272	–16.8	–13.4	12.3	0.26
CRYSTAL09	*2.07*	*–16.8*	*1.3995*	*0.6826*	*0.7169*	*–15.9*	*–12.8*	*11.9*	*0.25*
C5–H5	1.76	–13.6	1.0833	0.6895	0.3938	–15.7	–15.6	17.7	0.01
CRYSTAL09	*1.83*	*–15.8*	*1.0831*	*0.7226*	*0.3605*	*–18.0*	*–16.4*	*18.6*	*0.09*
C6–H6	1.84	–16.0	1.0827	0.6833	0.3994	–16.7	–15.6	16.2	0.07
CRYSTAL09	*1.83*	*–15.8*	*1.0831*	*0.7226*	*0.3605*	*–18.0*	*–16.4*	*18.6*	*0.09*
C9–C10	1.74	–11.5	1.5176	0.8038	0.7138	–12.5	–11.2	12.1	0.11
CRYSTAL09	*1.69*	*–9.8*	*1.5164*	*0.7892*	*0.7272*	*–11.7*	*–10.8*	*12.7*	*0.08*
C10–H10A	1.70	–15.8	1.0934	0.7340	0.3594	–16.7	–15.8	16.7	0.06
CRYSTAL09	*1.82*	*–15.8*	*1.0921*	*0.7279*	*0.3641*	*–17.4*	*–16.9*	*18.4*	*0.03*
C10–H10B	1.84	–18.8	1.0908	0.6692	0.4216	–16.9	–16.0	14.0	0.06
CRYSTAL09	*1.76*	*–13.7*	*1.0922*	*0.7097*	*0.3825*	*–16.1*	*–15.6*	*17.9*	*0.03*
C11–H11A	1.74	–15.0	1.0785	0.6822	0.3963	–15.7	–14.3	15.1	0.10
CRYSTAL09	*1.92*	*–16.7*	*1.0774*	*0.6969*	*0.3805*	*–17.7*	*–17.0*	*18.0*	*0.04*
C11–H11B	1.74	–14.0	1.0763	0.7345	0.3418	–16.8	–15.3	18.1	0.09
CRYSTAL09	*1.90*	*–16.6*	*1.0770*	*0.6969*	*0.3801*	*–17.6*	*–17.0*	*18.1*	*0.03*
C11–H11C	1.83	–18.5	1.0766	0.6085	0.4682	–16.0	–12.8	10.2	0.25
CRYSTAL09	*1.86*	*–16.1*	*1.0771*	*0.6967*	*0.3804*	*–17.1*	*–16.7*	*17.7*	*0.03*

Table 6: Topological parameters of intramolecular bonds from Experiment and Theory (italics) in **II**

Bond	**ρ ($e\AA^{-3}$)**	**$\nabla^2\rho$ ($e\AA^{-5}$)**	**R_{ij}(Å)**	**d_1 (Å)**	**d_2 (Å)**	**λ_1**	**λ_2**	**λ_3**	**ε**
O1-C1	2.67	-30.5	1.2543	0.8185	0.4358	-25.7	-22.6	17.8	0.13
CRYSTAL09	*2.59*	*-27.7*	*1.2543*	*0.7679*	*0.4864*	*-22.0*	*-19.8*	*14.1*	*0.11*
O2-C1	2.6	-35.1	1.2735	0.8071	0.4664	-24.0	-21.3	10.2	0.12
CRYSTAL09	*2.52*	*-26.7*	*1.2735*	*0.7650*	*0.5085*	*-21.0*	*-19.8*	*14.2*	*0.06*
O3-C5	2.08	-19.3	1.3507	0.8197	0.5309	-16.0	-15.3	12.0	0.04
CRYSTAL09	*2.03*	*-13.2*	*1.3505*	*0.7869*	*0.5636*	*-15.7*	*-14.2*	*16.7*	*0.10*
O3-H3O	2.07	-30	0.992	0.7743	0.2177	-32.7	-32.0	34.7	0.02
CRYSTAL09	*2.13*	*-24.6*	*0.9920*	*0.7521*	*0.2399*	*-31.4*	*-30.9*	*37.7*	*0.02*
N1-C8	1.65	-9.3	1.481	0.8509	0.6301	-10.7	-9.9	11.4	0.08
CRYSTAL09	*1.60*	*-6.4*	*1.4810*	*0.8388*	*0.6422*	*-10.5*	*-10.3*	*14.3*	*0.02*
N1-C9	1.71	-10	1.479	0.8407	0.6383	-11.2	-10.7	11.9	0.04
CRYSTAL09	*1.61*	*-6.5*	*1.4789*	*0.8358*	*0.6431*	*-10.7*	*-10.3*	*14.5*	*0.04*
N1-H1N	2.02	-27.7	1.036	0.7885	0.2475	-26.8	-26.5	25.7	0.01
CRYSTAL09	*2.09*	*-25.7*	*1.0360*	*0.7653*	*0.2707*	*-26.9*	*-26.7*	*27.9*	*0.01*
N1-H2N	2.08	-29.8	1.036	0.7709	0.265	-27.5	-27.2	24.8	0.01
CRYSTAL09	*2.07*	*-25.4*	*1.0360*	*0.7709*	*0.2651*	*-26.9*	*-26.7*	*28.2*	*0.01*
C1-C2	1.77	-12.8	1.4989	0.7788	0.72	-13.0	-10.7	10.8	0.21
CRYSTAL09	*1.73*	*-10.4*	*1.4989*	*0.7779*	*0.7210*	*-12.1*	*-10.7*	*12.5*	*0.13*
C2-C3	2.07	-16.5	1.4014	0.6941	0.7073	-15.6	-12.7	11.8	0.23
CRYSTAL09	*2.03*	*-15.2*	*1.4014*	*0.7021*	*0.6993*	*-14.9*	*-12.3*	*12.0*	*0.21*
C2-C7	2.16	-18.8	1.4014	0.6968	0.7046	-16.7	-14.0	11.9	0.19
CRYSTAL09	*2.04*	*-15.6*	*1.4015*	*0.6950*	*0.7065*	*-15.0*	*-12.6*	*12.0*	*0.19*
C3-C4	2.12	-18.5	1.3888	0.6857	0.7031	-16.4	-12.9	10.8	0.27
CRYSTAL09	*2.10*	*-17.1*	*1.3887*	*0.6951*	*0.6936*	*-15.8*	*-12.9*	*11.7*	*0.22*
C3-H3	1.84	-17.2	1.083	0.7021	0.3809	-17.5	-16.7	17.0	0.05
CRYSTAL09	*1.85*	*-17.3*	*1.0830*	*0.7002*	*0.3828*	*-17.4*	*-16.7*	*16.8*	*0.04*
C4-C5	2.18	-20.4	1.3996	0.673	0.7266	-17.0	-13.7	10.3	0.24
CRYSTAL09	*2.11*	*-17.8*	*1.3996*	*0.6834*	*0.7162*	*-16.3*	*-13.3*	*11.8*	*0.23*
C4-H4	1.82	-16.6	1.083	0.6927	0.3903	-17.1	-15.4	15.8	0.11
CRYSTAL09	*1.86*	*-17.1*	*1.0830*	*0.6944*	*0.3886*	*-17.6*	*-16.5*	*17.1*	*0.07*
C5-C6	2.08	-18.1	1.4028	0.7435	0.6593	-15.7	-12.6	10.2	0.25
CRYSTAL09	*2.05*	*-16.2*	*1.4029*	*0.7146*	*0.6883*	*-15.6*	*-12.6*	*12.0*	*0.24*
C6-C7	2.1	-18.8	1.3901	0.7139	0.6762	-16.3	-13.0	10.5	0.25
CRYSTAL09	*2.09*	*-16.9*	*1.3901*	*0.6931*	*0.6970*	*-15.6*	*-13.0*	*11.7*	*0.20*
C6-H6	1.83	-17.2	1.0831	0.695	0.3881	-17.1	-15.7	15.6	0.09
CRYSTAL09	*1.84*	*-16.9*	*1.0830*	*0.6996*	*0.3835*	*-17.5*	*-16.5*	*17.1*	*0.06*
C7-H7	1.86	-17.4	1.083	0.6993	0.3837	-17.9	-16.6	17.0	0.08
CRYSTAL09	*1.82*	*-15.0*	*1.0831*	*0.7048*	*0.3783*	*-16.8*	*-16.0*	*17.8*	*0.05*
C8-H8A	1.66	-13	1.0776	0.7283	0.3493	-14.9	-13.8	15.7	0.08
CRYSTAL09	*1.92*	*-19.2*	*1.0771*	*0.7135*	*0.3636*	*-18.9*	*-18.6*	*18.3*	*0.02*

C8-H8B	1.85	-17.7	1.0771	0.6291	0.448	-15.4	-13.3	11.0	0.16
CRYSTAL09	*1.90*	*-17.5*	*1.0771*	*0.7008*	*0.3763*	*-18.1*	*-17.8*	*18.4*	*0.02*
C8-H8C	1.84	-17.4	1.0773	0.7164	0.3609	-17.0	-15.8	15.3	0.07
CRYSTAL09	*1.88*	*-17.5*	*1.0770*	*0.7116*	*0.3655*	*-18.3*	*-17.9*	*18.8*	*0.02*
C9-H9A	1.81	-16.5	1.077	0.6895	0.3875	-15.9	-14.7	14.2	0.08
CRYSTAL09	*1.90*	*-18.8*	*1.0772*	*0.6935*	*0.3836*	*-18.2*	*-17.8*	*17.3*	*0.02*
C9-H9B	1.75	-15.4	1.0773	0.7066	0.3708	-15.7	-14.9	15.1	0.06
CRYSTAL09	*1.88*	*-17.3*	*1.0771*	*0.6969*	*0.3803*	*-17.7*	*-17.5*	*17.9*	*0.01*
C9-H9C	1.6	-14.3	1.077	0.7746	0.3025	-15.7	-14.9	16.2	0.05
CRYSTAL09	*1.92*	*-18.3*	*1.0770*	*0.7030*	*0.3740*	*-18.5*	*-18.2*	*18.3*	*0.01*

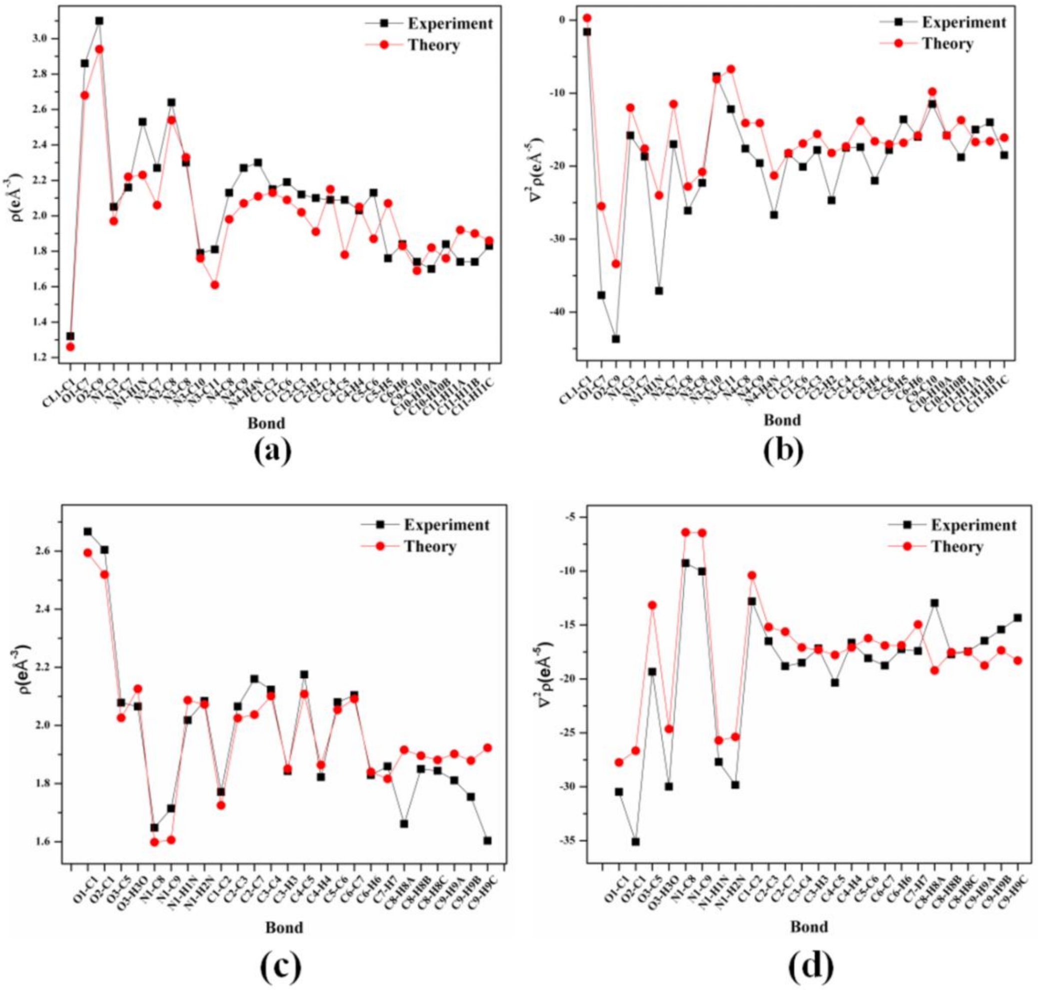
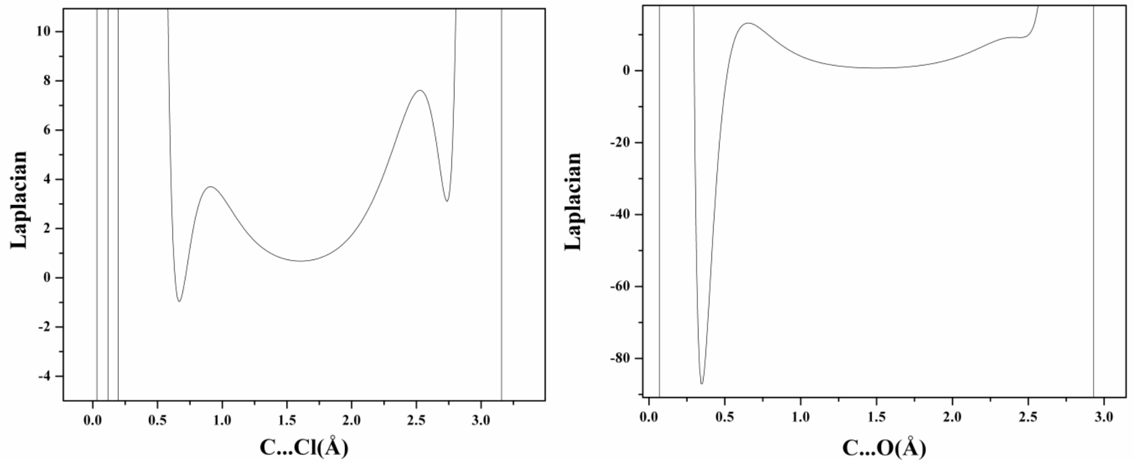
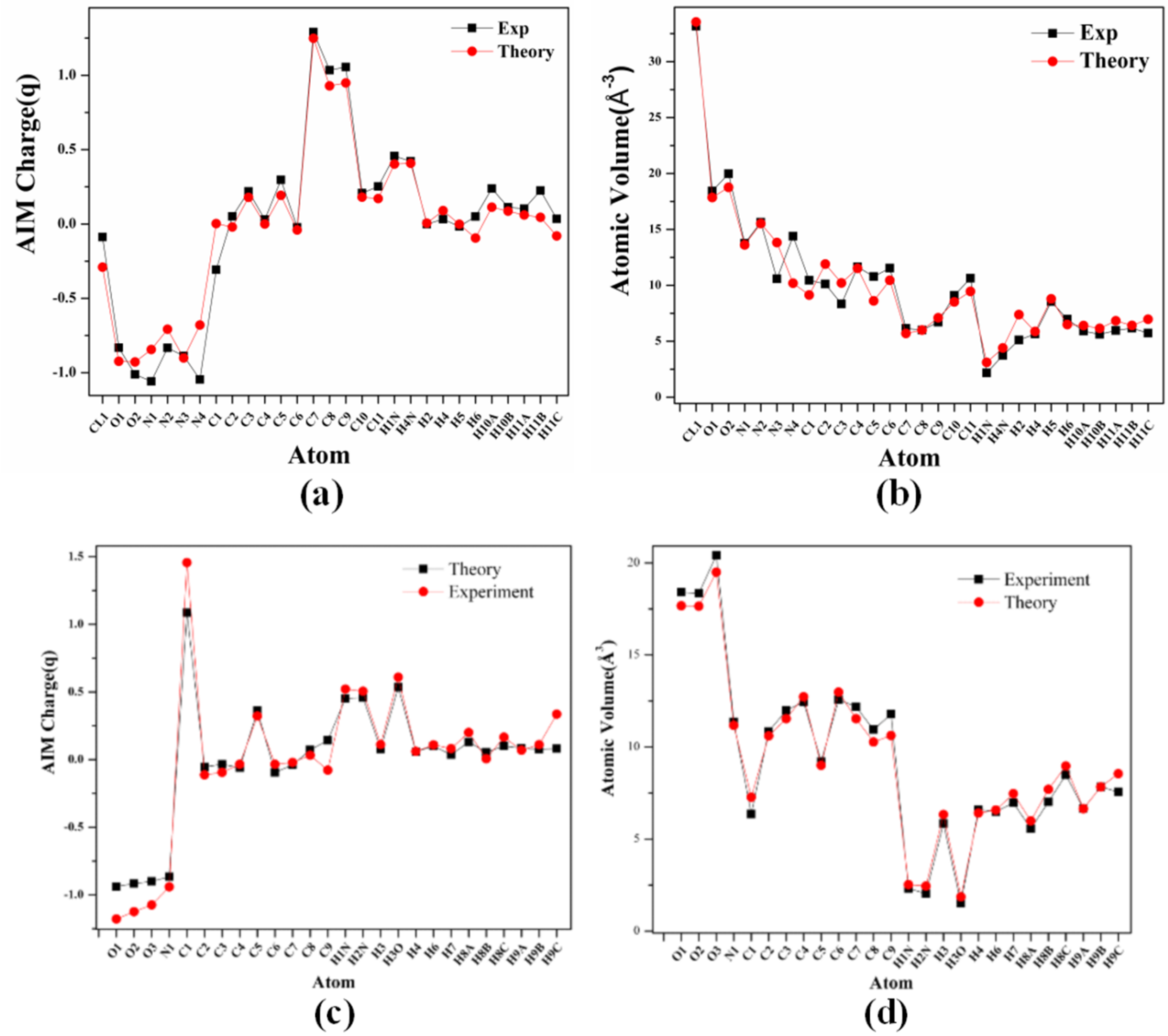


Figure 10: Comparison of intramolecular topological parameters in (a) and (b) **I** ;(b) and (d) **II**



(a) (b)

Figure 11: Laplacian plots for the (a) C-Cl···C (b) C-O···C interaction region



(a) (b) (c) (d)

Figure 12: Comparison between experiment and theory AIM charges (q) and atomic volumes in **I** (a) and (b); **II** (c) and (d)

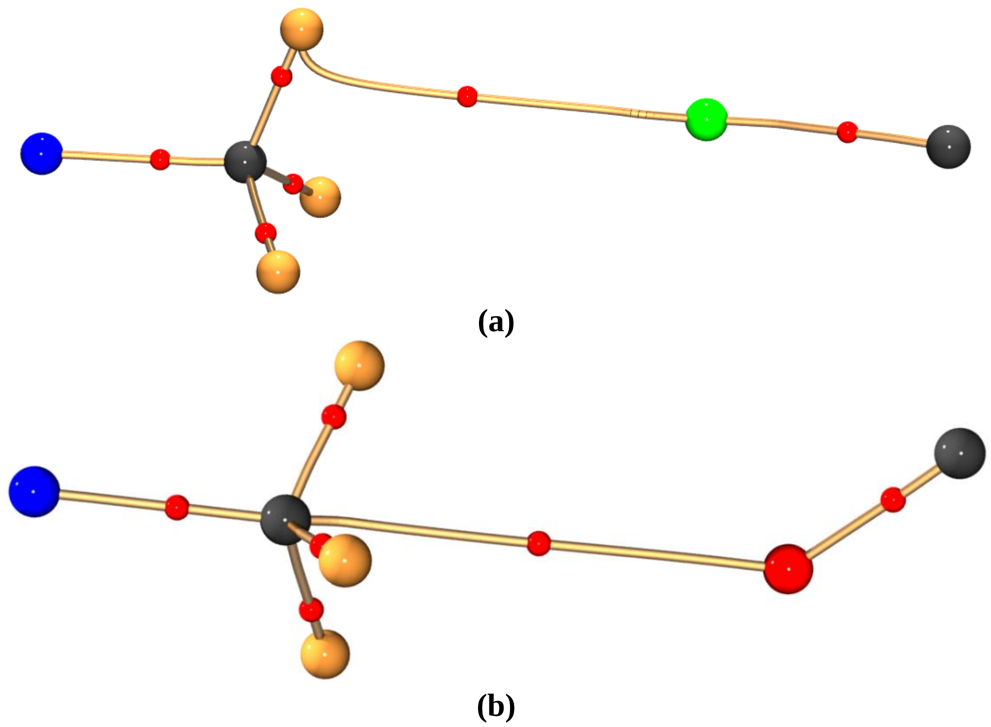


Figure 13: Theoretical bond paths together with bcp's in the intermolecular regions of (a) **I** (b) **II**

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