Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary material

Table S1. Rigid bond test for non-hydrogen atoms of (1)

Atom1	Atom2	Z^2A [Å²]	Z^2B [Å²]	ΔZ_{AB}^2 [Å2]
CL7	C7	0.0092	0.0096	-0.00037
CL4	C4	0.0091	0.0095	-0.00037
CL5	C5	0.0103	0.0106	-0.00037
CL6	C6	0.0109	0.0112	-0.00029
O9	C9	0.0086	0.0086	-0.00003
O2	C2	0.0088	0.0087	0.00004
N1	C2	0.0101	0.0103	-0.00021
N1	C9	0.0100	0.0103	-0.00027
N1	C10	0.0109	0.0117	-0.00073
C6	C5	0.0120	0.0120	0.00001
C6	C7	0.0120	0.0120	-0.00008
C3	C4	0.0103	0.0106	-0.00028
C3	C2	0.0115	0.0117	-0.00026
C3	C8	0.0085	0.0085	0.00003
C5	C4	0.0133	0.0131	0.00010
C8	C7	0.0104	0.0106	-0.00018
C8	C9	0.0110	0.0113	-0.00024
C10	C11	0.0157	0.0157	0.00004
C11	C12	0.0127	0.0128	-0.00011
C12	C13	0.0169	0.0169	-0.00006

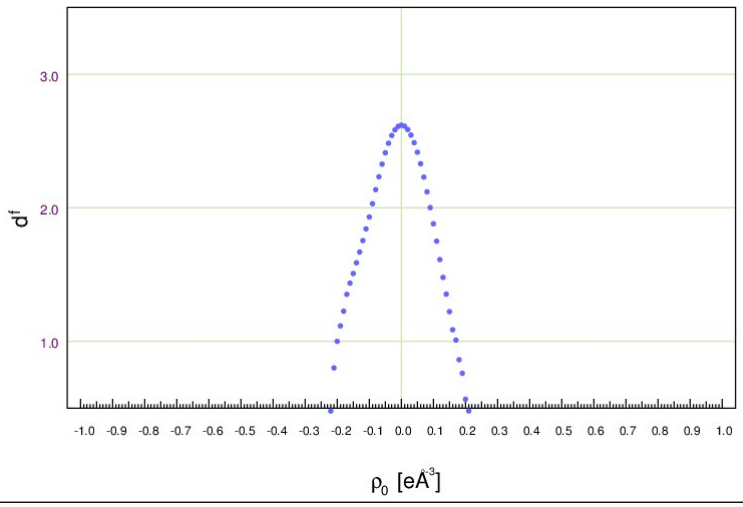


Figure S1. The RDA plots for N-n-Butyltetrachlororphthalimide

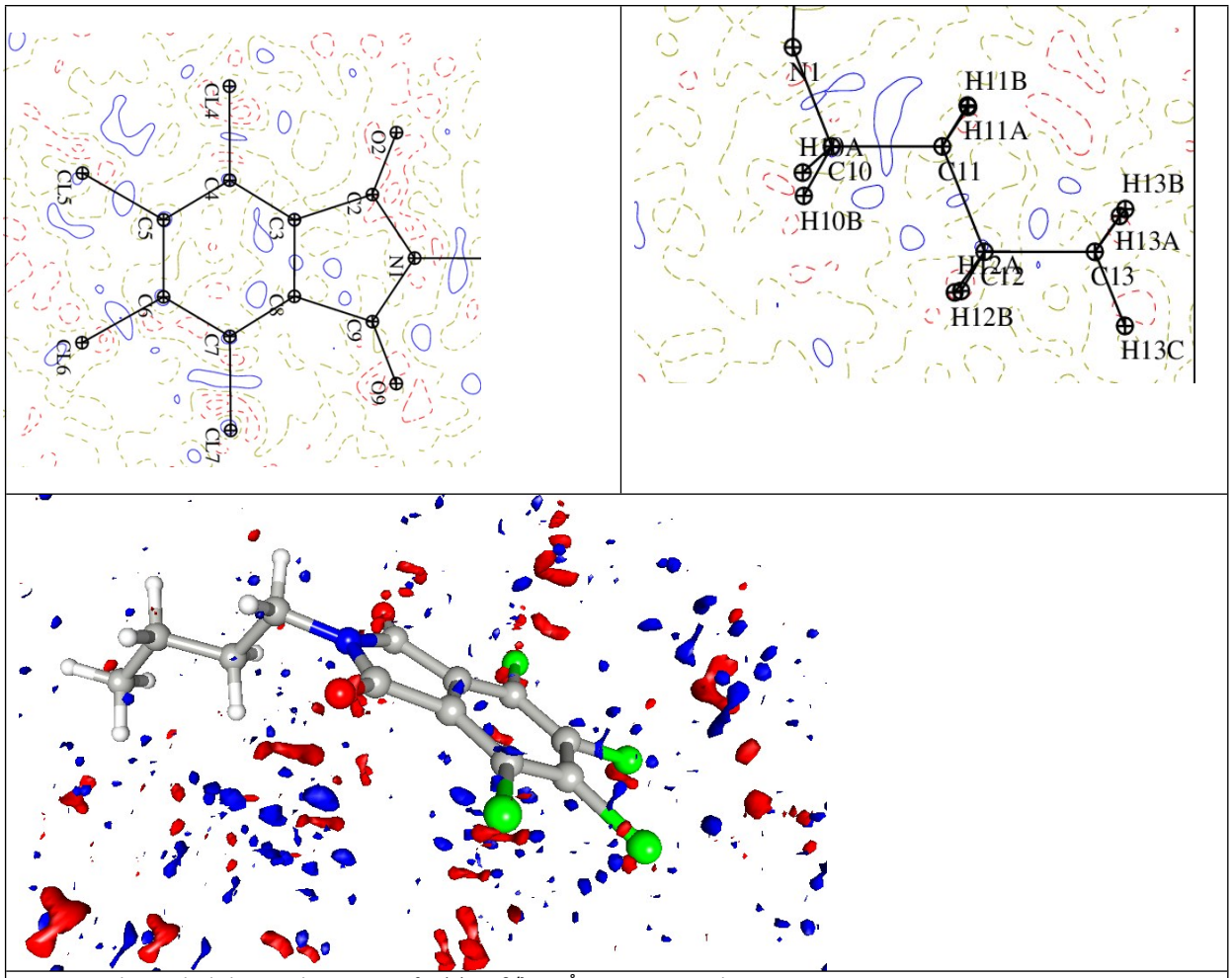


Figure S2. The residual electron density maps for (1), sinθ/λ>0.9Å-1 contours are drawn at intervals 0.05 e $Å^{-3}$3 (2dmaps), and 0.1e $Å^{-3}$ (3dmaps)

Table S2. Atomic Charges (e) in Molecule (1) by integration over atomic basins (Inte)

Atom	Atomic Charges (e)	Atom	Atomic Charges (e)
N1	-1,05862	O9	-0,97485
C2	1,265046	C10	0,351072
O2	-0,98243	C11	0,12537
C3	0,113848	C12	0,009775
C4	-0,02313	C13	-0,01669
CL4	-0,09949	H10A	0,085322
C5	-0,02281	H10B	0,08024
CL5	-0,12889	H11A	-0,01448
C6	-0,02248	H11B	0,008161
CL6	-0,11708	H12A	-0,00141
C7	-0,01638	H12B	0,000247
CL7	-0,10037	H13A	0,071445
C8	0,102588	H13B	0,032744
C9	1,257577	H13C	0,071285

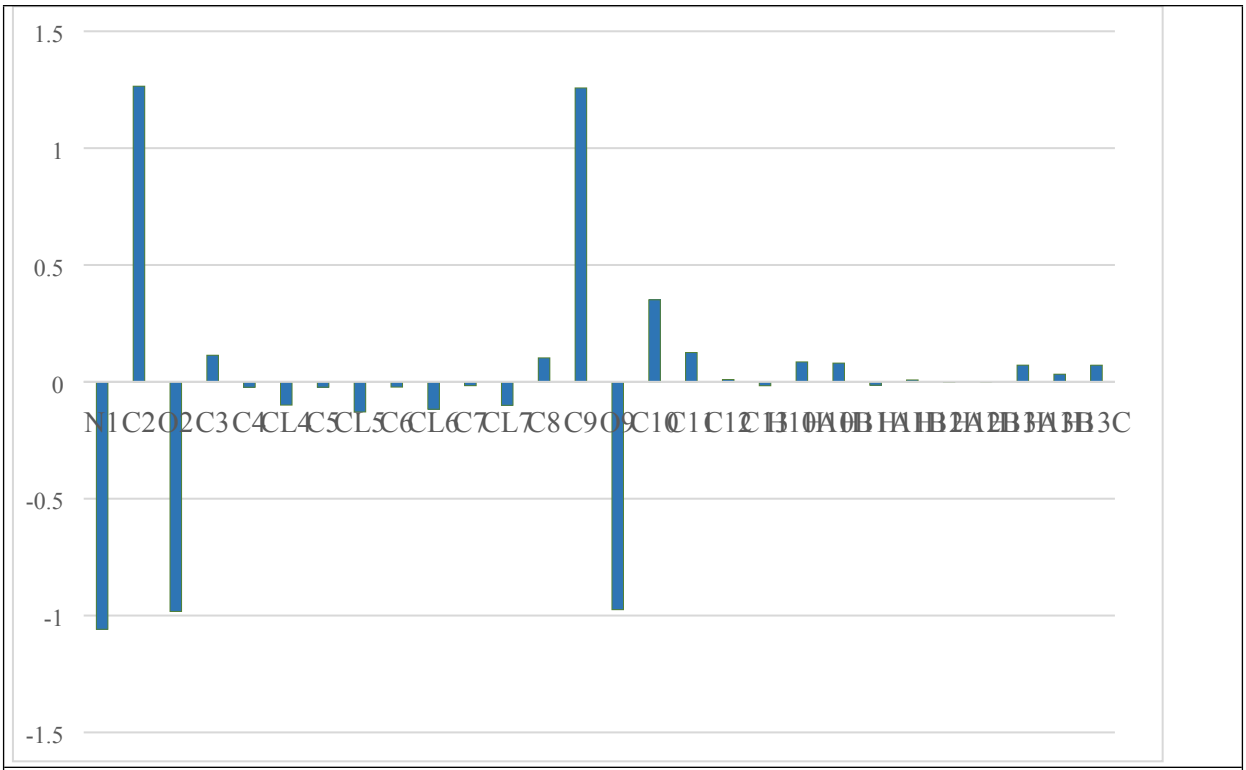


Figure S3. Graphical representation atomic charges (e) obtained by integration over atomic basins

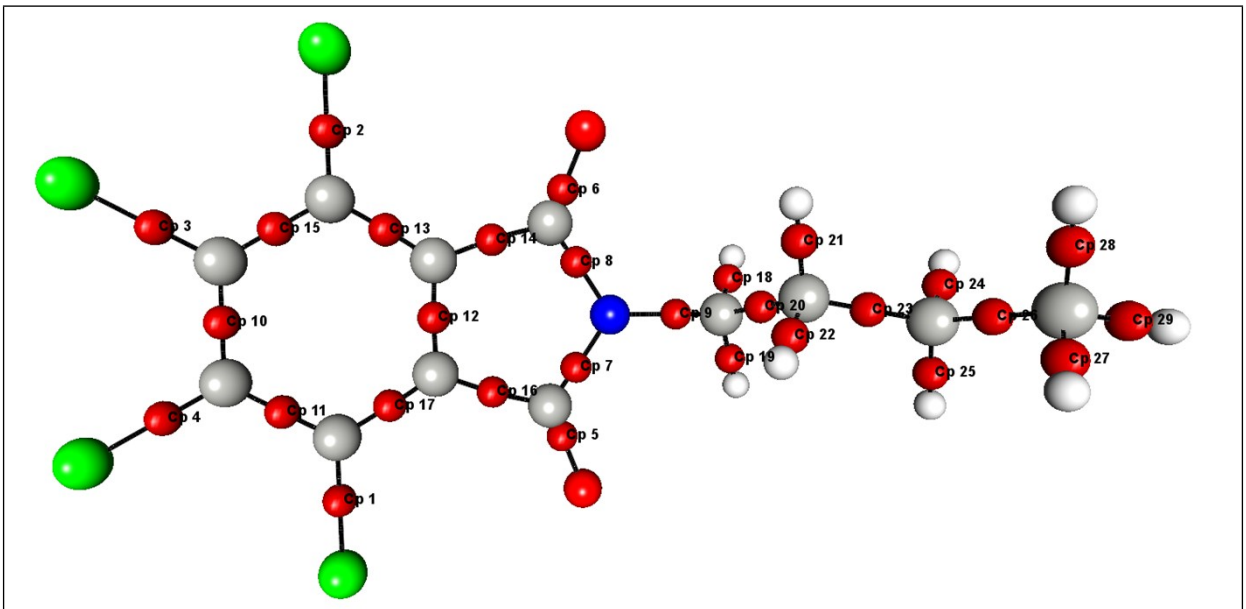


Figure S4. The bond critical point in molecule 1

Table S3. Characteristics of bond critical points (3,-1) .

Atom1	Atom2	$G(r_{CP})$ [kJ·mol^{-1}bohr^{-3}]	$V(r_{CP})$ [kJ·mol^{-1}bohr^{-3}]	D12[Å]	D1[Å]	D2[Å]	ρ_{tot} [e/Å^3]	∇^2 [e/Å^5]	λ_1	λ_2	λ_3	Ellip
O2	C2	1307,14	-3661,34	1,21	0,7695	0,4404	3,0487	-38,44	-30,71	-26,89	19,16	0,1419
O9	C9	1306,39	-3625,1	1,2105	0,771	0,4395	3,0269	-37,17	-30,43	-26,42	19,68	0,1516
C3	C4	771,86	-2081,97	1,3828	0,6715	0,7121	2,1619	-19,76	-17,56	-13,54	11,33	0,2969
C5	C4	791,86	-2082,15	1,408	0,704	0,7042	2,1544	-18,3	-16,96	-13,43	12,1	0,263
N1	C2	764,75	-2067,18	1,3901	0,803	0,5871	2,1533	-19,74	-17,67	-15,18	13,11	0,1639
N1	C9	770,01	-2068,84	1,3908	0,7998	0,5912	2,1526	-19,42	-17,73	-15,09	13,41	0,175
C8	C7	767,01	-2060,05	1,3839	0,6705	0,714	2,147	-19,31	-17,27	-13,41	11,37	0,2877
C6	C5	778,86	-2036,44	1,4045	0,7044	0,7004	2,1242	-17,58	-16,75	-13,01	12,18	0,2876
C6	C7	774,69	-2031,18	1,4077	0,7073	0,7006	2,1217	-17,69	-16,64	-13,05	12	0,2743
C3	C8	741,42	-1969,97	1,3935	0,696	0,6978	2,087	-17,88	-16,13	-13,32	11,57	0,2108
C13	H13B	563,14	-1561,27	1,0768	0,6731	0,4038	1,8257	-15,97	-15,9	-15,86	15,78	0,0028
C13	H13A	560,24	-1549,69	1,0767	0,6817	0,3951	1,8171	-15,76	-16,06	-15,83	16,13	0,0143
C12	H12A	556,34	-1538,19	1,0913	0,675	0,4163	1,8088	-15,62	-15,16	-15,1	14,64	0,0046
C12	H12B	555,57	-1532,5	1,0919	0,6756	0,4164	1,8043	-15,47	-15,13	-14,99	14,65	0,009
C10	H10B	553,1	-1529,32	1,0914	0,6812	0,4103	1,8026	-15,54	-16,02	-15,22	15,71	0,0526
C10	H10A	544,56	-1513,47	1,0913	0,6775	0,4138	1,7926	-15,58	-15,93	-14,99	15,34	0,0628
C8	C9	584,91	-1520,01	1,4951	0,741	0,7552	1,7807	-12,86	-13,19	-11,49	11,82	0,148
C11	H11A	546,37	-1492,08	1,0922	0,6773	0,415	1,7732	-14,66	-14,92	-14,67	14,92	0,0167
C3	C2	580,22	-1506,83	1,4954	0,7455	0,7506	1,7713	-12,72	-13,16	-11,36	11,81	0,1586
C13	H13C	535,12	-1482,02	1,0769	0,6742	0,4028	1,7693	-15,12	-15,32	-15,29	15,49	0,0019
C11	H11B	536,21	-1464,49	1,0911	0,674	0,4171	1,7535	-14,39	-14,6	-14,46	14,67	0,0101
N1	C10	574,79	-1389,84	1,4564	0,8554	0,6011	1,6695	-8,82	-11,19	-10,9	13,26	0,0263
C11	C12	526,26	-1300,8	1,5243	0,7557	0,7686	1,6099	-9,12	-10,35	-10,21	11,44	0,0138
C10	C11	529,18	-1297,72	1,528	0,7828	0,7452	1,6057	-8,79	-10,71	-10,11	12,03	0,0587
C12	C13	526,43	-1282,35	1,5246	0,761	0,7636	1,5926	-8,43	-10,29	-10,19	12,05	0,0104
CL5	C5	501,66	-1117,29	1,7088	0,9441	0,7647	1,4449	-4,18	-8,63	-7,63	12,07	0,1317
CL6	C6	488,74	-1097,54	1,7099	0,9473	0,7626	1,4315	-4,41	-8,59	-7,62	11,8	0,1278
CL4	C4	490,93	-1085,98	1,7118	0,9397	0,7722	1,4187	-3,82	-8,34	-7,42	11,94	0,1247

CL7	C7	482,27	-1061,94	1,7134	0,9387	0,7747	1,3987	-3,58	-8,13	-7,27	11,83	0,1184	

Table S4: Topological characteristic of the intermolecular critical points(3,-11)

Atom1	Atom2	Symm. codes	$G(r_{CP})$ [kJ·mol^{-1} bohr^{-3}]	$V(r_{CP})$[kJ·mol^{-1} bohr^{-3}]	D12[Å]	D1[Å]	D2[Å]	ρ_{tot} [e/Å^3]	∇^2 [e/Å^5]	λ_1	λ_2	λ_3	Ellip	$E(r_{CP})$ [kJ·mol^{-1} bohr^{-3}]	$\lvert V(r_{CP})\rvert / G(r_{CP})$
CL4	O2	57651	21,96	-16,92	2,953	1,5658	1,3874	0,0727	0,99	-0,2	-0,2	1,39	0,0014	5,04	0,770492
O2	CL4	57651	21,96	-16,92	2,953	1,3874	1,5658	0,0727	0,99	-0,2	-0,2	1,39	0,0014	5,04	0,770492
CL7	O9	76651	19,19	-14,52	3,0069	1,5988	1,4083	0,065	0,88	-0,18	-0,18	1,23	0,016	4,67	0,756644
O9	CL7	76651	19,19	-14,52	3,0069	1,4083	1,5988	0,065	0,88	-0,18	-0,18	1,23	0,016	4,67	0,756644
CL7	C5	65501	13,69	-10,49	3,3595	1,7406	1,6225	0,0542	0,62	-0,09	-0,07	0,79	0,2997	3,2	0,766253
C5	CL7	45501	13,69	-10,49	3,3595	1,6225	1,7406	0,0542	0,62	-0,09	-0,07	0,79	0,2997	3,2	0,766253
CL7	C9	66651	13,41	-10,14	3,2972	1,7603	1,5446	0,0523	0,61	-0,11	-0,04	0,76	1,5141	3,27	0,756152
C9	CL7	66651	13,41	-10,14	3,2972	1,5446	1,7603	0,0523	0,61	-0,11	-0,04	0,76	1,5141	3,27	0,756152
CL4	C8	45501	12,26	-9,2	3,3817	1,7669	1,619	0,0489	0,56	-0,09	-0,06	0,71	0,5136	3,06	0,750408
C8	CL4	65501	12,26	-9,2	3,3817	1,619	1,7669	0,0489	0,56	-0,09	-0,06	0,71	0,5136	3,06	0,750408
CL4	CL4	57651	11,76	-8,34	3,5412	1,7706	1,7706	0,0428	0,56	-0,09	-0,09	0,74	0,0175	3,42	0,709184
CL6	H11B	66651	12,31	-8,46	2,8568	1,7605	1,1313	0,0412	0,59	-0,12	-0,1	0,82	0,2359	3,85	0,687246
H11B	CL6	66651	12,31	-8,46	2,8568	1,1313	1,7605	0,0412	0,59	-0,12	-0,1	0,82	0,2363	3,85	0,687246
CL5	C13	45401	10,51	-7,43	3,4916	1,7732	1,7287	0,0398	0,5	-0,07	-0,05	0,62	0,5529	3,08	0,706946
C13	CL5	65601	10,51	-7,44	3,4916	1,7285	1,7733	0,0398	0,5	-0,07	-0,05	0,62	0,5639	3,07	0,707897
CL5	C13	55401	10,15	-7,16	3,5174	1,8057	1,7233	0,0387	0,48	-0,07	-0,04	0,6	0,6427	2,99	0,705419
C13	CL5	55601	10,15	-7,16	3,5174	1,7233	1,8057	0,0387	0,48	-0,07	-0,04	0,6	0,6427	2,99	0,705419
CL5	CL6	45501	9,57	-6,71	3,6374	1,8102	1,832	0,037	0,46	-0,07	-0,05	0,58	0,4702	2,86	0,701149
CL6	CL5	65501	9,57	-6,71	3,6374	1,832	1,8102	0,037	0,46	-0,07	-0,05	0,58	0,4698	2,86	0,701149
H12A	H13B	67751	8,82	-5,68	2,3213	1,2249	1,3011	0,0288	0,44	-0,07	-0,05	0,56	0,484	3,14	0,643991
H13B	H12A	67751	8,82	-5,68	2,3213	1,3011	1,2249	0,0288	0,44	-0,07	-0,05	0,56	0,484	3,14	0,643991
CL7	H11B	66651	9,89	-6,2	2,9131	1,8581	1,1023	0,0286	0,5	-0,07	-0,07	0,64	0,0126	3,69	0,626896
H11B	CL7	66651	9,89	-6,2	2,9131	1,1024	1,8581	0,0286	0,5	-0,07	-0,07	0,64	0,0136	3,69	0,626896
H12A	H12A	67751	7,51	-4,96	2,8157	1,4079	1,4079	0,0279	0,37	-0,04	-0,02	0,43	0,8363	2,55	0,660453
H12A	H12A	77751	7,69	-5,02	2,6633	1,3316	1,3316	0,0274	0,38	-0,07	-0,06	0,51	0,2685	2,67	0,652796

H11A	H12A	67751	7,6	-4,9	2,4402	1,3358	1,2935	0,0264	0,38	-0,05	-0,04	0,47	0,503	2,7	0,644737
H12A	H11A	67751	7,6	-4,9	2,4402	1,2935	1,336	0,0264	0,38	-0,05	-0,04	0,47	0,5067	2,7	0,644737
CL7	CL7	76651	6,9	-4,51	3,797	1,8985	1,8985	0,0259	0,34	-0,05	-0,04	0,43	0,1441	2,39	0,653623
H10A	H12A	77751	6,79	-4,36	2,7734	1,4557	1,3233	0,0243	0,34	-0,07	-0,04	0,45	0,4762	2,43	0,642121
H12A	H10A	77751	6,79	-4,36	2,7734	1,3234	1,4556	0,0243	0,34	-0,07	-0,04	0,45	0,4762	2,43	0,642121
O9	C11	76651	3,74	-2,19	3,8277	1,7538	2,0744	0,0126	0,19	-0,03	-0,01	0,24	0,8225	1,55	0,585561
O9	C11	65501	3,74	-2,19	3,8277	1,7538	2,0744	0,0126	0,19	-0,03	-0,01	0,24	0,8228	1,55	0,585561
C11	O9	45501	3,74	-2,19	3,8277	2,0744	1,7538	0,0126	0,19	-0,03	-0,01	0,24	0,8219	1,55	0,585561
O2	H13C	67751	3,63	-2,02	3,0362	1,7818	1,3723	0,0098	0,19	-0,02	-0,02	0,24	0,0502	1,61	0,556474
H13C	O2	67751	3,63	-2,02	3,0362	1,3723	1,7818	0,0098	0,19	-0,02	-0,02	0,24	0,0502	1,61	0,556474
H10B	H11A	65501	7,65	-3,98	2,2246	1,1203	1,1705	0,008	0,42	-0,04	-0,01	0,47	1,8893	3,67	0,520261
H11A	H10B	45501	7,66	-3,98	2,2246	1,1702	1,1201	0,008	0,42	-0,04	-0,01	0,47	1,8903	3,68	0,519582
H12B	H13B	65501	8,19	-4,2	2,2577	1,1385	1,1257	0,0064	0,45	-0,03	-0,01	0,49	2,3277	3,99	0,512821
H13B	H12B	45501	8,18	-4,19	2,2577	1,1255	1,1389	0,0064	0,45	-0,03	-0,01	0,49	2,3426	3,99	0,512225

Energy framework analysis on interaction energies

Intermolecular interaction energies, calculated for the energy framework analysis were obtained using CrystalExplorer 17. This calculation is estimated from a single point molecular wavefunction at B3LYP/6-31G(d,p) .The energy of interaction between molecules is expressed in terms of four key components: electrostatic(E_{ele}), polarization(E_{pol}), dispersion(E_{dis}), and exchange-repulsion(E_{repl}).The total interaction energy is the sum of scaled components, see table S5.

Relatively strong interactions we can observed in stacked pairs (-39,7/38,5 kJ mol−1; Table S5,).Between adjacent molecules connected by halogen bond (Cl···O) electrostatic contribution and dispersion is simila r(-10,2 kJ·mol^{-1} vs 10 kJ·mol^{-1}Table S5) Much smaller interaction energies between molecules where occurred halogen···halogen contact (-1.9 kJ mol−1).

The molecular pair-wise interaction energies calculated for the construction of energy frameworks are used to evaluate the net interaction energies. The total interaction energies are electrostatic (E_{ele}= −83.8 kJ·mol^{-1}), polarization (E_{pol}= −12.3 kJ·mol^{-1}), dispersion (E_{dis}= −235,7kJ·mol^{-1}), repulsion (E_{rep}= 208.8kJ·mol^{-1}), and total interaction energy (E_{tot} = −173.9 kJ·mol^{-1}). The dispersion energy framework is dominant over the electrostatic energy framework **(Figure S6)**

Table S5 Interaction energies (kJ mol^{-1}) between a reference molecule and its neighbours. R is the distance between molecular centroids (mean atomic position) in A˚ . The colours identify molecules in **Figure S5**

	Symmop	R	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}[i]
	-x, -y, -z	11.04	-0.1	-0.1	-7.7	8.1	-1.9
	x, y, z	12.40	-2.1	-0.1	-9.6	8.4	-5.5
	x, y, z	5.20	-16.7	-2.5	-54.0	43.5	-39.7
	x, y, z	12.08	-1.6	-0.1	-10.6	7.5	-6.3
	-x, -y, -z	8.35	-13.0	-2.1	-11.2	22.0	-11.5
	-x, -y, -z	5.31	-20.2	-2.3	-56.3	54.4	-38.5
	-x, -y, -z	6.14	-14.5	-1.7	-33.8	24.4	-30.9
	-x, -y, -z	12.70	-4.8	-1.2	-26.5	17.0	-18.5
	-x, -y, -z	8.58	-10.2	-1.8	-10.0	14.9	-11.6
	-x, -y, -z	12.80	-0.6	-0.4	-16.0	8.6	-9.5

i Scale factors used to determine E tot: k ele = 1.057, k pol = 0.740, k dis = 0.871, k rep = 0.618

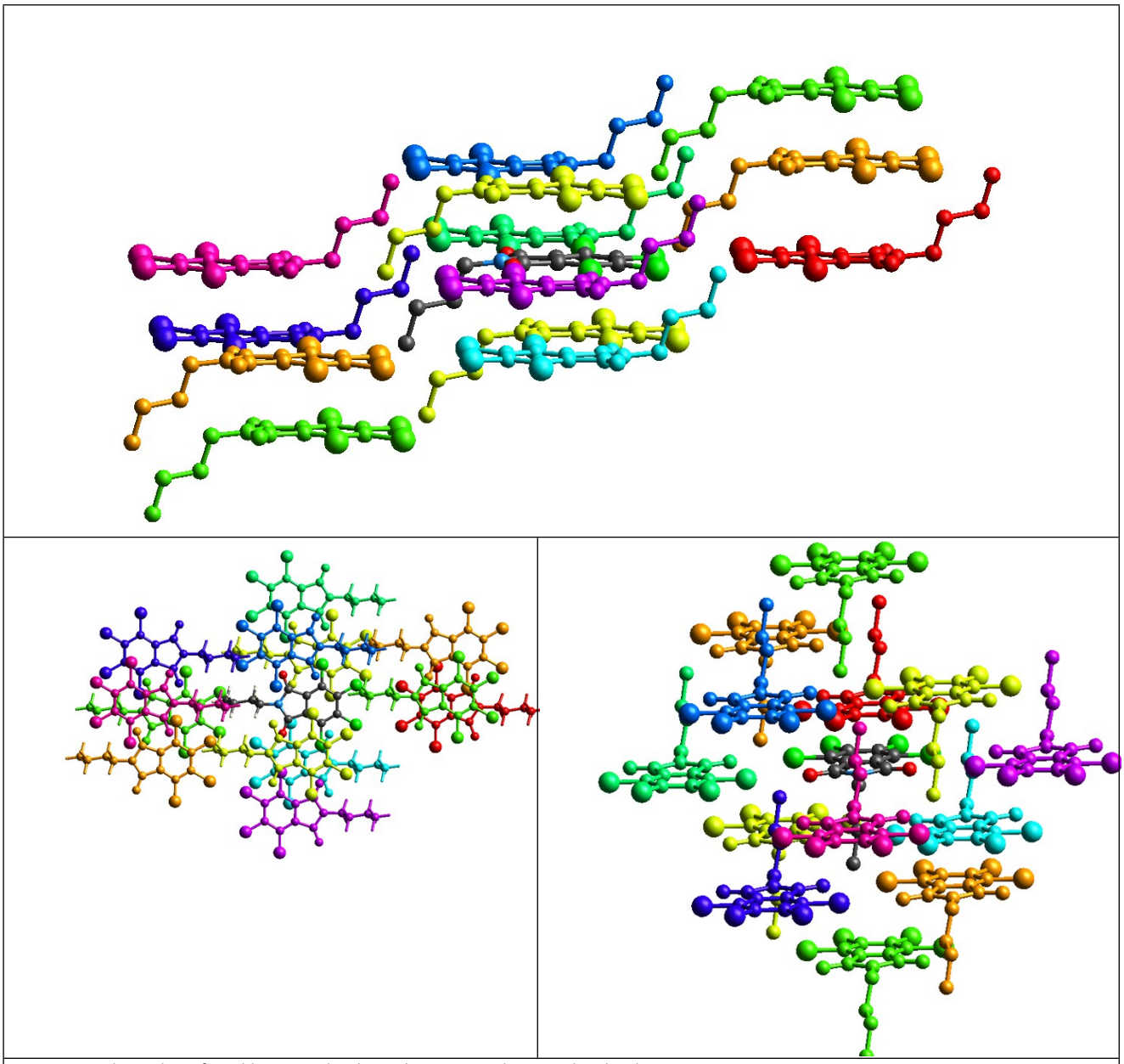
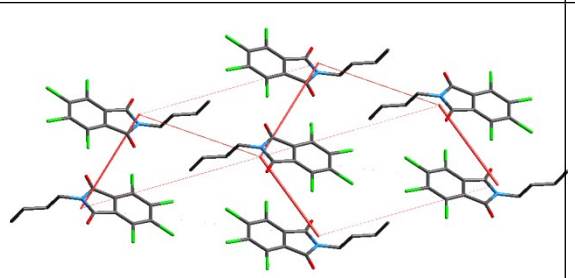
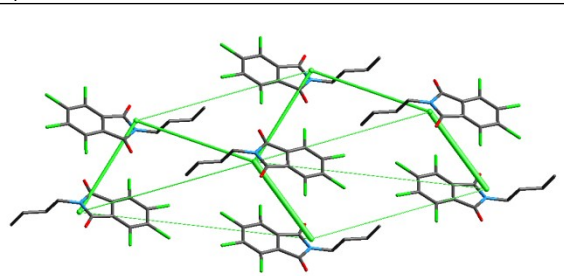
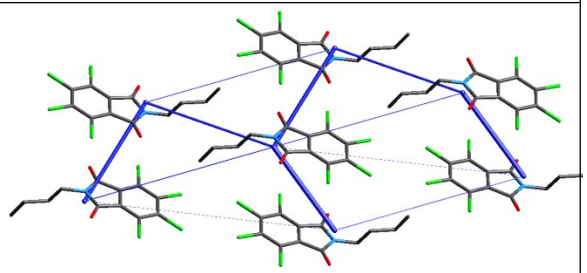
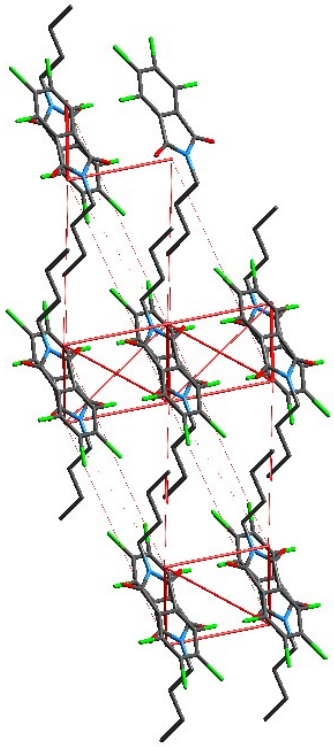
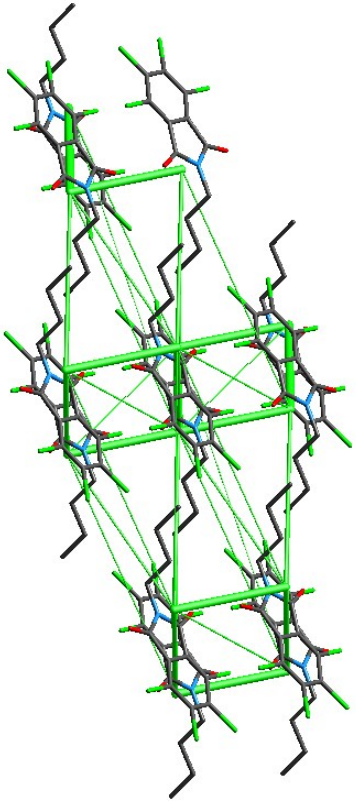
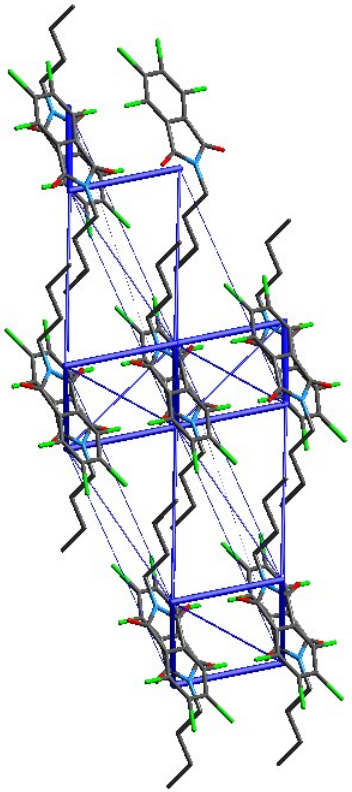


Figure S5: Color-coding of neighboring molecules with respect to the central molecule.

axis	Electrostatic termS	Dispersion terms	Total interactions energy
a			
b			

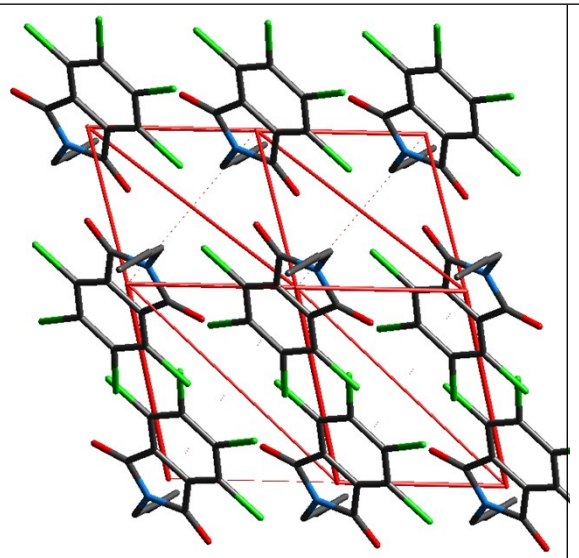
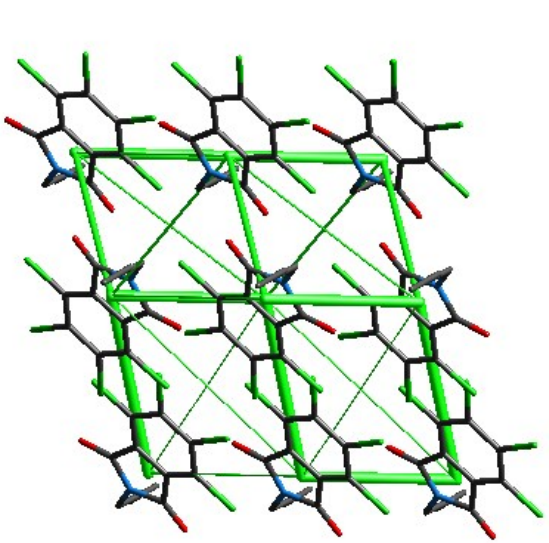
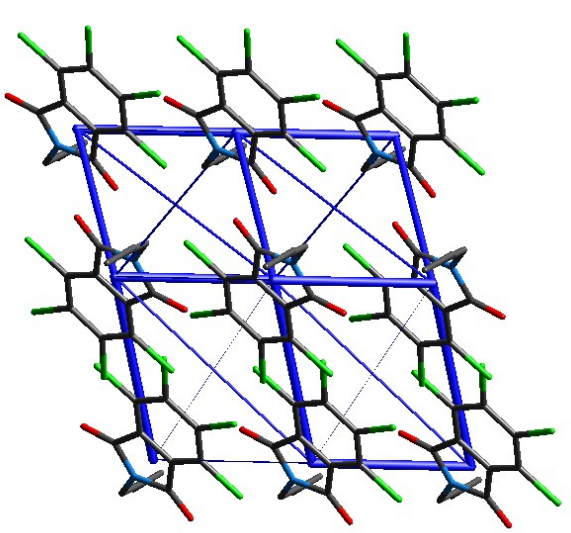
c			

Figure S6. Energy frameworks corresponding to the different energy components and the total interaction energy along a, b and c-axis. The tube size used in all the energy frameworks was 60.

Hirshfeld surface

The 2D fingerprint (Figure S7) of the Hirschfeld surface summarizes the complex information contained in a molecular crystal structure. The largest contribution (more than 29%) to the total Hirschfeld surface comes from the weak hydrogen bonds, CH···Cl, which are reflected as two wide wings, and H···H contacts, indicated by a large spike in the middle of the diagram. The Cl···C (π) contacts contribute 14.6% to the Hirschfeld surface, whereas 9.8% comes from the major halogen bond Cl···O. Apart from these interactions, there remain only Cl···Cl (7.5%) and other contacts observed in the central region of the diagram.

Figure S7 (a) Fingerprint plot of the Hirschfeld surface. (b) Percentage contributions to the Hirschfeld surface area for various intermolecular contacts