Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supporting Information

For paper

Role of Supramolecular Synthons in the Formation of Supramolecular Architecture of Molecular Crystals Revisited from Energetic Viewpoint

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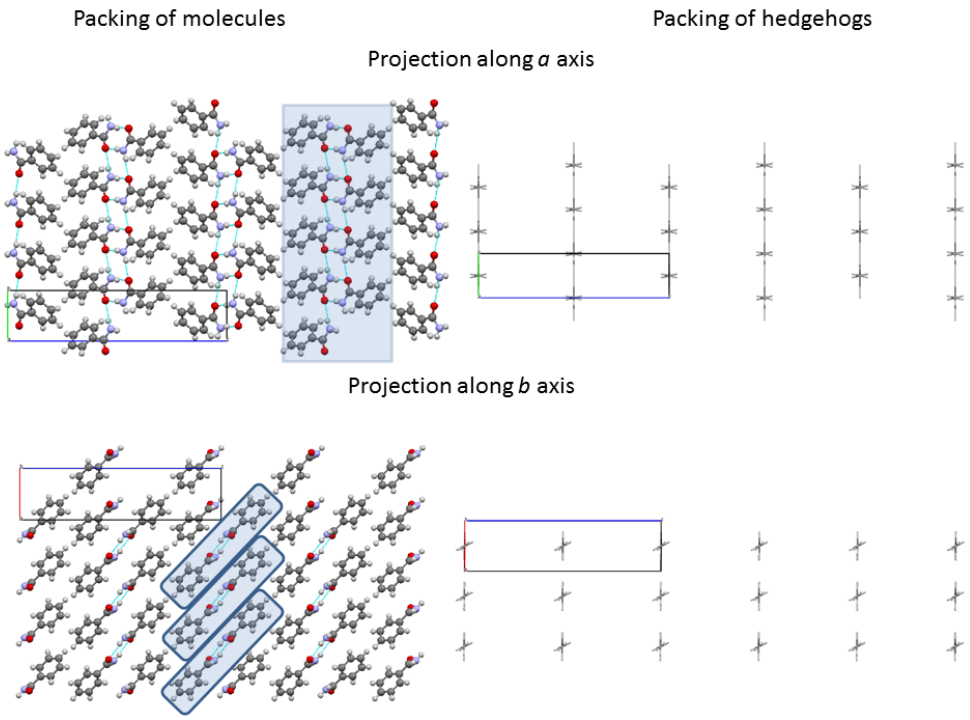

Figure S1. Supramolecular architecture of benzamide crystal 7 presented as packing of molecules and hedgehogs of intermolecular interactions for molecular complexes. Columns of molecular complexes are highlighted.

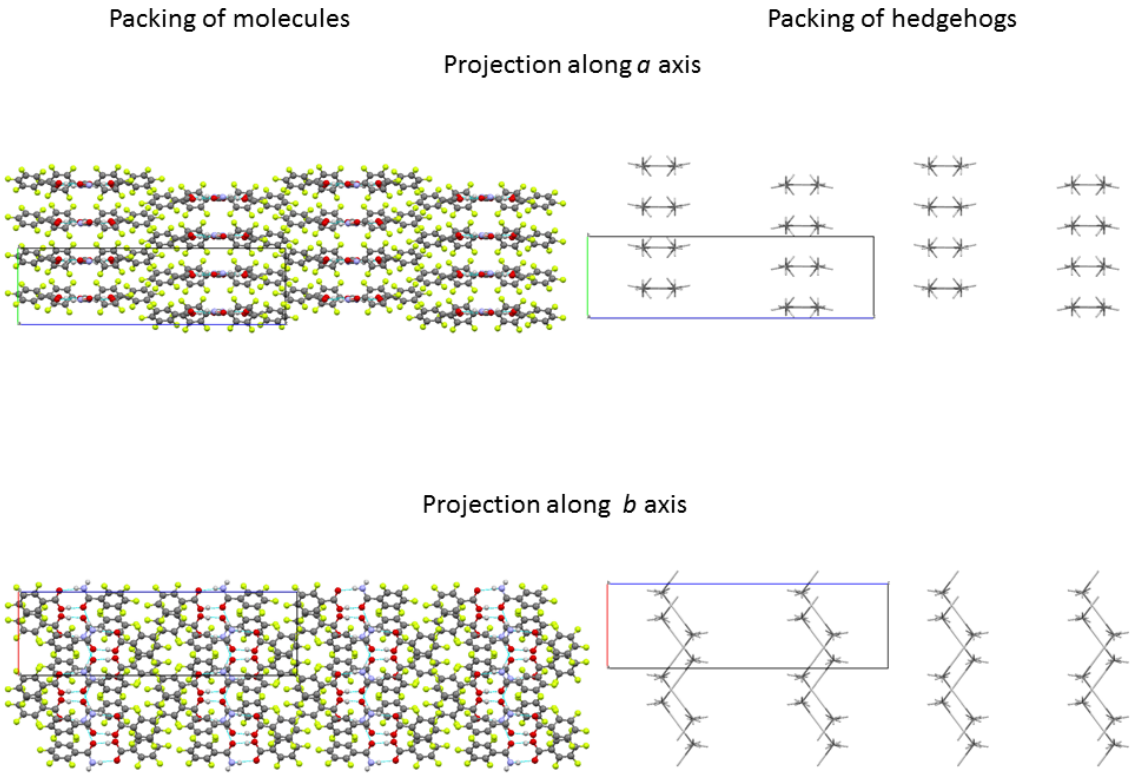

Figure S2. Supramolecular architecture of the co-crystal 8 presented as packing of molecules and hedgehogs of intermolecular interactions for molecular complexes.

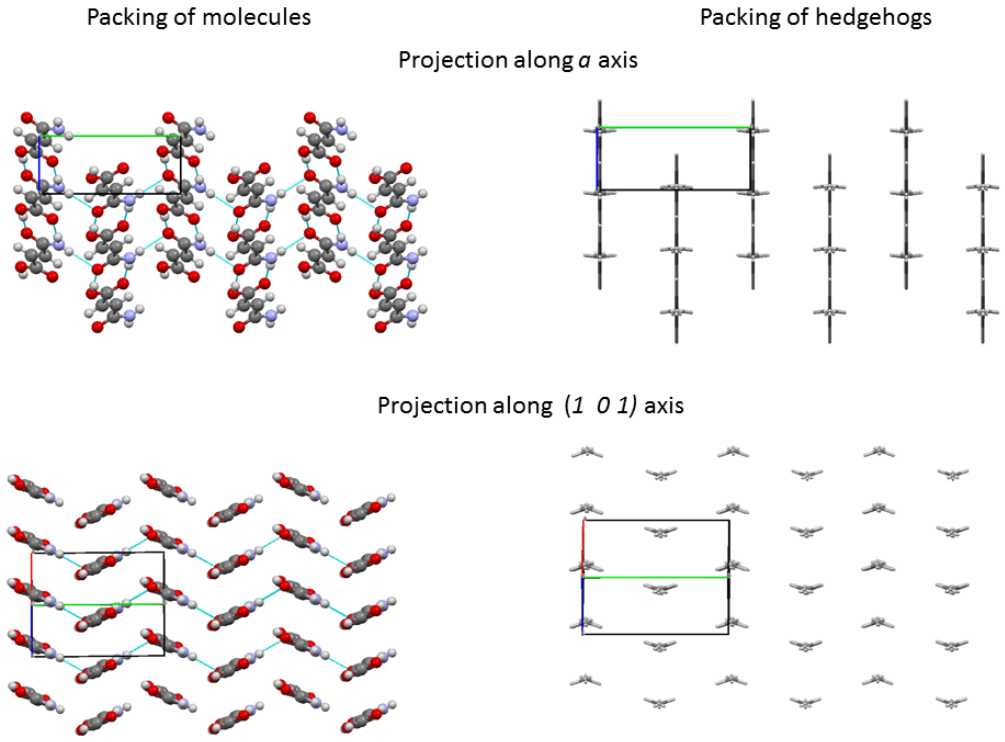

Figure S3. Supramolecular architecture of the crystal 9 presented as packing of molecules and hedgehogs of intermolecular interactions.

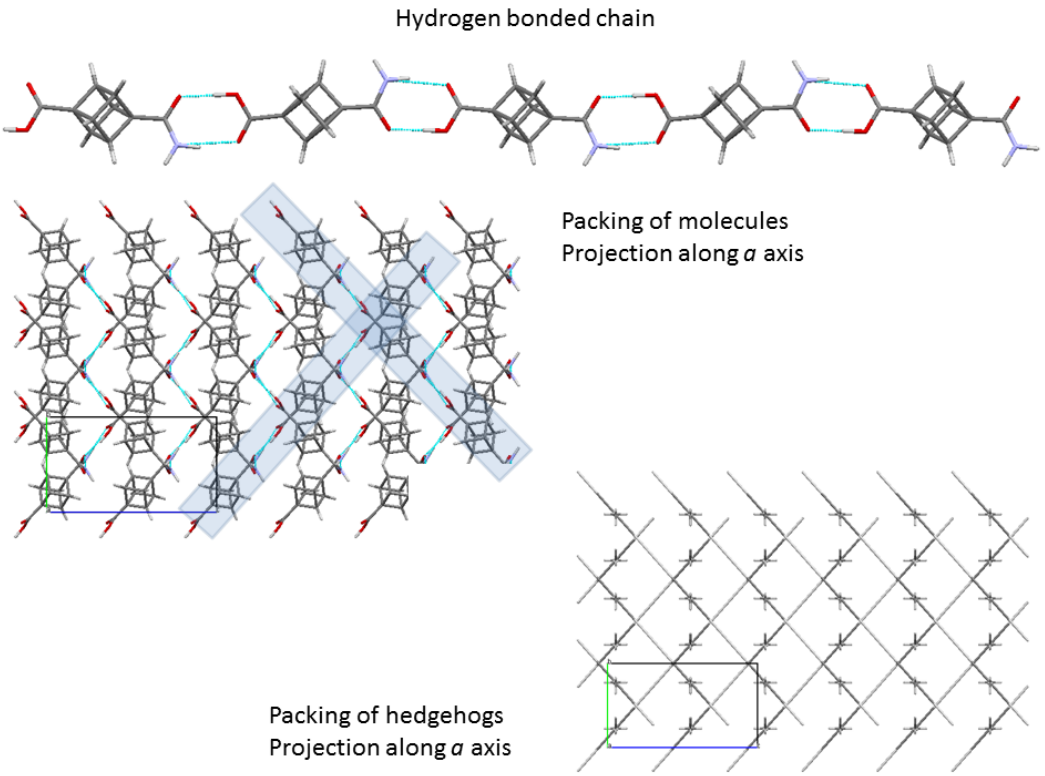

Figure S4. Supramolecular architecture of the crystal 10 presented as packing of molecules and hedgehogs of intermolecular interactions. Hydrogen bonded columns/chains are highlighted.

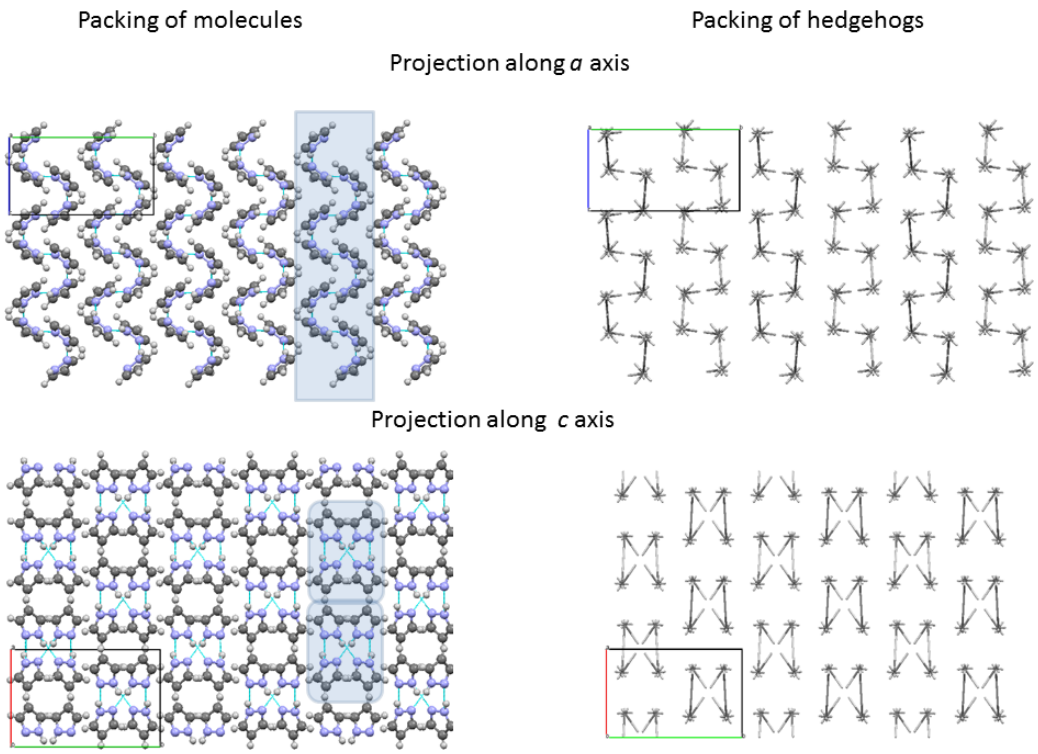

Figure S5. Supramolecular architecture of the crystal pyrazole 11 presented as packing of molecules and hedgehogs of intermolecular interactions. Hydrogen bonded columns/chains are highlighted.

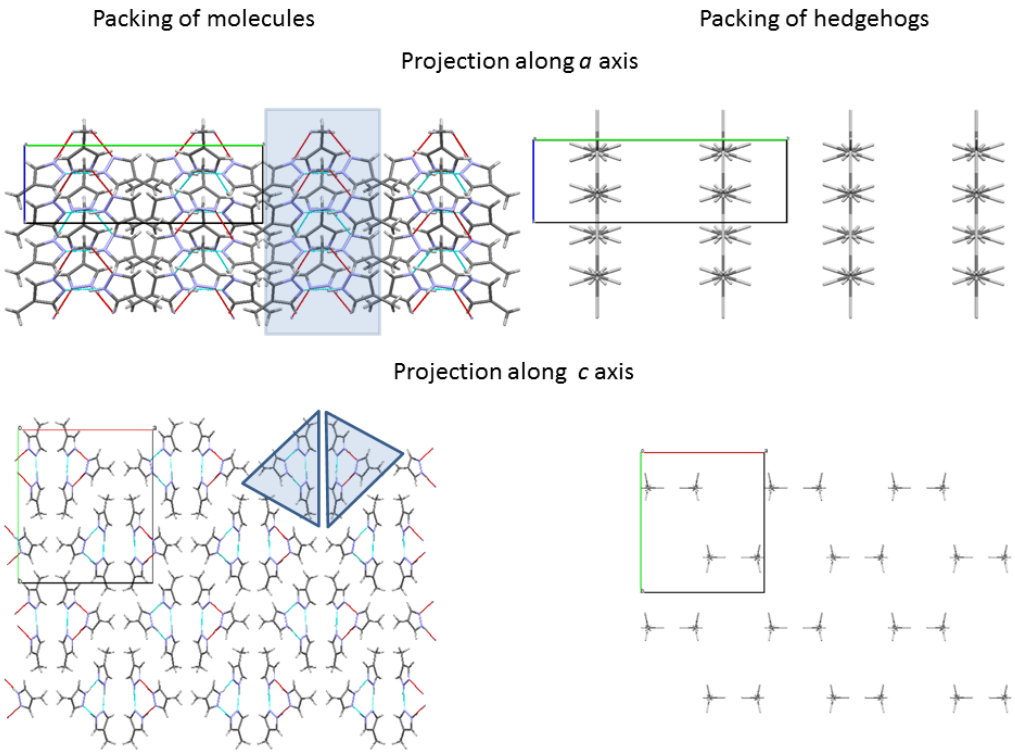

Figure S6. Supramolecular architecture of the crystal methylpyrazole 12 presented as packing of molecules and hedgehogs of intermolecular interactions for molecular complexes. Strongly bonded columns/chains are highlighted.

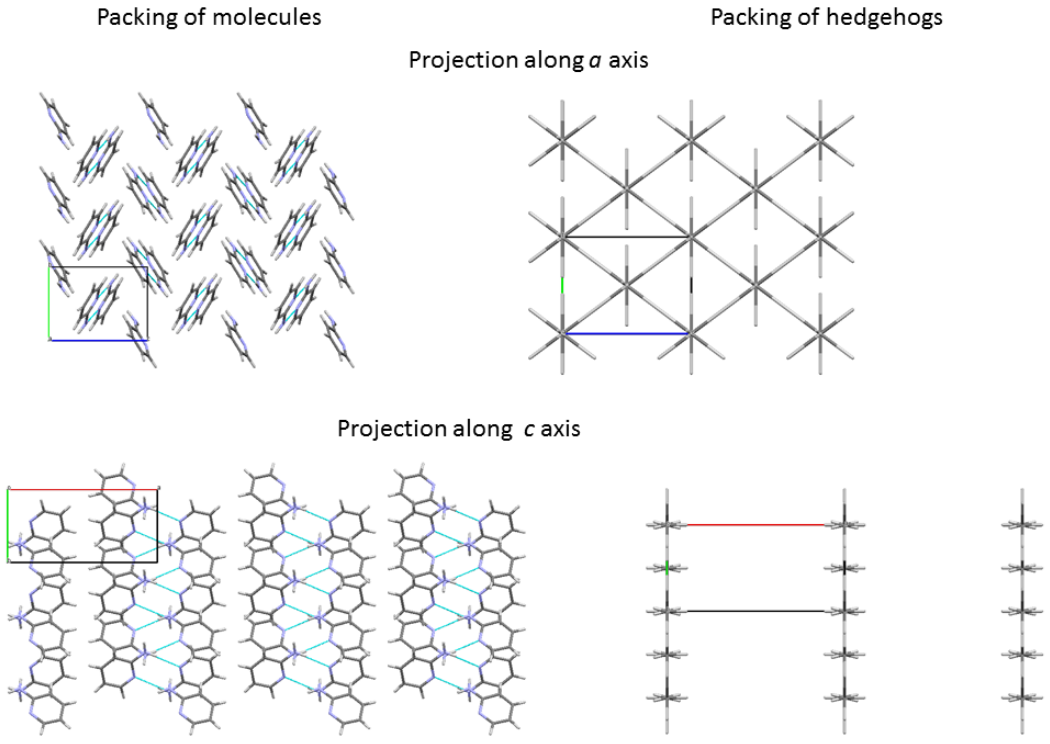

Figure S7. Supramolecular architecture of the crystal of 2-aminopyridine 13 presented as packing of molecules and hedgehogs of intermolecular interactions for molecular complexes.

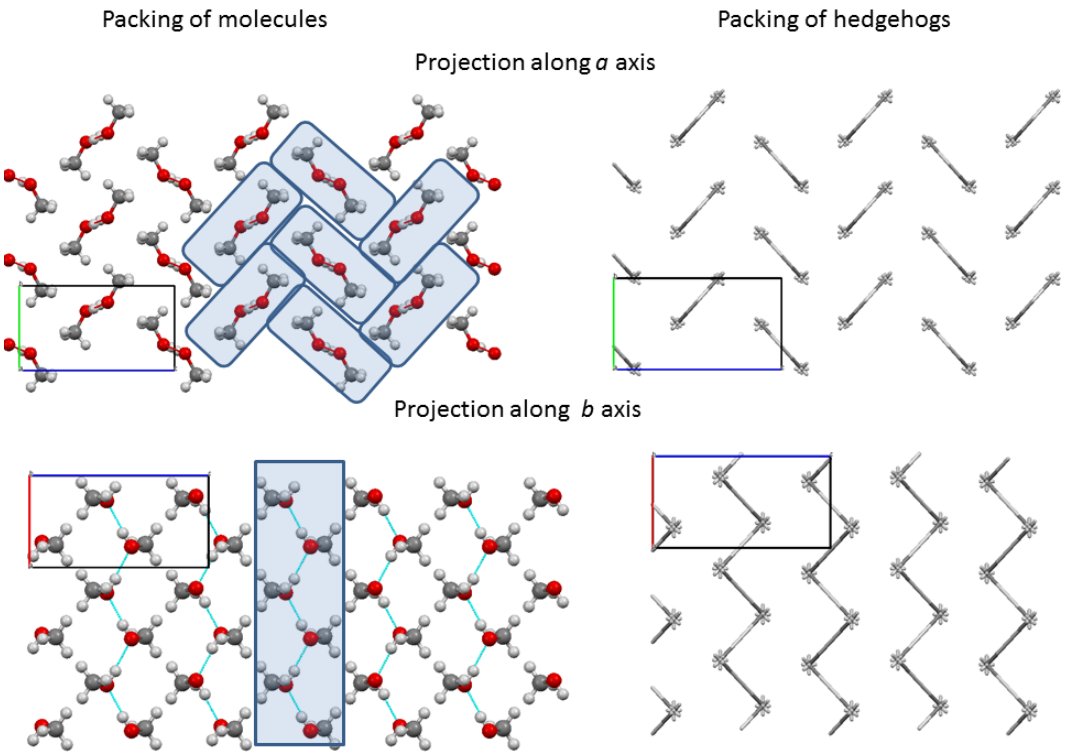

Figure S8. Supramolecular architecture of the methanol crystal 14 presented as packing of molecules and hedgehogs of intermolecular interactions of molecules.

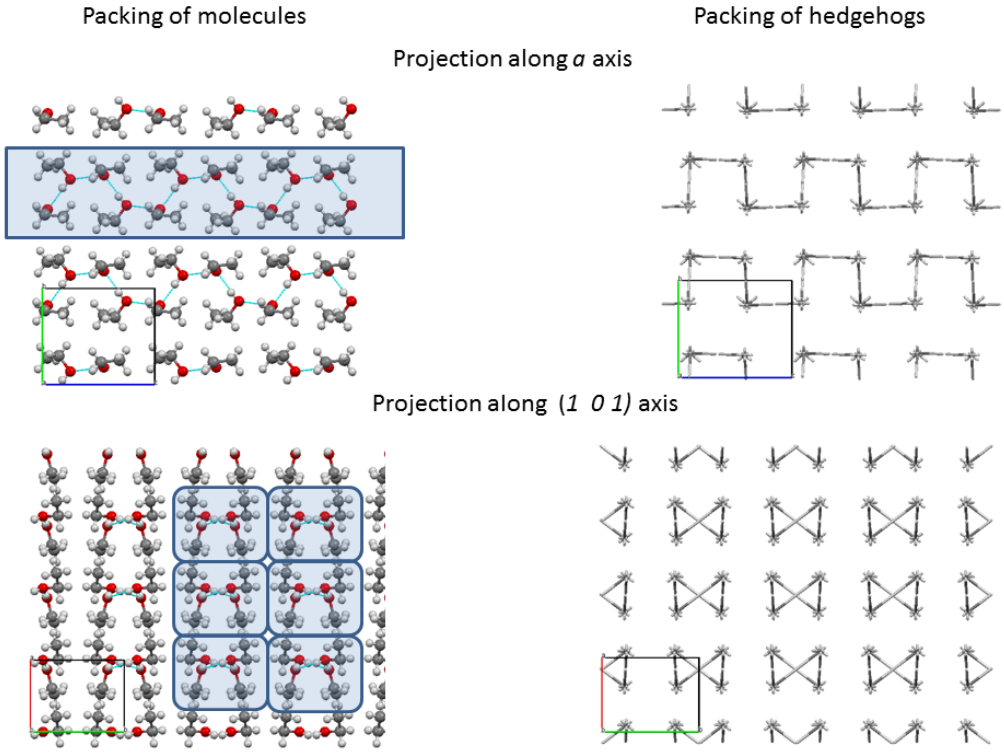

Figure S9. Supramolecular architecture of the ethanol crystal **15** presented as packing of molecules and hedgehogs of intermolecular interactions of molecules.

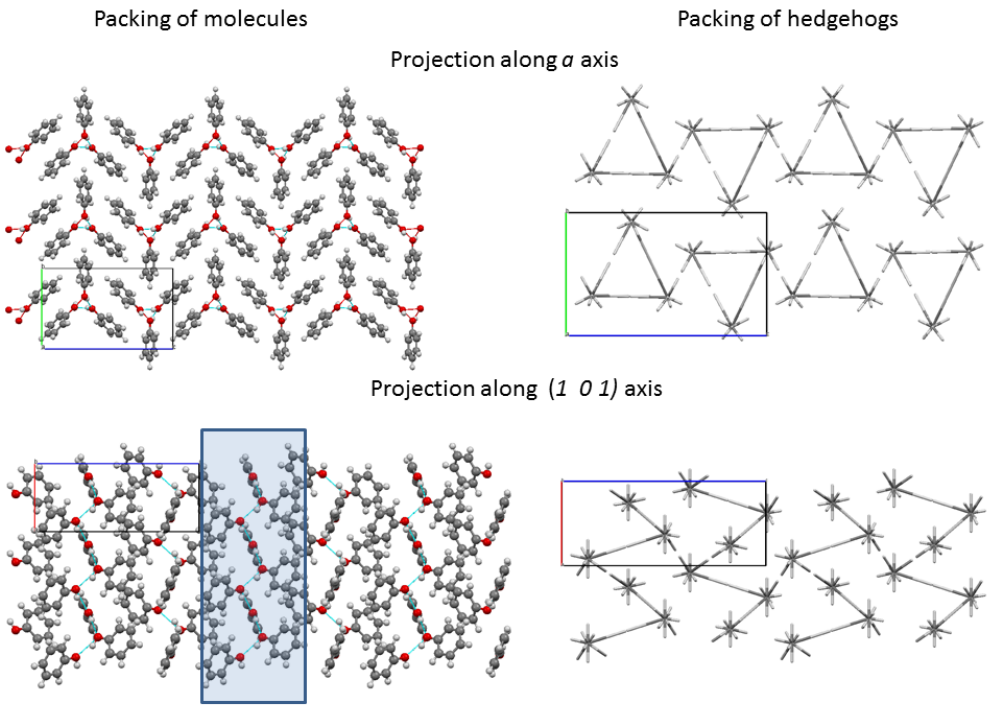

Figure S10. Supramolecular architecture of the ethanol crystal **16** presented as packing of molecules and hedgehogs of intermolecular interactions of molecules.

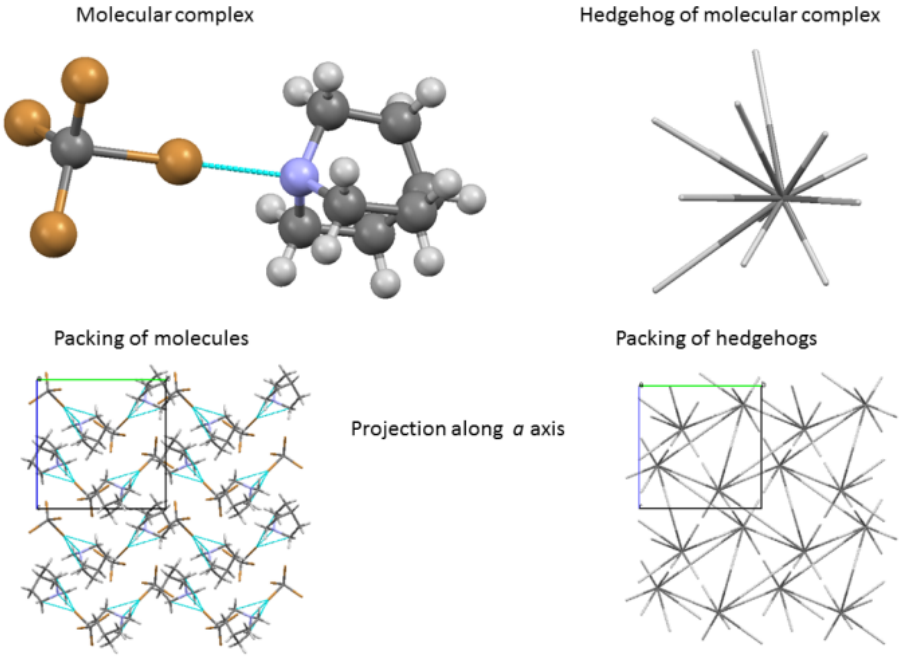

Figure S11. Supramolecular architecture of the co-crystal **17** presented as packing of molecules and hedgehogs of intermolecular interactions for molecular complexes.

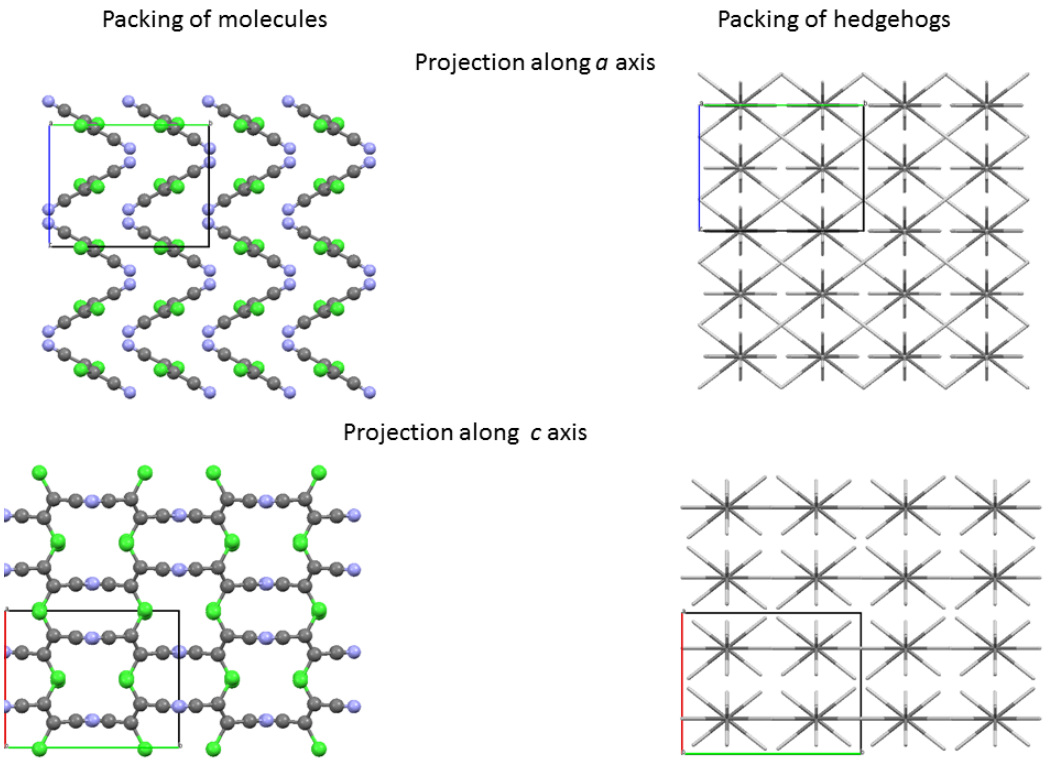

Figure S12. Supramolecular architecture of the crystal 18 presented as packing of molecules and hedgehogs of intermolecular interactions of molecules.

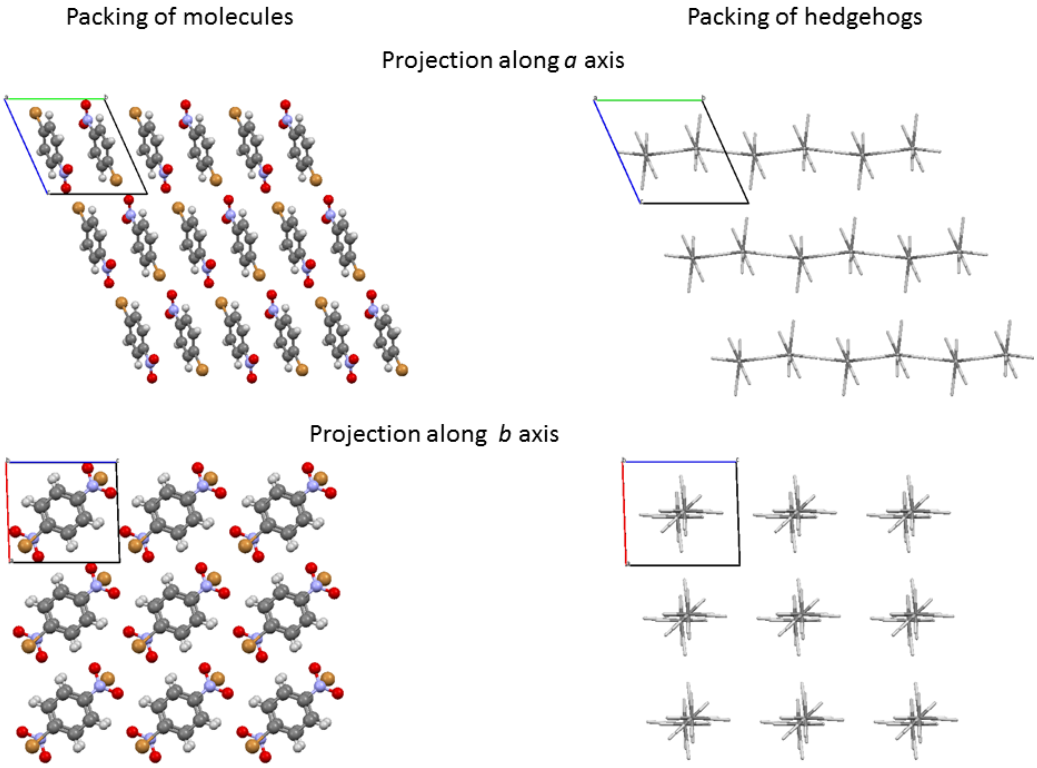

Figure S13. Supramolecular architecture of the crystal 19 presented as packing of molecules and hedgehogs of intermolecular interactions of molecules.

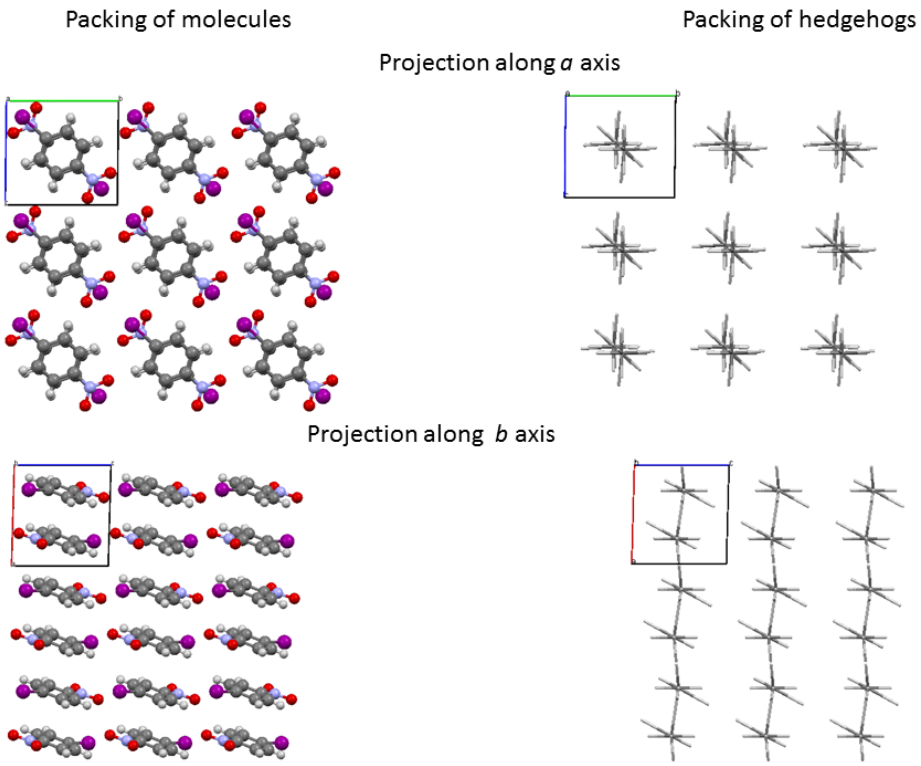

Figure S14. Supramolecular architecture of the crystal 20 presented as packing of molecules and hedgehogs of intermolecular interactions of molecules.

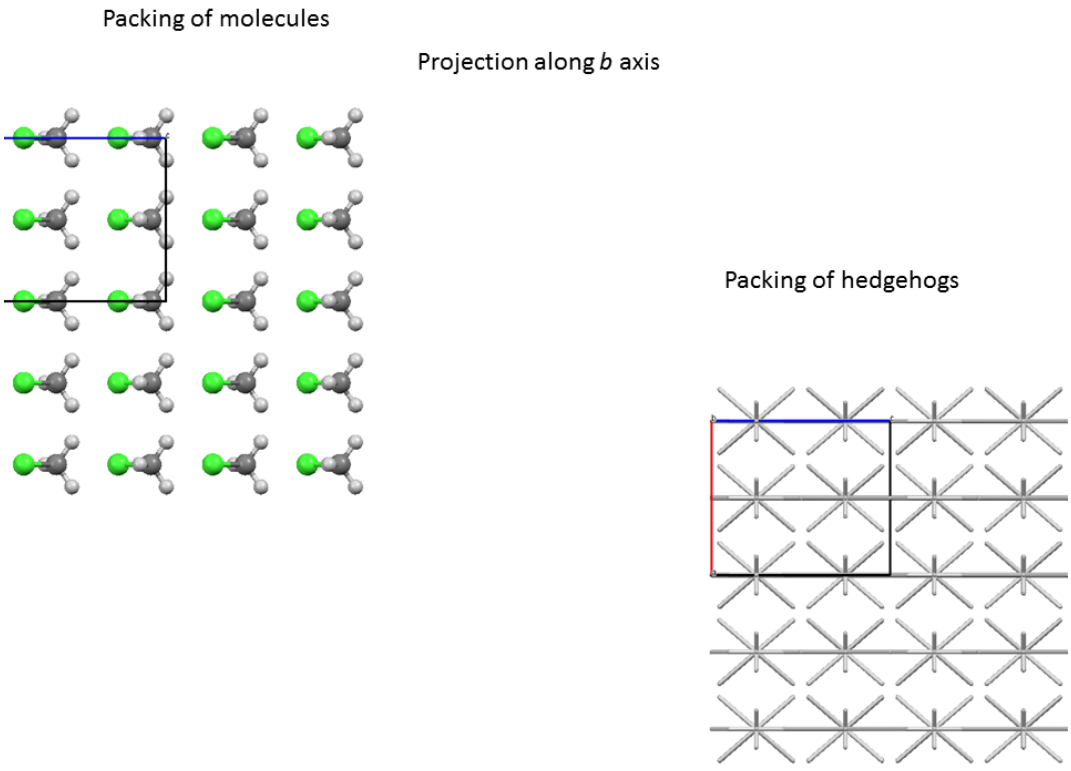

Figure S15. Supramolecular architecture of the crystal 21 presented as packing of molecules and hedgehogs of intermolecular interactions of molecules.

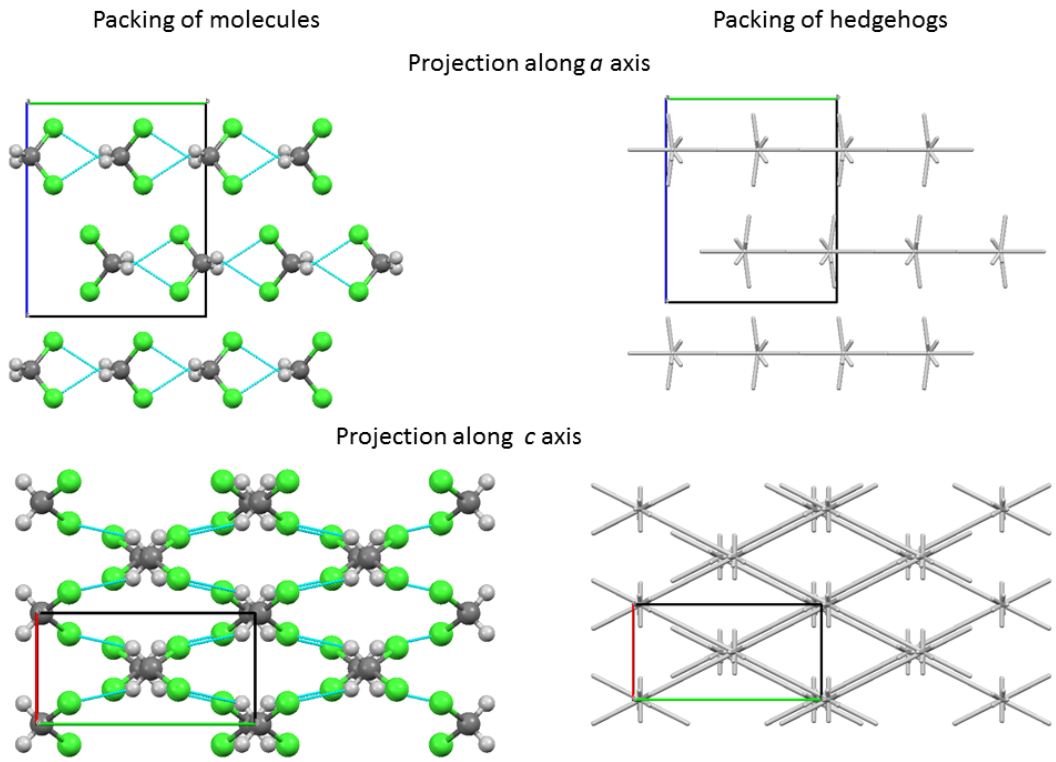

Figure S16. Supramolecular architecture of the crystal 22 presented as packing of molecules and hedgehogs of intermolecular interactions of molecules.

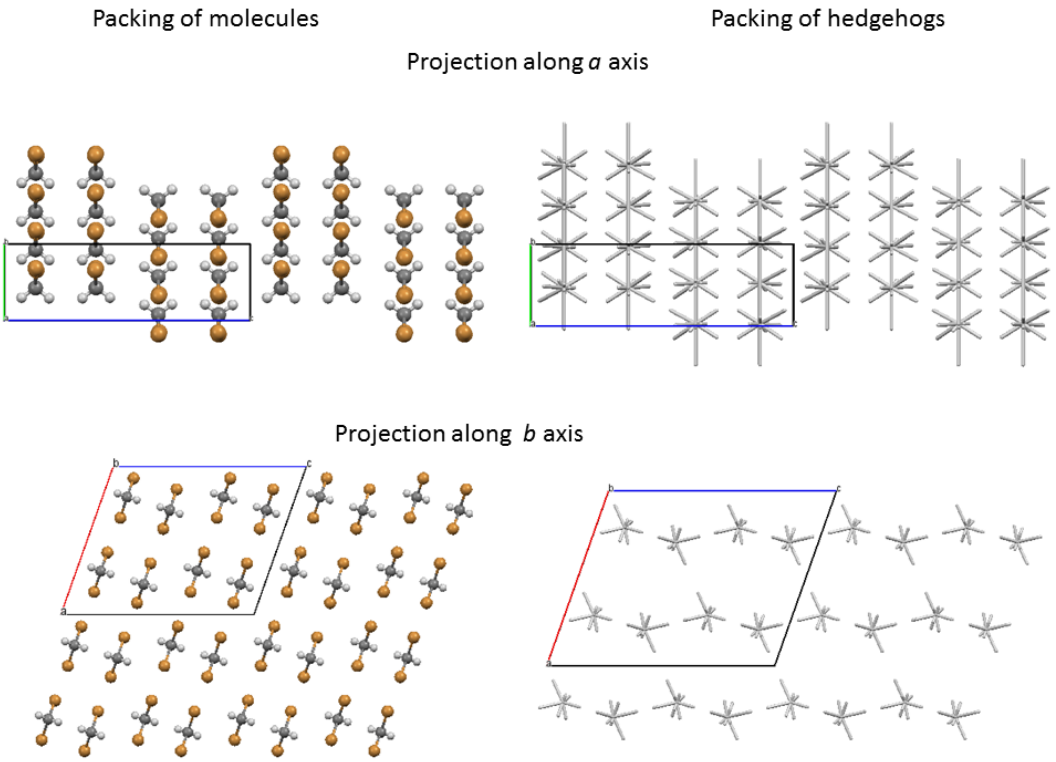

Figure S17. Supramolecular architecture of the crystal 23 presented as packing of molecules and hedgehogs of intermolecular interactions of molecules.

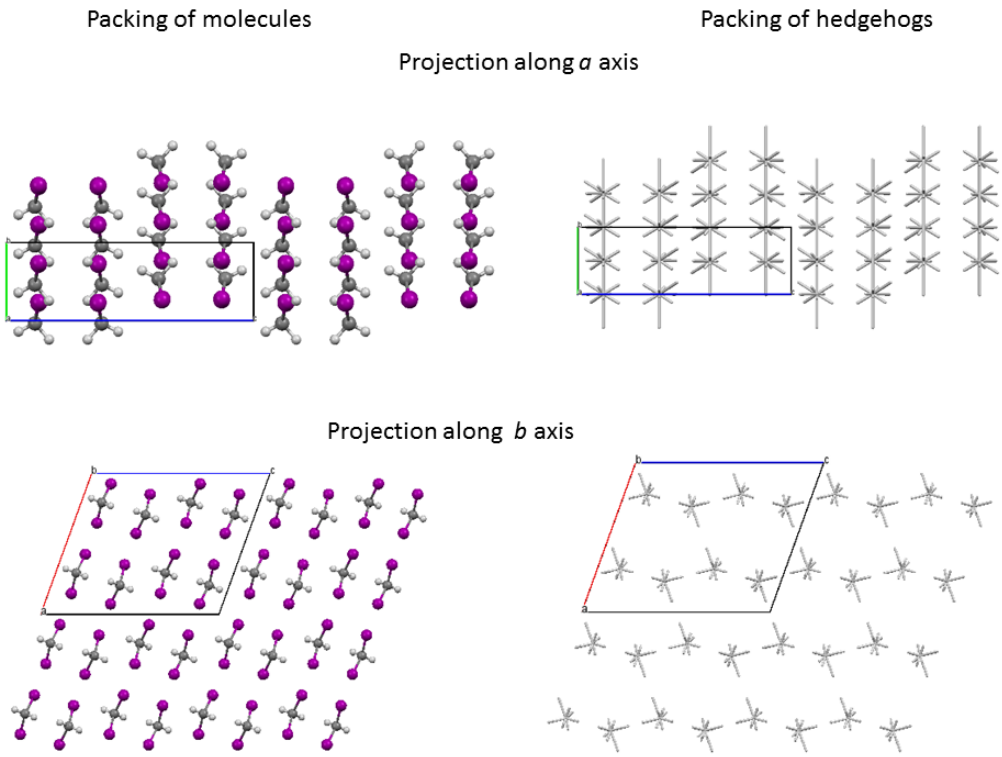

Figure S18. Supramolecular architecture of the crystal 24 presented as packing of molecules and hedgehogs of intermolecular interactions of molecules.

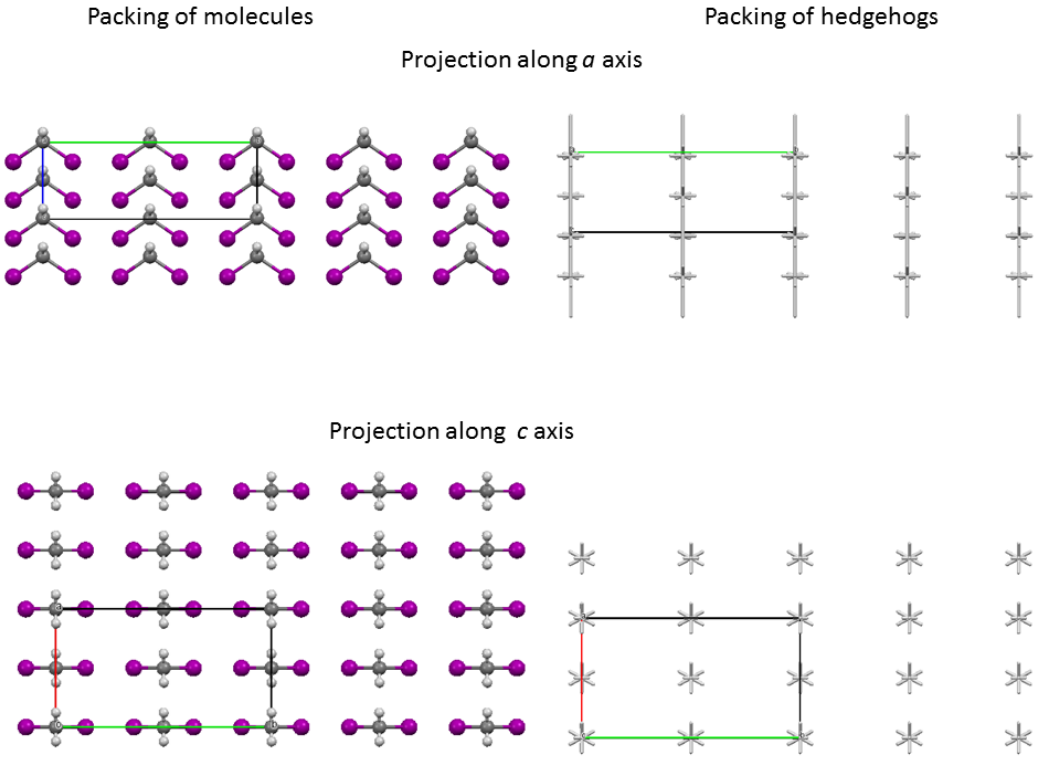

Figure S19. Supramolecular architecture of the crystal 25 presented as packing of molecules and hedgehogs of intermolecular interactions of molecules.

Table S1. Geometrical parameters of intermolecular interactions in crystals under consideration.

Structure	Refcode	D-X…A	X…A, Å	D-X…A, deg.
1	ACETAC07	O-H…O	1.84	157
		C-H…O	2.49	156
2	ACETAC09	O-H…O	1.85	162
		C-H…O	2.62	153
3	TFACET	O-H…O	1.78	162
4	BENZAC	O-H…O	1.62	178
		stacking	3.37	0
		C-H…O	2.46	149
5	ACEMID05	N-H…O	1.99	174
		N-H…O	1.99	169
6	ACEMID05	N-H…O	2.05	172
		N-H…O	2.03	178
		N-H…O	2.09	173
		N-H…O	2.01	168
		C-H…O	2.49	178
7	BZAMID05	N-H…O	2.07	169
		N-H…O	2.07	154
		stacking	3.45	26.3
		C-H…π(C)	2.84	138
8	HIBGOP	N-H…O	2.00	166
		O-H…O	1.73	168
		N-H…O	2.06	166
		O…π(C_{ar})	3.205	
		F…π(C_{ar})	3.148	
		F…π(C_{ar})	2.972	
		F…π(C_{ar})	2.953	
9	FUMRAM01	N-H…O	1.95	171
		O-H…O	1.78	176
		N-H…O	2.16	164
10	JUNQIS	N-H…O	1.87	166
		O-H…O	1.61	172
		N-H…O	2.00	152
11	PYRZOL05	N-H…N	1.98	163
		N-H…N	2.00	161
		C-H…N	2.61	135
		C-H…π	2.83	129
12	HOQHUQ	N-H…N	1.83	169
		N-H…N	2.01	166
		N-H…N	1.97	167
		stacking	3.404	4.5
		C-H…π	2.72	157
13	AMPYRD	N-H…N	2.20	171
		N-H…π	2.63	148
		C-H…π	2.89	158
		C-H…π	2.80	151
14	METHOL04	O-H…O	1.86	174
15	ETANOL	O-H…O	1.88	172
		O-H…O	1.93	176
16	PHENOL03	O-H…O	1.98	165

		O-H…O	1.81	157
		O-H…O	1.89	156
		C-H…π	2.78	116
		C-H…π	2.89	164
17	FEGYEV	C-Br…N	2.531	180.0
18	DCFUMN	N…C	3.381	
19	ULEBOD	stacking	3.370	0.0
		C-Br…O	3.227	164.6
		C-H…O	2.54	135
		C-H…O	2.53	147
20	ZONYIK	stacking	3.469	0.0
		C-I…O	3.327	163.8
		C-I…O	3.466	157.9
		C-H…O	2.59	150
21	CLMETH	C-H…Cl	3.00	172
		C-H…Cl	3.01	172
22	DCLMET	C-H…Cl	2.77	123
		C-Cl…Cl	3.358	168.7
23	DBRMET11	C-H…Br	3.12	110
		C-H…Br	3.04	140
		C-Br…Br	3.623	171.8
		C-Br…Br	3.490	112.7
24	DIMETH06	C-H…I	3.05	116
		C-H…I	3.10	119
		C-I…I	3.738	171.4
		C-I…I	3.648	174.0
25	DIMETH14	C-H…I	3.39	104
		C-I…I	3.626	106.7

Table S2. Numbering of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecule in the crystals of polymorphic modifications of acetic acid **1** and **2**. Dimers belonging to basic structural motif are highlighted in bold.

	Structure **1**		Structure **2**	
Dimer	Symmetry operation	E_{int}, kcal/mol	Symmetry operation	E_{int}, kcal/mol
1	x,y,1+z	-0,53	x,y,1+z	-0,46
2	x,y,-1+z	-0,53	x,y,-1+z	-0,46
3	x,1+y,z	-1,69	1+x,y,z	-1,51
4	x,-1+y,z	-1,69	-1+x,y,z	-1,51
5	1-x,1-y,1/2+z	-1,09	1/2+x,1/2-y,1/2+z	-2,36
6	1-x,1-y,-1/2+z	-1,09	**1/2+x,1/2-y,-1/2+z**	**-9,96**
7	1-x,2-y,1/2+z	-1,03	**-1/2+x,1/2-y,1/2+z**	**-9,96**
8	1-x,2-y,-1/2+z	-1,03	-1/2+x,1/2-y,-1/2+z	-2,36
9	1/2-x,1/2+y,1/2+z	-2,04	-x,1-y,1-z	-2,10
10	**1/2-x,1/2+y,-1/2+z**	**-8,77**	-x,1-y,2-z	-0,54
11	**1/2-x,-1/2+y,1/2+z**	**-8,77**	1-x,1-y,1-z	-1,05
12	1/2-x,-1/2+y,-1/2+z	-2,04	1-x,1-y,2-z	-0,20

Table S3. Numbering of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecule and basic molecular complex in the crystals of trifluoroacetic acid **3**. Dimers belonging to basic structural motif are highlighted in bold.

	BU=Molecule		BU=Molecular complex	
Dimer	Symmetry operation	E_{int}, kcal/mol	Symmetry operation	E_{int}, kcal/mol
1	x,1+y,z	-1,86	**x,1+y,z**	**-3,13**
2	x,-1+y,z	-1,86	**x,-1+y,z**	**-3,13**
3	-x,1/2+y,1/2-z	-2,98	1+x,y,z	-1,18
4	-x,-1/2+y,1/2-z	-2,98	1+x,1+y,z	-0,39
5	1-x,1/2+y,1/2-z	-0,24	-1+x,y,z	-1,18
6	1-x,-1/2+y,1/2-z	-0,24	-1+x,-1+y,z	-0,39
7	-x,-y,1-z	-15,95	**-x,1/2+y,1/2-z**	**-4,68**
8	-x,1-y,1-z	-0,56	**-x,1/2+y,3/2-z**	**-4,68**
9	-x,-1-y,1-z	1,41	**-x,-1/2+y,1/2-z**	**-4,68**
10	1-x,-y,1-z	-1,08	**-x,-1/2+y,3/2-z**	**-4,68**
11	1-x,1-y,1-z	-0,54	1-x,1/2+y,1/2-z	-0,49
12	x,1/2-y,1/2+z	-1,44	1-x,-1/2+y,1/2-z	-0,49
13	x,1/2-y,-1/2+z	-1,44	-1-x,1/2+y,3/2-z	-0,49
14	x,-1/2-y,1/2+z	-0,31	-1-x,-1/2+y,3/2-z	-0,49
15	x,-1/2-y,-1/2+z	-0,31	x,1+y,z	-3,13

Table S4. Numbering of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecule and basic molecular complex in the crystals of benzoic acid **4**. Dimers belonging to primary and secondary basic structural motifs are highlighted in bold and italic, respectively.

	BU=Molecule		BU=Molecular complex	
Dimer	Symmetry operation	E_{int}, kcal/mol	Symmetry operation	E_{int}, kcal/mol
1	x,1+y,z	-2,51	**x,1+y,z**	**-10,02**
2	x,-1+y,z	-2,51	**x,-1+y,z**	**-10,02**
3	1+x,y,z	-2,53	*1+x,y,z*	*-5,00*
4	1+x,1+y,z	-2,49	*1+x,1+y,z*	*-6,11*
5	-1+x,y,z	-2,46	*-1+x,y,z*	*-5,00*
6	-1+x,-1+y,z	-2,20	*-1+x,-1+y,z*	*-6,11*
7	-x,1/2+y,1/2-z	-1,30	-x,1/2+y,1/2-z	-1,41
8	-x,-1/2+y,1/2-z	-1,30	-x,1/2+y,-1/2-z	-1,41
9	1-x,1/2+y,1/2-z	-1,52	-x,-1/2+y,1/2-z	-1,41
10	1-x,-1/2+y,1/2-z	-1,52	-x,-1/2+y,-1/2-z	-1,41
11	-x,-y,-z	-33,10	1-x,1/2+y,1/2-z	-1,62
12	-x,1-y,-z	-5,12	1-x,-1/2+y,1/2-z	-1,62
13	1-x,-y,-z	-0,81	-1-x,1/2+y,-1/2-z	-1,62
14	1-x,1-y,-z	-1,86	-1-x,-1/2+y,-1/2-z	-1,62
15				

Table S5. Numbering of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecule in the crystals of polymorphic modifications of acetamide **5**.

Dimer	Symmetry operation	E_{int}, kcal/mol
1	-y,-1+x-y,z	0,85
2	1-y,x-y,z	-0,77
3	1+y-x,-x,z	0,83
4	1+y-x,1-x,z	-0,76
5	1/3-y,-1/3+x-y,-1/3+z	-2,20
6	2/3+y-x,1/3-x,1/3+z	-2,23
7	1/3-y,2/3-x,1/6+z	-1,19
8	2/3-y,1/3-x,-1/6+z	-1,20
9	1/3+y-x,-1/3+y,1/6+z	-9,75
10	1/3+x,-1/3+x-y,1/6+z	-8,49
11	2/3+y-x,1/3+y,-1/6+z	-9,75
12	-1/3+x,-2/3+x-y,-1/6+z	-8,53

Table S6. Numbering of dimers, type of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecules A and B (located in asymmetric part of unit cell) and basic molecular complex in the crystals of polymorphic modification of acetamide **6**. Dimers belonging to basic structural motif are highlighted in bold.

		BU=Molecule		BU=Molecular complex	
Dimer	Type	Symmetry operation	E_{int}, kcal/mol	Symmetry operation	E_{int}, kcal/mol
1	AB	x,y,z	-16,98	1/2+x,-1/2+y,1-z	-0,42
2	AB	-1/2+x,1/2+y,1-z	-0,16	-1/2+x,1/2+y,1-z	-0,42
3	AA	x,1/2-y,1/2+z	-7,99	**x,1/2-y,1/2+z**	**-8,01**
4	AB	x,1/2-y,1/2+z	0,06	**x,1/2-y,-1/2+z**	**-8,00**
5	AA	x,1/2-y,-1/2+z	-7,99	**3/2-x,y,1/2+z**	**-8,66**
6	AB	3/2-x,y,1/2+z	0,10	**3/2-x,y,-1/2+z**	**-8,66**
7	AA	1-x,-y,1-z	-4,31	1-x,-y,1-z	-5,57
8	AB	1-x,-y,1-z	-0,53	1-x,1-y,1-z	-1,43
9	AA	1-x,1-y,1-z	-1,57	**3/2-x,1/2-y,z**	**-4,96**
10	AB	3/2-x,1/2-y,z	-2,96	3/2-x,-1/2-y,z	-3,06
11	AA	1-x,1/2+y,1/2-z	-2,94	1-x,1/2+y,1/2-z	-2,18
12	AB	1-x,1/2+y,1/2-z	0,48	1-x,-1/2+y,1/2-z	-2,18
13	AA	1-x,-1/2+y,1/2-z	-2,94	1/2+x,-y,1/2-z	-0,52
14	AB	-1/2+x,-y,1/2-z	-0,27	-1/2+x,-y,1/2-z	-0,52
15	BA	x,y,z	-16,98		
16	BA	1/2+x,-1/2+y,1-z	-0,16		
17	BA	x,1/2-y,-1/2+z	0,06		
18	BB	3/2-x,y,1/2+z	-8,65		
19	BB	3/2-x,y,-1/2+z	-8,65		
20	BA	3/2-x,y,-1/2+z	0,10		
21	BA	1-x,-y,1-z	-0,53		
22	BB	3/2-x,1/2-y,z	-0,06		
23	BA	3/2-x,1/2-y,z	-2,96		
24	BB	3/2-x,-1/2-y,z	-1,65		
25	BA	1-x,-1/2+y,1/2-z	0,43		
26	BA	1/2+x,-y,1/2-z	-0,27		

Table S7. Numbering of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecule and basic molecular complex in the crystals of benzamide **7**. Dimers belonging to primary and secondary basic structural motifs are highlighted in bold and italic, respectively.

	BU=Molecule		BU=Molecular complex	
Dimer	Symmetry operation	E_{int}, kcal/mol	Symmetry operation	E_{int}, kcal/mol
1	x,1+y,z	-9,42	**x,1+y,z**	**-17,43**
2	x,-1+y,z	-9,42	**x,-1+y,z**	**-17,43**
3	1+x,y,z	-1,42	*1+x,y,z*	*-9,58*
4	1+x,-1+y,z	-2,05	*1+x,-1+y,z*	*-5,72*
5	-1+x,y,z	-1,30	*-1+x,y,z*	*-9,58*
6	-1+x,1+y,z	-2,01	*-1+x,1+y,z*	*-5,72*
7	-x,1/2+y,3/2-z	-2,57	-x,1/2+y,3/2-z	-2,69
8	-x,-1/2+y,3/2-z	-2,57	-x,-1/2+y,3/2-z	-2,69
9	1-x,1/2+y,3/2-z	-1,16	1-x,1/2+y,3/2-z	-1,30
10	1-x,-1/2+y,3/2-z	-1,16	1-x,-1/2+y,3/2-z	-1,30
11	-x,-y,2-z	-2,01	-2-x,1/2+y,5/2-z	-2,69
12	-x,1-y,2-z	-6,77	-2-x,-1/2+y,5/2-z	-2,69
13	-1-x,-y,2-z	0,42	-2+x,1/2-y,1/2+z	-1,30
14	-1-x,1-y,2-z	-15,38	-2+x,3/2-y,1/2+z	-1,30

Table S8. Numbering of dimers, type of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecules of perfluorobenzoic acid (A) and perfluorobenzamide (B) and basic molecular complex (AB) in the co-crystal **8**. Dimers belonging to primary and secondary basic structural motifs are highlighted in bold and italic, respectively.

		BU=Molecule		BU=Molecular complex	
Dimer	Type	Symmetry operation	E_{int}, kcal/mol	Symmetry operation	E_{int}, kcal/mol
1	AB	x,y,z	-3,47	1/2-x,1-y,1/2+z	-0,60
2	AB	-1+x,y,z	-2,08	1/2-x,1-y,-1/2+z	-0,60
3	AA	-x,1/2+y,1/2-z	-2,94	*-x,1/2+y,1/2-z*	*-6,87*
4	AA	-x,-1/2+y,1/2-z	-2,94	*-x,-1/2+y,1/2-z*	*-6,87*
5	AB	-1/2+x,1/2-y,1-z	-1,08	1/2+x,1/2-y,-z	-1,78
6	AB	1-x,1-y,1-z	-0,60	-1/2+x,1/2-y,-z	-1,78
7	AA	1/2+x,y,1/2-z	-8,18	-x,1-y,-z	-3,73
8	AA	-1/2+x,y,1/2-z	-8,18	1-x,1-y,-z	-0,32
9	AB	-1/2+x,y,1/2-z	-18,43	**1/2+x,y,1/2-z**	**-14,43**
10	AB	1/2-x,1/2+y,z	-1,19	**-1/2+x,y,1/2-z**	**-14,43**
11	AA	1/2-x,1/2+y,z	-2,66	x,1/2-y,1/2+z	-1,09
12	AA	1/2-x,-1/2+y,z	-2,66	x,1/2-y,-1/2+z	-1,09
13	AB	1/2-x,-1/2+y,z	-2,58	*1/2-x,1/2+y,z*	*-5,95*
14	BA	x,y,z	-3,47	*1/2-x,-1/2+y,z*	*-5,95*
15	BA	1+x,y,z	-2,08		
16	BA	1/2+x,1/2-y,1-z	-1,08		
17	BB	1/2+x,1/2-y,1-z	-1,75		
18	BB	-1/2+x,1/2-y,1-z	-1,75		
19	BA	1-x,1-y,1-z	-0,53		
20	BB	1-x,1-y,1-z	-3,58		
21	BB	2-x,1-y,1-z	-0,58		
22	BA	1/2+x,y,1/2-z	-18,43		
23	BA	1/2-x,1/2+y,z	-2,58		
24	BA	1/2-x,-1/2+y,z	-1,19		
25	BB	3/2-x,1/2+y,z	-2,53		
26	BB	3/2-x,-1/2+y,z	-2,53		

Table S9. Numbering of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecule in the crystals **9**. Dimers belonging to primary and secondary basic structural motifs are highlighted in bold and italic, respectively.

Dimer	Symmetry operation	E_{int}, kcal/mol
1	x,y,1+z	-2,38
2	x,y,-1+z	-2,38
3	1+x,y,z	-2,19
4	**1+x,y,1+z**	**-19,55**
5	-1+x,y,z	-2,19
6	**-1+x,y,-1+z**	**-19,55**
7	*-x,1/2+y,-z*	*-7,64*
8	-x,1/2+y,-1-z	-1,91
9	*-x,-1/2+y,-z*	*-7,64*
10	-x,-1/2+y,-1-z	-1,91
11	1-x,1/2+y,-z	-2,49
12	*1-x,1/2+y,1-z*	*0,28*
13	1-x,-1/2+y,-z	-2,49
14	*1-x,-1/2+y,1-z*	*0,28*

Table S10. Numbering of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecule in the crystals **10**. Dimers belonging to basic structural motifs are highlighted in bold.

Dimer	Symmetry operation	E_{int}, kcal/mol
1	x,1+y,z	-2,23
2	x,-1+y,z	-2,23
3	1-x,-y,1/2+z	0,39
4	1-x,-y,-1/2+z	0,43
5	1-x,1-y,1/2+z	-0,80
6	1-x,1-y,-1/2+z	-0,80
7	2-x,-y,1/2+z	-0,95
8	2-x,-y,-1/2+z	-0,95
9	3/2-x,y,1/2+z	-5,69
10	3/2-x,y,-1/2+z	-5,69
11	**3/2-x,1+y,1/2+z**	**-19,98**
12	**3/2-x,-1+y,-1/2+z**	**-19,98**
13	1/2+x,-y,z	-3,60
14	1/2+x,1-y,z	-9,43
15	-1/2+x,-y,z	-3,60
16	-1/2+x,1-y,z	-9,43

Table S11. Numbering of dimers, type of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecules A and B (located in asymmetric part of unit cell) in the crystals **11**. Dimers belonging basic structural motifs are highlighted in bold.

Dimer	Type	Symmetry operation	E_{int}, kcal/mol
1	**AB**	**x,y,z**	**-7,46**
2	**AB**	**x,y,1+z**	**-1,57**
3	AB	1+x,y,z	-0,77
4	AB	1+x,y,1+z	-1,41
5	**AA**	**x,1/2-y,1/2+z**	**-3,51**
6	**AB**	**x,1/2-y,1/2+z**	**-5,84**
7	**AA**	**x,1/2-y,-1/2+z**	**-3,51**
8	AB	1+x,1/2-y,1/2+z	-1,35
9	AB	1/2+x,-y,-z	-1,82
10	AA	1/2+x,-y,1-z	-1,1
11	AB	1/2+x,-y,1-z	-2,88
12	AA	-1/2+x,-y,1-z	-1,1
13	BA	x,y,z	-7,46
14	**BA**	**x,y,-1+z**	**-1,57**
15	BA	-1+x,y,z	-0,77
16	BA	-1+x,y,-1+z	-1,41
17	**BB**	**x,1/2-y,1/2+z**	**-2,21**
18	**BA**	**x,1/2-y,-1/2+z**	**-5,84**
19	**BB**	**x,1/2-y,-1/2+z**	**-2,21**
20	BA	-1+x,1/2-y,-1/2+z	-1,35
21	BB	1/2+x,-y,-z	-2,03
22	BA	-1/2+x,-y,-z	-1,82
23	BB	-1/2+x,-y,-z	-2,03
24	BA	-1/2+x,-y,1-z	-2,88

Table S12. Numbering of dimers, type of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecules (A, B and C, located in asymmetric part of unit cell) and basic molecular complex (ABC) in the crystal **12**. Dimers belonging to basic structural motifs are highlighted in bold.

		BU=Molecule		BU=Molecular complex	
Dimer	Type	Symmetry operation	E_{int}, kcal/mol	Symmetry operation	E_{int}, kcal/mol
1	AC	x,y,z	-8,68	**x,y,1+z**	**-10,21**
2	AB	x,y,z	-8,82	**x,y,-1+z**	**-10,21**
3	AA	x,y,1+z	-1,64	2-x,1-y,1/2+z	-3,62
4	AB	x,y,1+z	-3,88	2-x,1-y,3/2+z	-1,29
5	AA	x,y,-1+z	-1,64	2-x,1-y,-1/2+z	-3,62
6	AA	2-x,1-y,1/2+z	-2,28	2-x,1-y,-3/2+z	-1,29
7	AB	2-x,1-y,1/2+z	-1,31	2-x,2-y,1/2+z	-4,24
8	AB	2-x,1-y,3/2+z	-1,19	2-x,2-y,3/2+z	-1,22
9	AA	2-x,1-y,-1/2+z	-2,28	2-x,2-y,-1/2+z	-4,24
10	AB	-1/2+x,1-y,1+z	-0,65	2-x,2-y,-3/2+z	-1,22
11	AA	3/2-x,y,1/2+z	-2,34	1/2+x,1-y,-1+z	-0,77
12	AA	3/2-x,y,-1/2+z	-2,34	1/2+x,2-y,-1+z	-0,69
13	BA	x,y,z	-8,82	-1/2+x,1-y,1+z	-0,77
14	BC	x,y,z	-9,00	-1/2+x,2-y,1+z	-0,69
15	BB	x,y,1+z	-1,37	3/2-x,y,1/2+z	-6,52
16	BA	x,y,-1+z	-3,88	3/2-x,y,-1/2+z	-6,51
17	BC	x,y,-1+z	-1,67	5/2-x,y,1/2+z	-1,67
18	BB	x,y,-1+z	-1,37	5/2-x,y,-1/2+z	-1,67
19	BA	2-x,1-y,-1/2+z	-1,31		
20	BA	2-x,1-y,-3/2+z	-1,19		
21	BC	2-x,2-y,-1/2+z	-2,24		
22	BC	2-x,2-y,-3/2+z	-1,09		
23	BA	1/2+x,1-y,-1+z	-0,65		
24	BC	1/2+x,2-y,-1+z	-0,61		
25	BB	5/2-x,y,1/2+z	-1,51		
26	BB	5/2-x,y,-1/2+z	-1,51		
27	CB	x,y,z	-9,00		
28	CA	x,y,z	-8,68		
29	CB	x,y,1+z	-1,67		
30	CC	x,y,1+z	-2,14		
31	CC	x,y,-1+z	-2,14		
32	CB	2-x,2-y,1/2+z	-2,24		
33	CC	2-x,2-y,1/2+z	-1,78		
34	CB	2-x,2-y,3/2+z	-1,09		
35	CC	2-x,2-y,-1/2+z	-1,78		
36	CB	-1/2+x,2-y,1+z	-0,61		
37	CC	3/2-x,y,1/2+z	-2,76		
38	CC	3/2-x,y,-1/2+z	-2,76		

Table S13. Numbering of dimers, type of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecule and basic molecular complex in the crystal **13**. Dimers belonging to basic structural motifs are highlighted in bold.

	BU=Molecule		BU=Molecular complex	
Dimer	Symmetry operation	E_{int}, kcal/mol	Symmetry operation	E_{int}, kcal/mol
1	x,1+y,z	-2.83	**x,1+y,z**	**-7,15**
2	x,-1+y,z	-2.83	**x,-1+y,z**	**-7,15**
3	-x,1/2+y,1/2-z	-0.77	1+x,y,z	-1,93
4	-x,-1/2+y,1/2-z	-0.77	1+x,-1+y,z	-0,19
5	-1-x,1/2+y,1/2-z	-1.17	-1+x,y,z	-1,93
6	-1-x,-1/2+y,1/2-z	-1.17	-1+x,1+y,z	-0,19
7	-x,-y,1-z	-1.79	**-x,1/2+y,1/2-z**	**-8,78**
8	-x,1-y,1-z	-12.20	**-x,1/2+y,3/2-z**	**-8,78**
9	-1-x,1-y,1-z	-1.95	**-x,-1/2+y,1/2-z**	**-8,78**
10	-1-x,2-y,1-z	-0.22	**-x,-1/2+y,3/2-z**	**-8,78**
11	x,1/2-y,1/2+z	-6.27	1-x,1/2+y,3/2-z	-1,22
12	x,1/2-y,-1/2+z	-6.27	1-x,-1/2+y,3/2-z	-1,22
13	x,3/2-y,1/2+z	-2.01	-1-x,1/2+y,1/2-z	-1,22
14	x,3/2-y,-1/2+z	-2.01	-1-x,-1/2+y,1/2-z	-1,22

Table S14. Numbering of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecule in the crystals **14**. Dimers belonging to basic structural motifs are highlighted in bold.

Dimer	Symmetry operation	E_{int}, kcal/mol
1	x,1+y,z	-0,47
2	x,-1+y,z	-0,47
3	**1+x,y,z**	**-1,02**
4	**-1+x,y,z**	**-1,02**
5	1/2-x,1-y,1/2+z	-0,74
6	1/2-x,1-y,-1/2+z	-0,74
7	-x,1/2+y,3/2-z	-1,26
8	-x,-1/2+y,3/2-z	-1,26
9	1-x,1/2+y,3/2-z	-1,17
10	1-x,-1/2+y,3/2-z	-1,17
11	**1/2+x,1/2-y,2-z**	**-5,32**
12	1/2+x,3/2-y,2-z	-0,66
13	**-1/2+x,1/2-y,2-z**	**-5,32**
14	-1/2+x,3/2-y,2-z	-0,66

Table S15. Numbering of dimers, type of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecules A and B (located in asymmetric part of unit cell) in the crystals **15**. Dimers belonging to basic structural motifs are highlighted in bold.

Dimer	Type	Symmetry operation	E_{int}, kcal/mol
1	**AB**	**x,y,z**	**-1,31**
2	**AB**	**x,y,1+z**	**-5,17**
3	AA	1+x,y,z	-0,44
4	AB	1+x,y,z	-0,62
5	AB	1+x,y,1+z	-1,55
6	AA	-1+x,y,z	-0,45
7	**AB**	**x,-y,1/2+z**	**-5,61**
8	**AA**	**x,-y,1/2+z**	**-1,82**
9	**AA**	**x,-y,-1/2+z**	**-1,82**
10	AA	x,1-y,1/2+z	-0,54
11	AB	x,1-y,1/2+z	-1,42
12	AA	x,1-y,-1/2+z	-0,54
13	AB	1+x,-y,1/2+z	-1,09
14	AB	1+x,1-y,1/2+z	-0,91
15	BA	x,y,z	-1,31
16	**BA**	**x,y,-1+z**	**-5,17**
17	BB	1+x,y,z	-1,03
18	BB	-1+x,y,z	-1,03
19	BA	-1+x,y,z	-0,63
20	BA	-1+x,y,-1+z	-1,55
21	**BB**	**x,-y,1/2+z**	**-1,17**
22	**BA**	**x,-y,-1/2+z**	**-5,61**
23	**BB**	**x,-y,-1/2+z**	**-1,17**
24	BB	x,1-y,1/2+z	-0,41
25	BA	x,1-y,-1/2+z	-1,42
26	BB	x,1-y,-1/2+z	-0,41
27	BA	-1+x,-y,-1/2+z	-1,09
28	BA	-1+x,1-y,-1/2+z	-0,91

Table S16. Numbering of dimers, type of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecules (A, B and C, located in asymmetric part of unit cell) in the crystal **16**. Dimers belonging to primary and secondary basic structural motifs are highlighted in bold and italic, respectively.

Dimer	Type	Symmetry operation	E_{int}, kcal/mol
1	**AB**	**x,y,z**	**-5,03**
2	**AC**	**x,y,z**	**-1,34**
3	AC	x,-1+y,z	-1,50
4	**AC**	**1+x,y,z**	**-4,52**
5	**AA**	**1+x,y,z**	**-2,27**
6	AC	1+x,-1+y,z	-2,39
7	**AA**	**-1+x,y,z**	**-2,27**
8	AB	1-x,-y,-1/2+z	-1,11
9	AB	1-x,1-y,-1/2+z	-2,41
10	AC	1-x,1-y,-1/2+z	-2,70
11	AB	2-x,-y,-1/2+z	-1,24
12	AB	2-x,1-y,-1/2+z	-4,25
13	AC	2-x,1-y,-1/2+z	-0,63
14	BA	x,y,z	-5,03
15	**BC**	**x,y,z**	**-5,21**
16	BC	x,-1+y,z	-2,86
17	**BB**	**1+x,y,z**	**-2,27**
18	**BC**	**1+x,y,z**	**-1,81**
19	BC	1+x,-1+y,z	-1,54
20	**BB**	**-1+x,y,z**	**-2,27**
21	BC	-x,1-y,1/2+z	-0,67
22	BA	1-x,-y,1/2+z	-1,11
23	BA	1-x,1-y,1/2+z	-2,41
24	BC	1-x,1-y,1/2+z	-2,14
25	BA	2-x,-y,1/2+z	-1,24
26	BA	2-x,1-y,1/2+z	-4,25
27	CB	x,y,z	-5,21
28	CA	x,y,z	-1,34
29	CA	x,1+y,z	-1,50
30	CB	x,1+y,z	-2,86
31	**CC**	**1+x,y,z**	**-2,12**
32	**CA**	**-1+x,y,z**	**-4,52**
33	**CB**	**-1+x,y,z**	**-1,81**
34	**CC**	**-1+x,y,z**	**-2,12**
35	CA	-1+x,1+y,z	-2,39
36	CB	-1+x,1+y,z	-1,54
37	CB	-x,1-y,-1/2+z	-0,67
38	CA	1-x,1-y,1/2+z	-2,70
39	CB	1-x,1-y,-1/2+z	-2,14
40	CA	2-x,1-y,1/2+z	-0,63

Table S17. Numbering of dimers, type of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecules A and B (located in asymmetric part of unit cell) and basic molecular complex in the crystals **17**.

		BU=Molecule		BU=Molecular complex	
Dimer	Type	Symmetry operation	E_{int}, kcal/mol	Symmetry operation	E_{int}, kcal/mol
1	AB	x,y,z	-8.81	1/2+x,1/2-y,-z 0 0	-5.57
2	AA	1/2+x,1/2-y,-z 0 0	-1.99	1/2+x,1/2-y,1-z 0 0	-4.87
3	AB	-1/2+x,1/2-y,-z 0 1	-2.86	-1/2+x,1/2-y,-z 0 0	-5.57
4	AA	-1/2+x,1/2-y,-z 0 0	-1.99	-1/2+x,1/2-y,1-z 0 0	-4.87
5	AB	-1/2+x,1/2-y,1-z 0 1	-2.88	-x,1/2+y,1/2-z 0 0	-5.57
6	AA	-x,1/2+y,1/2-z 0 0	-2.00	-x,-1/2+y,1/2-z 0 0	-5.57
7	AB	-x,-1/2+y,1/2-z 0 1	-2.86	1-x,1/2+y,1/2-z 0 0	-4.87
8	AA	-x,-1/2+y,1/2-z 0 0	-1.98	1-x,-1/2+y,1/2-z 0 0	-4.87
9	AB	1-x,-1/2+y,1/2-z 0 1	-2.88	1/2-x,-y,1/2+z 0 0	-5.57
10	AA	1/2-x,-y,1/2+z 0 0	-1.99	1/2-x,-y,-1/2+z 0 0	-5.57
11	AB	1/2-x,-y,-1/2+z 0 1	-2.86	1/2-x,1-y,1/2+z 0 0	-4.87
12	AA	1/2-x,-y,-1/2+z 0 0	-1.99	1/2-x,1-y,-1/2+z 0 0	-4.87
13	AB	1/2-x,1-y,-1/2+z 0 1	-2.88		
14	BA	x,y,z 1 0	-8.79		
15	BA	1/2+x,1/2-y,-z 1 0	-2.86		
16	BA	1/2+x,1/2-y,1-z 1 0	-2.88		
17	BB	1/2+x,1/2-y,1-z 1 1	-1.27		
18	BB	-1/2+x,1/2-y,1-z 1 1	-1.27		
19	BA	-x,1/2+y,1/2-z 1 0	-2.86		
20	BA	1-x,1/2+y,1/2-z 1 0	-2.88		
21	BB	1-x,1/2+y,1/2-z 1 1	-1.27		
22	BB	1-x,-1/2+y,1/2-z 1 1	-1.27		
23	BA	1/2-x,-y,1/2+z 1 0	-2.86		
24	BB	1/2-x,1-y,1/2+z 1 1	-1.27		
25	BA	1/2-x,1-y,1/2+z 1 0	-2.88		
26	BB	1/2-x,1-y,-1/2+z 1 1	-1.27		

Table S18. Numbering of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecule in the crystals **18**. Dimers belonging to basic structural motifs are highlighted in bold.

Dimer	Symmetry operation	E_{int}, kcal/mol
1	1+x,y,z	-0,38
2	-1+x,y,z	-0,38
3	1/2+x,1/2+y,z	-2,55
4	1/2+x,-1/2+y,z	-2,92
5	-1/2+x,1/2+y,z	-2,92
6	-1/2+x,-1/2+y,z	-2,55
7	-x,y,1/2-z	-1,13
8	-x,y,-1/2-z	-2,49
9	1-x,y,1/2-z	-2,55
10	1-x,y,-1/2-z	-1,13
11	**1/2-x,1/2+y,1/2-z**	**-3,40**
12	**1/2-x,1/2+y,-1/2-z**	**-3,40**
13	**1/2-x,-1/2+y,1/2-z**	**-3,40**
14	**1/2-x,-1/2+y,-1/2-z**	**-3,40**

Table S19. Numbering of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecule in the crystals **19**. Dimers belonging to basic structural motifs are highlighted in bold.

Dimer	Symmetry operation	E_{int}, kcal/mol
1	-1+x,y,z	-3.24
2	-1+x,y,1+z	-1.96
3	x,y,-1+z	-3.01
4	x,y,1+z	-3.01
5	1+x,y,-1+z	-1.96
6	1+x,y,z	-3.24
7	-x,1-y,1-z	-4.89
8	**1-x,-y,1-z**	**-6.47**
9	1-x,-y,2-z	-4.81
10	1-x,1-y,-z	-2.66
11	**1-x,1-y,1-z**	**-6.93**
12	2-x,-y,1-z	-2.31
13	2-x,1-y,-z	-0.72

Table S20. Numbering of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecule in the crystals **20**. Dimers belonging to basic structural motifs are highlighted in bold.

Dimer	Symmetry operation	E_{int}, kcal/mol
1	x,-1+y,-1+z	-2.32
2	x,-1+y,z	-3.16
3	x,y,-1+z	-3.36
4	x,y,1+z	-3.36
5	x,1+y,z	-3.16
6	x,1+y,1+z	-2.32
7	-x,1-y,-2-z	-2.68
8	**-x,1-y,-1-z**	**-6.62**
9	-x,2-y,-1-z	-4.45
10	1-x,-y,-2-z	-0.33
11	1-x,-y,-1-z	-2.79
12	**1-x,1-y,-1-z**	**-7.14**
13	1-x,1-y,-z	-4.78

Table S21. Numbering of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecule in the crystals **21**.

Dimer	Symmetry operation	E_{int}, kcal/mol
1	x,-1+y,z	-1.06
2	x,1+y,z	-1.06
3	x,-y,-1/2+z	-0.92
4	x,-y,1/2+z	-0.92
5	x,1-y,-1/2+z	-1.51
6	x,1-y,1/2+z	-1.51
7	-1/2+x,-1/2+y,z	-0.72
8	-1/2+x,1/2+y,z	-0.72
9	1/2+x,-1/2+y,z	-0.72
10	1/2+x,1/2+y,z	-0.72
11	-1/2+x,1/2-y,-1/2+z	-1.25
12	-1/2+x,1/2-y,1/2+z	-1.25
13	1/2+x,1/2-y,-1/2+z	-1.25
14	1/2+x,1/2-y,1/2+z	-1.25

Table S22. Numbering of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecule in the crystals **22**. Dimers belonging to basic structural motifs are highlighted in bold.

Dimer	Symmetry operation	E_{int}, kcal/mol
1	**x-1,y,z**	**-0.95**
2	**1+x,y,z**	**-0.95**
3	-1/2-x,1/2-y,-1/2+z	-0.49
4	-1/2-x,1/2-y,1/2+z	-0.49
5	1/2-x,1/2-y,-1/2+z	-0.49
6	1/2-x,1/2-y,1/2+z	-0.49
7	-1-x,-y,1-z	-0.40
8	-x,-y,-z	-1.47
9	-x,-y,1-z	-1.47
10	1-x,-y,-z	-0.40
11	**-1/2+x,-1/2+y,1/2-z**	**-2.15**
12	**-1/2+x,1/2+y,1/2-z**	**-2.15**
13	**1/2+x,-1/2+y,1/2-z**	**-2.15**
14	**1/2+x,1/2+y,1/2-z**	**-2.15**

Table S23. Numbering of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecule in the crystals **23**. Dimers belonging to primary and secondary basic structural motifs are highlighted in bold and italic, respectively.

Dimer	Symmetry operation	E_{int}, kcal/mol
1	**x,-1+y,z**	**-3.39**
2	**x,1+y,z**	**-3.39**
3	-1/2+x,-1/2+y,z	-0.39
4	-1/2+x,1/2+y,z	-0.58
5	1/2+x,-1/2+y,z	-1.05
6	1/2+x,1/2+y,z	-0.56
7	-x,y,1/2-z	-0.56
8	1-x,y,1/2-z	-1.05
9	*1/2-x,-1/2+y,1/2-z*	*-2.23*
10	*1/2-x,1/2+y,1/2-z*	*-2.23*
11	-x,1-y,-z	-2.03
12	-x,2-y,-z	-0.55
13	*1/2-x,1/2-y,-z*	*-2.50*
14	*1/2-x,1.5-y,-z*	*-2.15*

Table S24. Numbering of dimers, symmetry operation of second molecule of dimer and energy of intermolecular interactions in dimers formed by the basic molecule in the crystals of polymorphic modifications of diiodomethane **24** and **25**. Dimers belonging to primary and secondary basic structural motifs are highlighted in bold and italic, respectively.

	Structure **24**		Structure **25**	
Dimer	Symmetry operation	E_{int}, kcal/mol	Symmetry operation	E_{int}, kcal/mol
1	**x,-1+y,z**	**-4.15**	**x,y,-1+z**	**-4.16**
2	**x,1+y,z**	**-4.15**	**x,y,1+z**	**-4.16**
3	-x,y,1/2-z	-0.76	x,-1/2+y,-1/2+z	-0.49
4	1-x,y,1/2-z	-1.05	x,-1/2+y,1/2+z	-0.49
5	-1/2+x,-1/2+y,z	-1.08	x,1/2+y,-1/2+z	-0.49
6	-1/2+x,1/2+y,z	-0.68	x,1/2+y,1/2+z	-0.49
7	1/2+x,-1/2+y,z	-0.68	*-1/2+x,y,-1/2+z*	*-2.01*
8	1/2+x,1/2+y,z	-1.08	*-1/2+x,y,1/2+z*	*-2.01*
9	*1/2-x,-1/2+y,1/2-z*	*-2.23*	*1/2+x,y,-1/2+z*	*-2.01*
10	*1/2-x,1/2+y,1/2-z*	*-2.23*	*1/2+x,y,1/2+z*	*-2.01*
11	-x,1-y,-z	-2.68	-1/2+x,-1/2+y,z	-0.88
12	-x,2-y,-z	-0.82	-1/2+x,1/2+y,z	-0.88
13	*1/2-x,1/2-y,-z*	*-2.01*	1/2+x,-1/2+y,z	-0.88
14	*1/2-x,1.5-y,-z*	*-2.92*	1/2+x,1/2+y,z	-0.88