

The role of hydrogen bond interactions in crystal formation of pyrrolo-azines alcohols

Marcel Mirel Popa, Mihai Răducă*, Isabela C. Man and Florea Dumitrascu*

Institute of Organic and Supramolecular Chemistry "C. D. Nenițescu", Romanian Academy, 202 B Splaiul Independenței,
060023 Bucharest, Romania

-= SUPPLEMENTARY MATERIAL =-

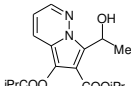
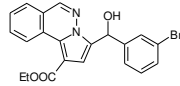
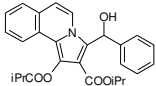
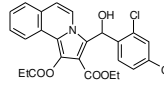
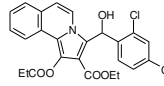
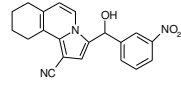
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1. Single crystal X-Ray diffraction

Table S1. Molecular structures and X-ray diffraction parameters for compounds **1-5** – Extended Table

Compound	1	2	3A	3B	4	5
Formula						
Empirical formula	C ₁₇ H ₂₂ N ₂ O ₅	C ₂₁ H ₁₇ BrN ₂ O ₃	C ₂₇ H ₂₇ NO ₅	C ₂₇ H ₂₇ NO ₅	C ₂₅ H ₂₁ Cl ₂ NO ₅	C ₂₀ H ₁₇ N ₃ O ₃
Formula weight	334.36	425.27	445.49	445.49	486.33	347.36
Temperature/K	293(2)	293(2)	293(2)	293(2)	293(2)	160.00(10)
Crystal system	monoclinic	triclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	P2 ₁ /c	P-1	P2 ₁ /c	P-1	P-1	C2/c
a/Å	8.8876(5)	8.3116(5)	9.4337(8)	10.0519(8)	8.8989(3)	21.988(3)
b/Å	9.4076(5)	9.6349(9)	11.7570(11)	11.4464(10)	10.0904(4)	14.771(2)
c/Å	21.6068(14)	12.3873(8)	21.510(2)	11.4996(9)	12.9124(5)	15.662(2)
α/°	90	89.768(7)	90	72.018(8)	98.447(3)	90
β/°	100.146(6)	86.326(5)	94.695(8)	80.535(6)	92.114(3)	40.541(13)
γ/°	90	70.903(7)	90	71.772(8)	91.975(3)	90
Volume/Å ³	1778.32(18)	935.32(13)	2377.7(4)	1191.96(18)	1145.16(7)	3306.4(10)
Z	4	2	4	2	2	8
ρ _{calc} /cm ³	1.249	1.510	1.244	1.241	1.410	1.396
μ/mm ⁻¹	0.092	2.221	0.086	0.085	0.321	0.096
F(000)	712.0	432.0	944.0	472.0	504.0	1456
Crystal size/mm ³	0.21 × 0.17 × 0.11	0.321 × 0.224 × 0.102	0.33 × 0.21 × 0.14	0.41 × 0.35 × 0.1	0.21 × 0.18 × 0.1	0.4 × 0.2 × 0.2
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2θ range for data collection/°	4.656 to 62.096	4.474 to 61.866	4.332 to 49.994	4.278 to 61.85	4.084 to 61.972	3.794 to 50.044
Index ranges	-11 ≤ h ≤ 12, -12 ≤ k ≤ 13, -27 ≤ l ≤ 22	-11 ≤ h ≤ 10, -12 ≤ k ≤ 12, -16 ≤ l ≤ 15	-11 ≤ h ≤ 10, -12 ≤ k ≤ 13, 13 ≤ k ≤ 13, -15 ≤ k ≤ 16, 25 ≤ l ≤ 22	-12 ≤ h ≤ 13, -15 ≤ k ≤ 16, -16 ≤ l ≤ 15	-12 ≤ h ≤ 12, -13 ≤ k ≤ 14, -17 ≤ l ≤ 17	-25 ≤ h ≤ 26, -17 ≤ k ≤ 10, -12 ≤ l ≤ 18
Reflections collected	11773	12023	14106	14783	17512	6817
Independent reflections	4413 [R _{int} = 0.0240, R _{sigma} = 0.0311]	4568 [R _{int} = 0.0379, R _{sigma} = 0.0585]	4167 [R _{int} = 0.0601, R _{sigma} = 0.0741]	5965 [R _{int} = 0.0238, R _{sigma} = 0.0295]	5686 [R _{int} = 0.0265, R _{sigma} = 0.0286]	2915 [R _{int} = 0.0274, R _{sigma} = 0.0416]
Data/restraints/parameters	4413/0/234	4568/0/248	4167/0/315	5965/0/303	5686/0/301	2915/0/236
Goodness-of-fit on F ²	0.901	1.021	1.022	1.026	1.102	1.057
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0520, wR ₂ = 0.1608	R ₁ = 0.0645, wR ₂ = 0.1270	R ₁ = 0.0515, wR ₂ = 0.1426	R ₁ = 0.0461, wR ₂ = 0.1423	R ₁ = 0.0549, wR ₂ = 0.1522	R ₁ = 0.0662, wR ₂ = 0.1717
Final R indexes [all data]	R ₁ = 0.0787, wR ₂ = 0.1828	R ₁ = 0.1317, wR ₂ = 0.1476	R ₁ = 0.0692, wR ₂ = 0.1575	R ₁ = 0.0660, wR ₂ = 0.1580	R ₁ = 0.0761, wR ₂ = 0.1669	R ₁ = 0.0824, wR ₂ = 0.1828
Largest diff. peak/hole / e Å ⁻³	0.34/-0.20	0.60/-0.65	0.20/-0.20	0.17/-0.20	0.71/-0.45	1.09/-0.36

1. Energy Frameworks

The energy frameworks were generated by CrystalExplorer v17.

Compound 1 – Energy Frameworks Report

Interaction Energies (kJ/mol)

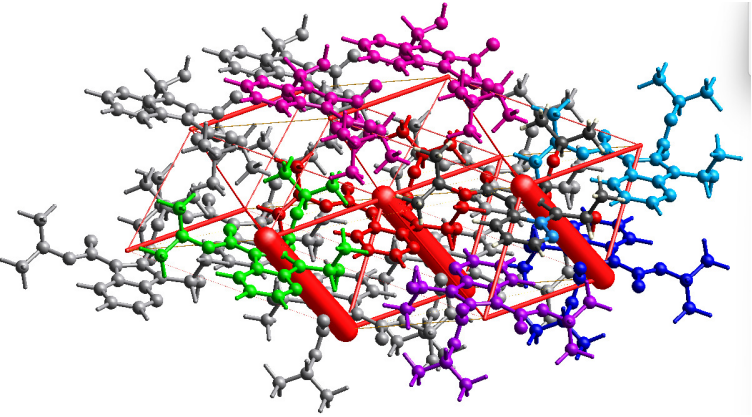
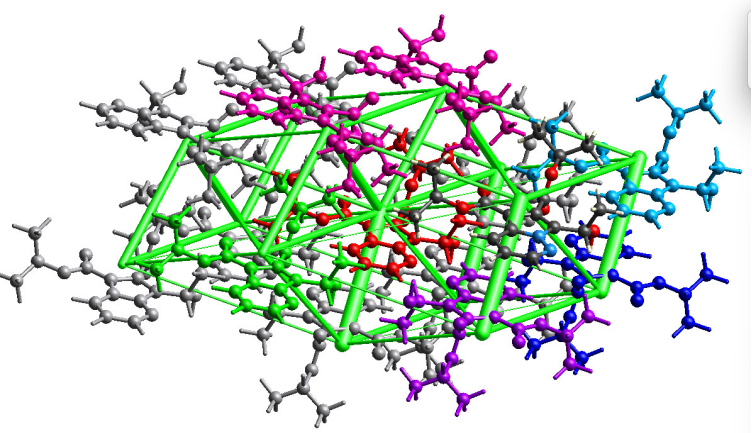
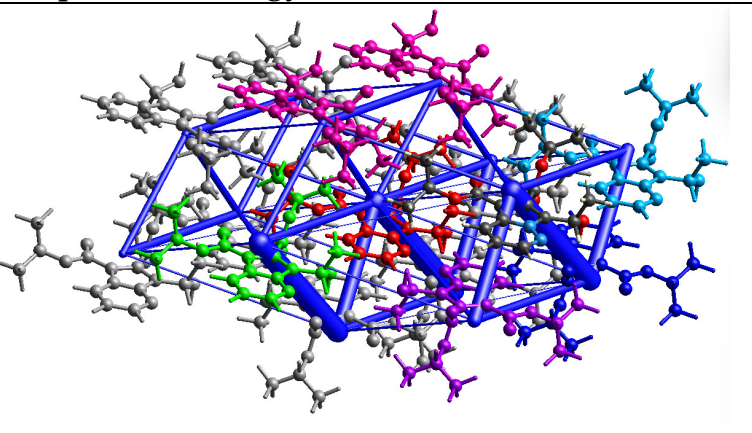
R is the distance between molecular centroids (mean atomic position) in Å.

Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	x, y, z	8.89	HF/3-21G	2.6	-2.3	-13.8	3.2	-8.7
	0	-x, -y, -z	11.00	HF/3-21G	-0.7	-0.5	-10.1	2.2	-8.4
	0	-x, -y, -z	10.66	HF/3-21G	-7.8	-2.2	-14.6	5.1	-18.4
	1	x, y, z	12.94	HF/3-21G	0.5	-0.2	-4.8	0.0	-4.0
	0	-x, y+1/2, -z+1/2	7.52	HF/3-21G	-4.5	-2.0	-38.1	17.2	-26.2
	1	x, y, z	9.41	HF/3-21G	-17.9	-5.2	-27.5	17.3	-32.4
	1	-x, -y, -z	7.12	HF/3-21G	-89.7	-28.4	-21.3	58.4	-81.7
	1	-x, -y, -z	6.57	HF/3-21G	-15.9	-3.6	-63.6	27.9	-53.2
	2	-x, y+1/2, -z+1/2	10.50	HF/3-21G	-4.6	-2.7	-18.4	10.1	-14.9

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811

Table S2. Energy Frameworks for compound 1

Energy Framework

Electrostatic Energy Framework

Dispersive Energy Framework

Total Energy Framework

Compound 2 – Energy Frameworks report

Interaction Energies (kJ/mol)

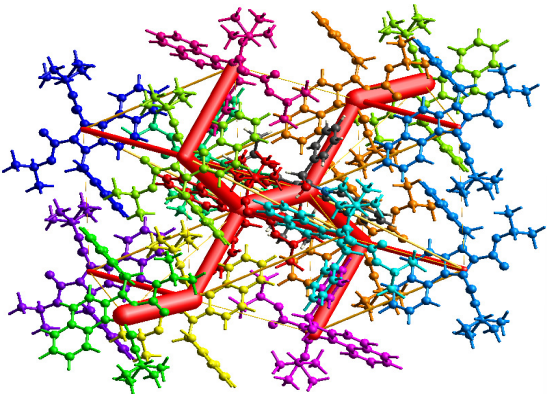
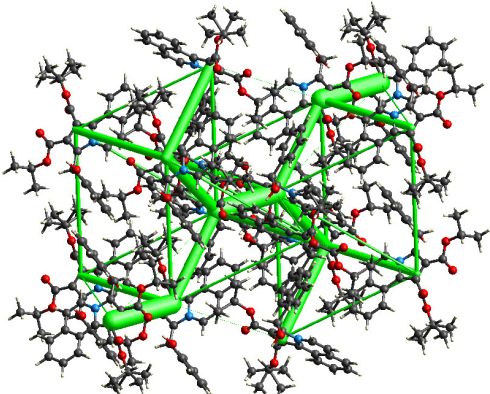
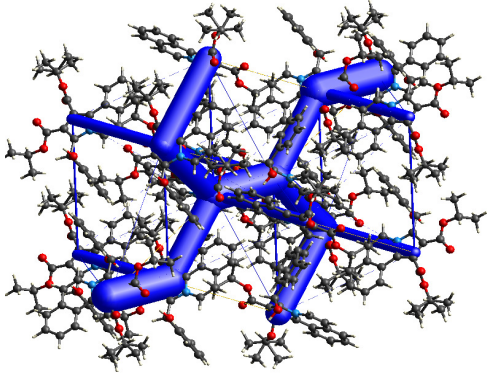
R is the distance between molecular centroids (mean atomic position) in Å.

Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-x, -y, -z	5.71	HF/3-21G	-118.7	-53.6	-123.9	81.8	-201.2
	2	-x, y+1/2, -z+1/2	7.96	HF/3-21G	-79.5	-38.5	-72.5	28.0	-148.7
	1	x, -y+1/2, z+1/2	12.59	HF/3-21G	0.0	-1.0	0.0	0.0	-0.6
	2	x, -y+1/2, z+1/2	11.95	HF/3-21G	5.2	-0.9	-1.9	0.0	3.0
	1	-x, y+1/2, -z+1/2	17.36	HF/3-21G	0.0	-0.0	0.0	0.0	-0.0
	1	x, y, z	9.43	HF/3-21G	-33.2	-20.3	-48.2	26.8	-68.8
	1	-x, -y, -z	9.46	HF/3-21G	5.9	-3.4	-8.7	0.2	-3.9
	2	-x, y+1/2, -z+1/2	11.70	HF/3-21G	12.6	-5.0	-16.4	5.0	-1.1
	1	x, -y+1/2, z+1/2	15.76	HF/3-21G	0.0	-0.3	0.0	0.0	-0.2
	1	x, -y+1/2, z+1/2	16.25	HF/3-21G	0.0	-0.4	0.0	0.0	-0.2
	1	x, y, z	11.76	HF/3-21G	2.1	-6.4	-26.4	17.0	-12.0
	1	-x, -y, -z	12.47	HF/3-21G	0.0	-4.1	0.0	0.0	-2.7

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811

Table S3. Energy Frameworks for compound 2

Energy Framework
 A 3D molecular model of compound 2 showing the total energy framework. The molecule is composed of various atoms represented by different colors (blue, green, yellow, orange, red, purple). The energy framework is highlighted by a network of red and orange lines connecting the atoms, indicating the distribution of total energy across the molecular structure.
Electrostatic Energy Framework
 A 3D molecular model of compound 2 showing the electrostatic energy framework. The molecule is represented by a grey ball-and-stick model. The electrostatic energy framework is highlighted by a network of green lines connecting the atoms, indicating the distribution of electrostatic energy across the molecular structure.
Dispersive Energy Framework
 A 3D molecular model of compound 2 showing the dispersive energy framework. The molecule is represented by a grey ball-and-stick model. The dispersive energy framework is highlighted by a network of blue lines connecting the atoms, indicating the distribution of dispersive energy across the molecular structure.
Total Energy Framework

Compound 3A – Energy Frameworks report

Interaction Energies (kJ/mol)

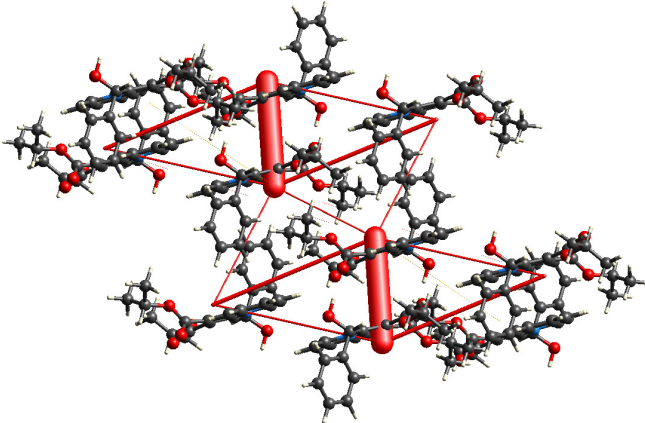
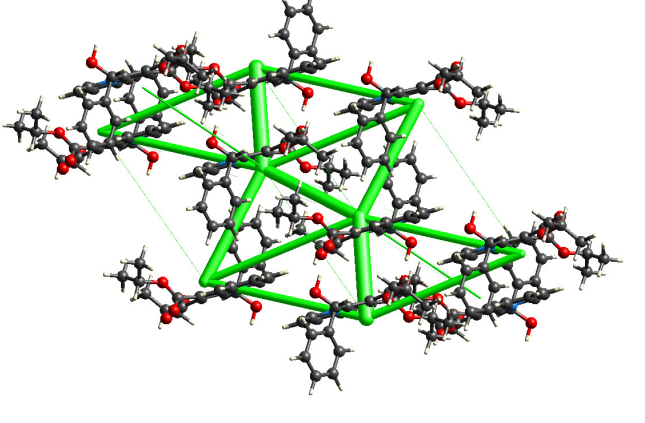
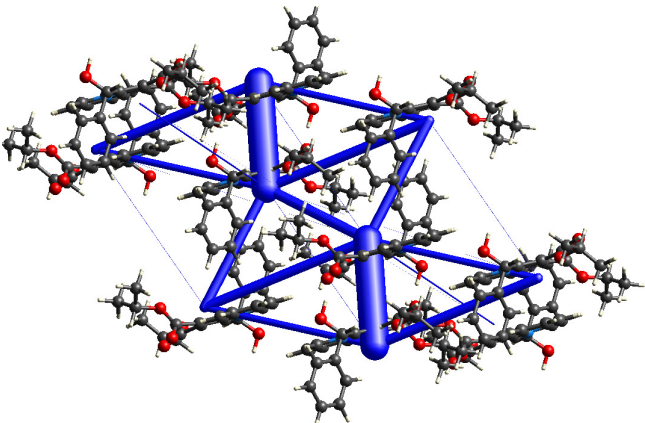
R is the distance between molecular centroids (mean atomic position) in Å.

Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-x, -y, -z	7.91	HF/3-21G	-6.7	-2.9	-57.9	21.0	-43.9
	1	x, y, z	11.45	HF/3-21G	0.0	-0.1	-1.6	0.0	-1.5
	1	-x, -y, -z	5.50	HF/3-21G	-90.6	-34.6	-75.2	79.5	-118.2
	1	x, y, z	10.05	HF/3-21G	-17.2	-5.9	-38.7	19.5	-40.5
	1	-x, -y, -z	7.34	HF/3-21G	-6.8	-2.2	-58.4	23.7	-41.8
	1	x, y, z	17.44	HF/3-21G	-0.2	-0.0	-0.2	0.0	-0.4
	1	-x, -y, -z	9.67	HF/3-21G	-8.9	-2.4	-39.6	22.6	-27.9
	1	x, y, z	11.50	HF/3-21G	1.1	-0.5	-9.4	1.5	-6.4
	1	-x, -y, -z	15.61	HF/3-21G	-0.0	-0.0	-0.5	0.0	-0.5

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811

Table S4. Energy Frameworks for compound **3A**

Energy Framework
 A 3D molecular model of compound 3A, which is a complex polycyclic aromatic hydrocarbon with multiple hydroxyl groups. The model is overlaid with a network of red lines and red cylindrical volumes, representing the energy framework. The red cylinders are positioned at various points within the molecule, and the red lines connect them, forming a complex web that highlights the energy distribution across the structure.
Electrostatic Energy Framework
 A 3D molecular model of compound 3A, similar to the first one. The model is overlaid with a network of green lines and green cylindrical volumes, representing the electrostatic energy framework. The green cylinders are positioned at various points within the molecule, and the green lines connect them, forming a complex web that highlights the electrostatic energy distribution across the structure.
Dispersive Energy Framework
 A 3D molecular model of compound 3A, similar to the first one. The model is overlaid with a network of blue lines and blue cylindrical volumes, representing the dispersive energy framework. The blue cylinders are positioned at various points within the molecule, and the blue lines connect them, forming a complex web that highlights the dispersive energy distribution across the structure.
Total Energy Framework

Compound 3B - Energy Frameworks report

Interaction Energies (kJ/mol)

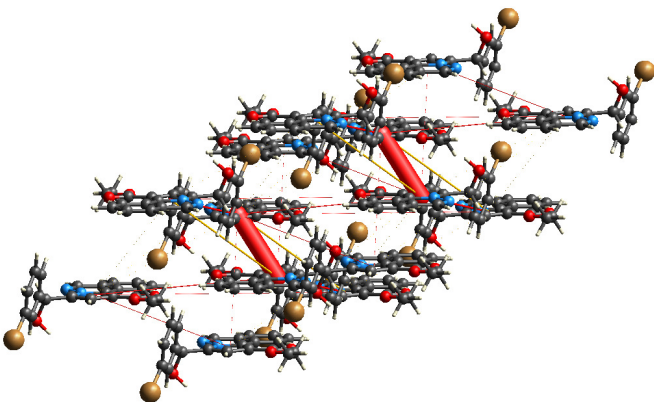
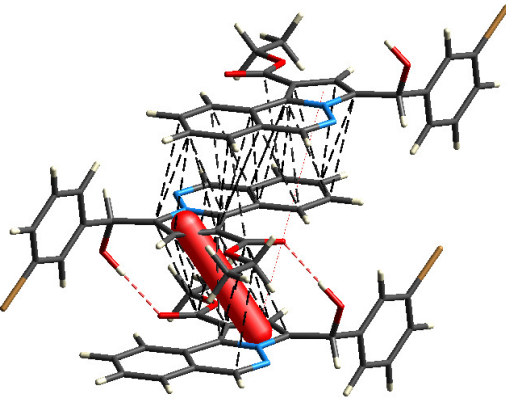
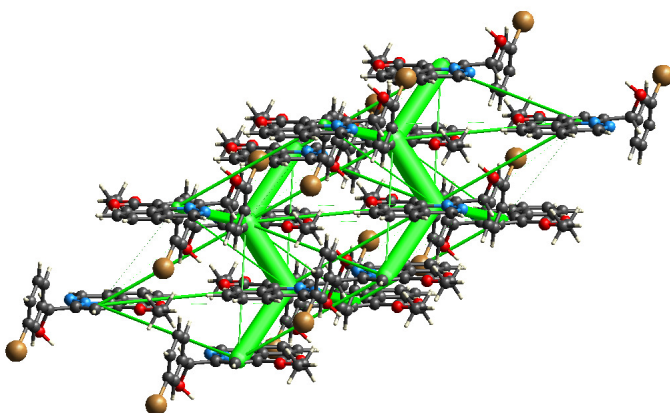
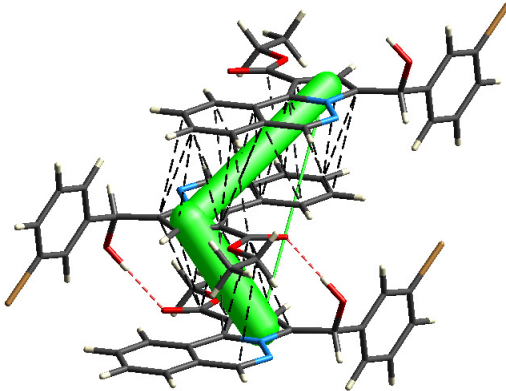
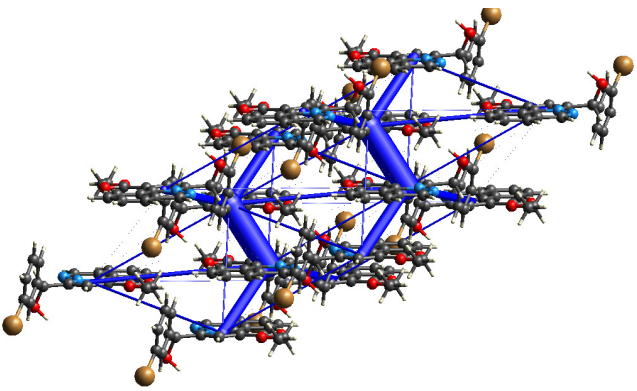
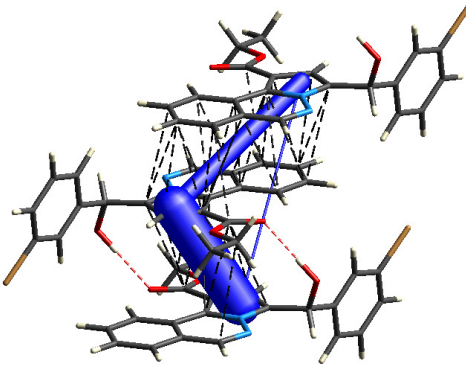
R is the distance between molecular centroids (mean atomic position) in Å.

Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-x, -y, -z	8.14	HF/3-21G	-8.1	-2.1	-47.8	22.8	-34.1
	1	x, y, z	12.39	HF/3-21G	7.7	-0.5	-8.0	0.0	0.3
	0	-x, -y, -z	5.28	HF/3-21G	-72.3	-17.3	-108.0	88.8	-110.2
	0	-x, -y, -z	8.83	HF/3-21G	-0.0	-3.8	-85.6	35.5	-50.9
	0	x, y, z	8.31	HF/3-21G	-0.9	-0.2	-8.3	1.3	-7.5
	0	-x, -y, -z	12.23	HF/3-21G	-3.8	-2.4	-15.1	0.0	-19.1
	1	x, y, z	9.63	HF/3-21G	0.2	-1.5	-15.1	6.9	-8.8
	1	-x, -y, -z	13.68	HF/3-21G	0.3	-0.0	-0.6	0.0	-0.3
	1	x, y, z	15.72	HF/3-21G	-1.4	-0.1	-0.8	0.0	-2.3
	0	-x, -y, -z	15.88	HF/3-21G	0.2	-0.0	-0.4	0.0	-0.2
	0	x, y, z	10.46	HF/3-21G	-2.4	-1.2	-14.2	5.8	-11.2
	0	-x, -y, -z	21.38	HF/3-21G	-0.0	-0.0	-0.0	0.0	-0.1

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811

Table S5. Energy Frameworks for compound **3B**

Energy Framework	
	
Electrostatic Energy Framework	
	
Dispersive Energy Framework	
	
Total Energy Framework	

Compound 4- Energy Frameworks report

Interaction Energies (kJ/mol)

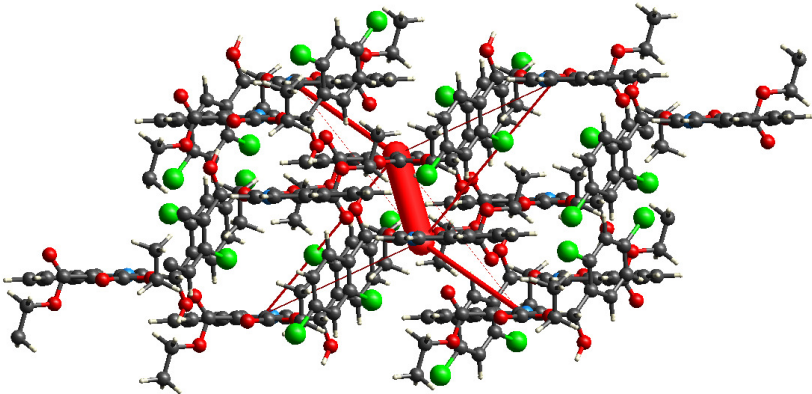
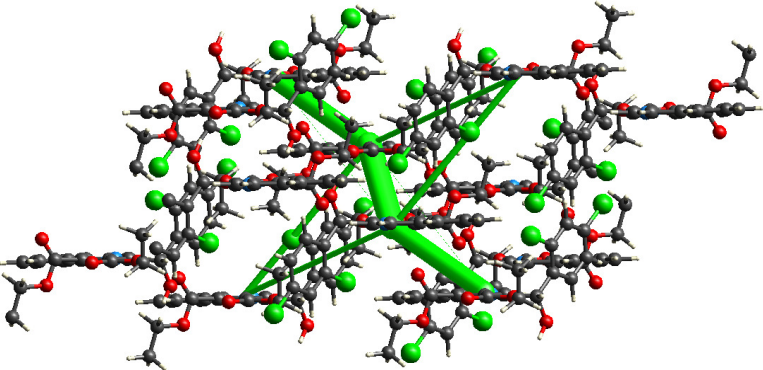
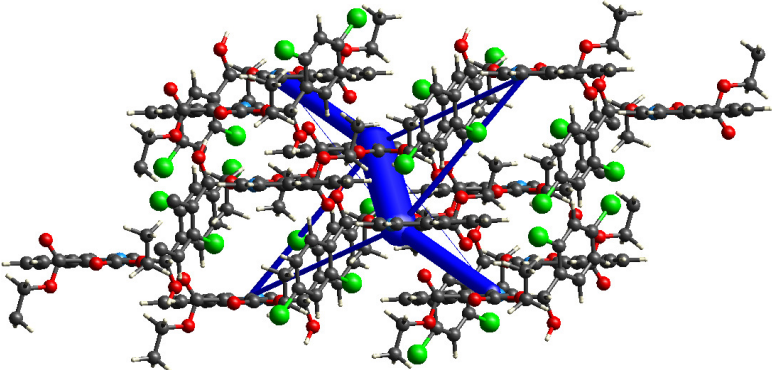
R is the distance between molecular centroids (mean atomic position) in Å.

Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-x, -y, -z	6.81	HF/3-21G	-91.1	-27.9	-100.2	83.9	-133.2
	1	-x, -y, -z	10.74	HF/3-21G	-4.2	-1.0	-22.5	8.5	-18.3
	1	x, y, z	10.09	HF/3-21G	-8.6	-1.6	-28.0	15.0	-22.9
	1	-x, -y, -z	7.47	HF/3-21G	-19.9	-8.8	-80.8	40.1	-66.3
	1	x, y, z	12.91	HF/3-21G	-1.1	-0.1	-1.1	0.0	-2.2

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811

Table S6. Energy Frameworks for compound 4

Energy Framework

Electrostatic Energy Framework

Dispersive Energy Framework

Total Energy Framework

Compound 5- Energy Frameworks report

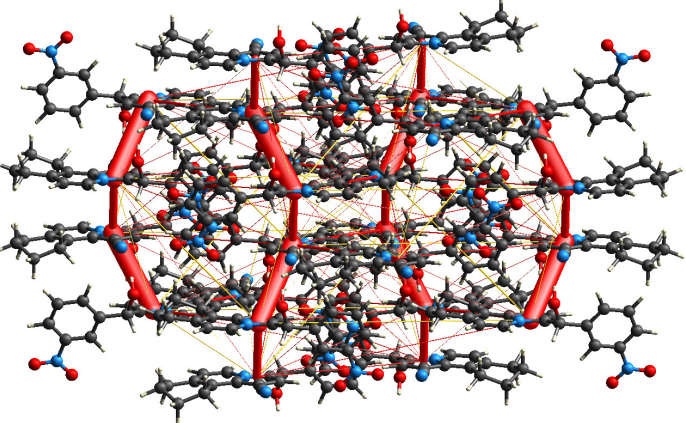
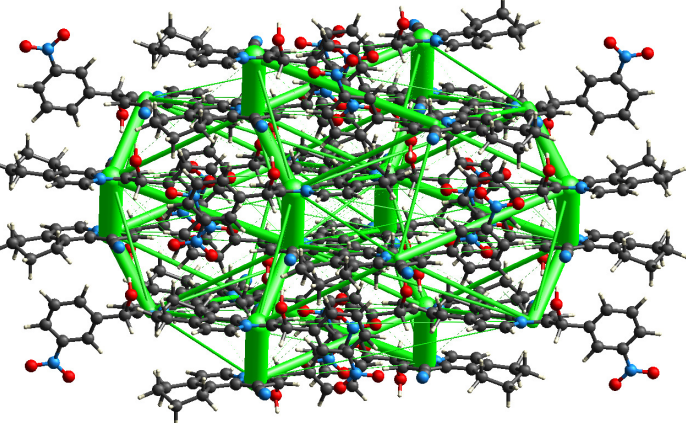
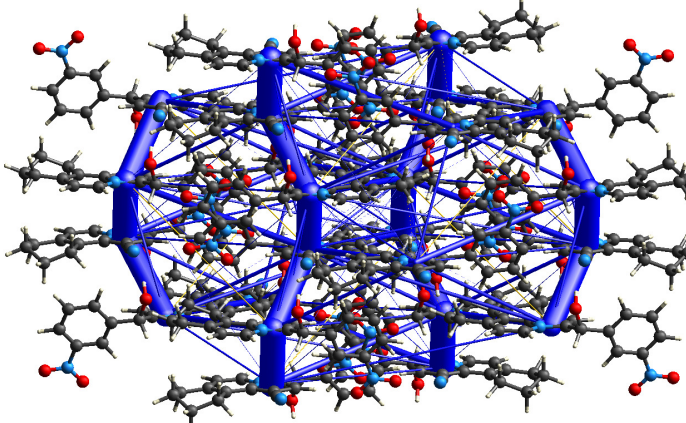
Interaction Energies (kJ/mol)

R is the distance between molecular centroids (mean atomic position) in Å.

Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-x+1/2, -y+1/2, -z+1/2	10.02	HF/3-21G	-2.7	-0.4	-1.1	0.0	-4.0
	1	-x, -y, -z	9.95	HF/3-21G	-3.2	-1.7	-46.5	24.3	-26.6
	1	x+1/2, y+1/2, z+1/2	12.61	HF/3-21G	-1.9	-0.2	-0.7	0.0	-2.8
	1	x, y, z	14.77	HF/3-21G	4.1	-0.7	-4.5	0.0	-0.3
	2	x, -y+1/2, z+1/2	7.19	HF/3-21G	2.7	-3.9	-16.1	4.4	-10.7
	1	x+1/2, -y, z	11.16	HF/3-21G	-4.5	-1.0	-3.3	0.1	-8.2
	1	-x, y+1/2, -z+1/2	13.61	HF/3-21G	-1.6	-0.1	-0.3	0.0	-2.0
	1	-x+1/2, y, -z	15.21	HF/3-21G	-3.3	-1.9	-5.4	0.0	-9.5
	1	-x, -y, -z	9.06	HF/3-21G	2.8	-1.8	-12.8	2.4	-7.8
	2	x+1/2, -y, z	10.38	HF/3-21G	-10.8	-5.6	-20.1	10.4	-24.3
	1	-x+1/2, y, -z	3.64	HF/3-21G	-32.2	-8.8	-102.7	39.9	-98.7
	1	-x+1/2, -y+1/2, -z+1/2	13.44	HF/3-21G	1.5	-0.0	-0.4	0.0	1.1
	1	x+1/2, y+1/2, z+1/2	12.61	HF/3-21G	-1.1	-0.2	-0.9	0.0	-2.1
	2	-x, y+1/2, -z+1/2	9.89	HF/3-21G	-1.9	-2.8	-23.1	11.8	-15.1
	1	-x+1/2, y, -z	13.45	HF/3-21G	0.9	-0.0	-0.3	0.0	0.6
	1	-x+1/2, -y+1/2, -z+1/2	5.43	HF/3-21G	-75.4	-22.1	-63.3	75.0	-87.4
	1	x+1/2, y+1/2, z+1/2	13.24	HF/3-21G	0.4	-0.1	-0.3	0.0	0.1
	1	-x+1/2, -y+1/2, -z+1/2	15.19	HF/3-21G	-1.9	-0.7	-14.4	0.0	-15.4
	1	x+1/2, y+1/2, z+1/2	13.24	HF/3-21G	5.4	-0.2	-1.2	0.0	4.4
	1	x, -y+1/2, z+1/2	15.91	HF/3-21G	0.0	-0.1	-0.7	0.0	-0.6
Energy Model					k_ele	k_pol	k_disp	k_rep	
CE-HF ... HF/3-21G electron densities					1.019	0.651	0.901	0.811	

Table S7. Energy Frameworks for compound 5

Energy Framework

Electrostatic Energy Framework

Dispersive Energy Framework

Total Energy Framework