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Toward Low-sensitive and High-energetic Cocrystal III: Thermodynamics of the Energetic-energetic Cocrystal Formation

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Table s1. Summary of intermolecular hydrogen bonding interactions (A–H···B; Å, º) operating in the crystal structures of CL-20 polymorphs and co-crystals regarding a CL-20 molecule involved in crystal. The distance of H···B and the angle of A-H···B are limited to shorter than 2.6 Å and bigger than 120º.

	A	H	B	A-H	H···B	A···B	A-H···B	Symmetry operation
β-CL-20	C4	H4	O4	0.933	2.542	3.272	135.4	1-x,1/2+y,1-z; 1-x,-1/2+y,1-z
	C5	H5	O5	0.852	2.576	3.233	134.8	1/2+x,y,1-z; -1/2+x,y,1-z
	C6	H6	O9	0.898	2.539	3.161	126.9	-1/2+x,y,-z; 1/2+x,y,-z
CL-20/HMX	C4	H4	O3	1.000	2.584	3.327	131.1	1-x,-1/2+y,1/2-z; x,1/2-y,-1/2+z; x,1/2-y,-1/2+z; 1-x,1/2+y,1/2-z
	C3	H3	O4	0.999	2.391	3.377	168.9	1-x,-1/2+y,1/2-z; x,1/2-y,-1/2+z; x,1.5-y,-1/2+z; 1-x,1/2+y,1/2-z
	C7	H7A	O7	0.990	2.288	3.140	143.6	-x,1-y,-z; x,1+y,z; -x,1-y,-z; 1+x,y,z;
	C7	H7A	O9	0.990	2.311	2.967	122.9	-x,1-y,-z; -x,2-y,-z; -x,1-y,-z; 1+x,y,z
	C8	H8B	O10	0.990	2.319	3.137	139.4	-x,2-y,-z; 1-x,1-y,-z; x, y, z
	C8	H8A	O7	0.991	2.421	3.335	153.1	-x,1-y,-z; x,1+y,z; 1+x,y,z
	C2	H2	O16	0.999	2.357	3.259	149.6	x,1.5-y,-1/2+z; 1-x,-1/2+y,1/2-z; -x,1/2+y,-1/2-z; x,1.5-y,1/2+z
	C7	H7B	O15	0.991	2.515	3.433	154.0	-x,1/2+y,1/2-z; -x,1/2+y,-1/2-z; x,1.5-y,1/2+z
CL-20/TNT	C13	H11	O13	1.000	2.439	3.360	152.7	-1/2+x,y,1.5-z; 1/2+x,y,1.5-z
	C6	H5	O17	0.951	2.506	3.442	168.0	-1/2+x,y,1.5-z; 1/2+x,y,1.5-z
	C11	H9	O5	1.001	2.367	3.185	138.4	1+x,y,z; -1+x,y,z
	C8	H6	O7	1.000	2.395	3.308	151.4	-1/2+x,1/2-y,1-z; 1/2+x,1/2-y,1-z
	C4	H4	O13	0.949	2.422	3.319	157.6	2.5-x,-1/2+y,z; 2.5-x,1/2+y,z
	C1	H1B	O15	0.981	2.595	3.268	125.9	x, y, z
CL-20/BTF	C6	H6	N18	0.980	2.448	3.338	150.7	-x,-1/2+y,-1/2-z; -x,1/2+y,-1/2-z

S2. Geometries of O···O contacts in BTF and BTF-based EECCs.

Table s2. Summary of intermolecular O···O interactions operating in the crystal structures of BTF and BTF-based cocrystals regarding a BTF molecule involved in crystal. The O···O distances are limited to shorter than 3.3 Å.

Energetic-energetic	Atom1	Atom2	Length, Å	Symmetry Operation
BTF	O4	O5	2.954	1/2+x, 1/2-y, z ; -1/2+x, 1/2-y, z
	O1	O5	3.046	x, y, 1+z; x, y, -1+z
	O2	O3	3.070	2-x, -y, 1/2+z; 2-x, -y, -1/2+z
	O1	O4	3.088	-1+x, y, 1+z; 1+x, y, -1+z
	O1	O3	3.197	-1+x,y, z; 1+x,y, z
	O4	O6	3.245	1+x,y,-1+z; -1+x,y,1+z
	O2	O4	3.245	x, y, 1+z; -x, y, 1+z
BTF/CL-20	O1	O15	3.062	1/2+x, 1/2-y, -z; -1/2+x, 1/2-y, -z
	O3	O16	3.139	1/2+x, 1.5-y, -z; -1/2+x, 1.5-y, -z
	O3	O18	3.272	1+x, y, z; -1+x, y, z
	O4	O13	3.271	1/2+x, 1.5-y, -z; -1/2+x, 1.5-y, -z
	O4	O15	3.028	x, y, z
	O6	O13	3.270	x, -1+y, z; x, 1+y, z
	O7	O15	3.224	1/2+x, 1/2-y, -z; -1/2+x, 1/2-y, -z
	O8	O17	2.803	-x, -1/2+y, -1/2-z; -x, 1/2+y, -1/2-z
	O8	O13	3.172	x, -1+y, z; x, 1+y, z
	O9	O13	2.962	1-x, -1/2+y, -1/2-z; 1-x, 1/2+y, -1/2-z
	O10	O17	3.192	-x, -1/2+y, -1/2-z; -x, 1/2+y, -1/2-z
	O12	O14	3.028	-x, -1/2+y, -1/2-z; -x, 1/2+y, -1/2-z
	O12	O18	3.176	x, y, z
	O5	O15	2.998	x, y, z
	O5	O17	3.167	-1/2+x, y, 1.5-z; 1/2+x, y, 1.5-z
	O5	O18	2.942	-1/2+x, y, 1.5-z; 1/2+x, y, 1.5-z
	O6	O10	3.036	-1+x, y, z; 1+x, y, z
	O6	O12	3.185	1.5-x, -1/2+y, z; 1.5-x, 1/2+y, z
BTF/MATNB	O1	O2	2.945	1-x, 2-y, 1-z (2)
	O1	O10	3.144	1+x, 1+y, z; -1+x, -1+y, z
	O2	O10	3.170	1+x, 1+y, z; -1+x, -1+y, z
	O3	O6	2.992	x, 1.5-y, -1/2+z; x, 1.5-y, 1/2+z
	O3	O8	3.192	x, 1+y, z; x, -1+y, z
	O4	O9	2.951	x, 1+y, z; x, -1+y, z
	O4	O12	2.876	-x, 1/2+y, 1/2-z; -x, -1/2+y, 1/2-z
	O5	O7	2.777	x, y, z
	O5	O12	3.110	-x, 1-y, 1-z (2)
	O6	O6	2.812	1-x, 1-y, 1-z
	O6	O12	3.111	-x, 1-y, 1-z (2)
BTF/TNA	O1	O7	3.253	1-x, -y, -z (2)
	O1	O12	2.833	x, 1+y, z; x, -1+y, z

	O2	O12	3.259	-x, -y, -z (2)
	O3	O9	3.181	-1+y, y, z; 1+y, y, z
	O4	O9	3.110	-1+x, y, z; 1+x, y, z
	O5	O11	3.205	x, y, z
	O6	O10	2.990	x, y, z
BTF/TNB	O1	O7	2.999	1+x, 1+y, z; -1+x, -1+y, z
	O1	O10	3.247	1-x, 1/2+y, 1/2-z; 1-x, -1/2+y, 1/2-z
	O1	O11	3.123	1-x, 1-y, -z; 1-x, 1-y, -z
	O1	O12	3.264	1-x, 1-y, -z; 1-x, 1-y, -z
	O2	O7	3.282	-x, 1-y, -z; -x, 1-y, -z
	O4	O10	3.101	x, y, z
	O5	O12	3.15	1+x, 1/2-y, 1/2+z; -1+x, 1/2-y, -1/2+z
	O6	O9	3.07	1+x, y, z; -1+x, y, z
BTF/TNAZ	O10	O5A	3.284	x,1+y,z; x,-1+y,z
	O11	O5A	2.916	1+x,1+y,z; -1+x,-1+y,z
	O12	O5A	3.265	1+x,1+y,z; -1+x,-1+y,z
BTF/TNT	O2	O13A	2.853	1+x, 1+y, z; -1+x, -1+y, z
	O2	O17	3.265	1-x, 1-y, 1-z; 1-x,1-y, 1-z
	O3	O15	3.001	1+x, y, z; -1+x, y, z
	O4	O14	3.19	-1+x, y, z; 1+x, y, z
	O5	O16	3.112	x, y, z
	O6	O16	3.154	x, y, z
	O7	O18	3.258	-x, 1-y, 1-z; -x, 1-y, 1-z
	O8	O21	3.112	1+x, y, z; -1+x, y, z
	O11	O15	3.272	x, 1+y, z; x, -1+y, z
	O11	O16	3.287	x, 1+y, z; x, -1+y, z
	O11	O24	3.090	x, 1+y, z; x, -1+y, z
	O12	O22	2.982	x, y, z
BTF/DNB	O2	O7	3.236	-1+x, 1.5-y, -1/2+z; 1+x, 1.5-y, 1/2+z
	O2	O11	3.275	x, y, z
	O3	O11	3.180	x, y, z

S3. Summary of synthesis conditions of observed EECCs

Table s3. Synthesis conditions of **observed** EECCs

Cocrystals	Temperature (℃)	Solvent
CL-20/HMX	23	2-propanol
CL-20/TNT	23	ethanol
CL-20/BTF	room temperature	ethanol
TNT/TNB	room temperature	ethanol
BTF/TNA	room temperature	acetone
BTF/TNB	room temperature	acetone
BTF/MATNB	room temperature	acetone
BTF/TNAZ	room temperature	acetone
BTF/TNT	room temperature	acetone
BTF/DNB	room temperature	ethanol
DADP/TCTNB	room temperature	acetonitrile
DADP/TBCTNB	room temperature	acetonitrile