Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information for: First-Principles Stability Ranking of Molecular Crystal Polymorphs with the DFT+MBD Approach

Johannes Hoja[1] and Alexandre Tkatchenko[1]

[1] *Physics and Materials Science Research Unit, University of Luxembourg, L-1511 Luxembourg, Luxembourg*

CONTENTS

OPTIMIZED GEOMETRIES

All optimized structures are available in the attached file *Structures.cif*.

TABLE S1. Errors of PBE+TS-optimized structures using light settings w.r.t. experimental structures. This table shows the relative error in % for cell lengths (a,b,c), angles (α,β,γ), cell volume, and density. In addition the $RMSD_{20}$ is shown in Å.[34]

Exp. str.	a	b	c	α	β	γ	Volume	Density	$RMSD_{20}$
XXII	0.46	0.94	2.07		0.76		2.99	-2.90	0.103
XXIII-A	-1.25	-2.12	0.06		-1.42		-3.09	3.18	0.198
XXIII-B	1.13	-0.92	-3.95	4.28	0.26	-1.39	-4.53	4.71	0.277
XXIII-C	-1.43	-1.24	-0.97	2.47	2.01	0.11	-3.19	3.30	0.237
XXIII-D	-3.56	0.74	1.24		2.11		-3.51	3.67	0.447
XXIII-E	-1.15	-3.63	-1.69	-3.05	0.93	-0.55	-4.73	4.96	0.479
XXIV	2.17	-0.99	-0.78		1.04		0.11	-0.06	0.119
XXV	-0.06	-1.30	-1.61		0.72		-3.43	3.51	0.129
XXVI	-1.02	-0.67	-1.95	3.30	0.73	0.86	-2.47	2.53	0.268

TABLE S2. Errors of PBE+MBD-optimized structures using light settings w.r.t. experimental structures. This table shows the relative error in % for cell lengths (a,b,c), angles (α,β,γ), cell volume, and density. In addition the $RMSD_{20}$ is shown in Å.

Exp. str.	a	b	c	α	β	γ	Volume	Density	$RMSD_{20}$
XXII	1.62	0.96	2.01		1.24		3.80	-3.71	0.119
XXIII-A	-1.21	-0.32	-0.03		-1.52		-1.33	1.33	0.161
XXIII-B	2.45	-0.32	-3.28	3.02	1.04	-1.53	-1.83	1.81	0.243
XXIII-C	-1.57	-1.11	-0.21	2.26	1.91	1.11	-2.25	2.30	0.232
XXIII-D	-2.56	1.53	1.19		2.22		-1.92	2.02	0.414
XXIII-E	-0.27	-2.35	-2.02	-2.63	0.99	-0.40	-3.10	3.18	0.453
XXIV	4.69	-1.11	-1.32		0.06		2.15	-2.10	0.158
XXV	0.08	-1.03	-0.75		0.70		-2.16	2.15	0.102
XXVI	-0.56	-0.21	-2.13	3.18	1.04	1.62	-1.27	1.34	0.271

TABLE S3. Errors of PBE0+MBD-optimized structures using light settings w.r.t. experimental structures. This table shows the relative error in % for cell lengths (a,b,c), angles (α,β,γ), cell volume, and density. In addition the $RMSD_{20}$ is shown in Å.

Exp. str.	a	b	c	α	β	γ	Volume	Density	$RMSD_{20}$
XXII	0.22	0.18	0.64		0.62		0.63	-0.64	0.059
XXIII-A	-1.98	-2.30	-0.32		-1.41		-4.34	4.52	0.181
XXIII-B	1.58	-1.78	-3.81	3.14	0.65	-1.37	-4.61	4.86	0.251
XXIII-C	-2.64	-1.99	-1.20	2.54	1.88	0.50	-5.24	5.52	0.237
XXIII-D	-2.34	-0.14	-0.21		1.18		-3.71	3.90	0.272
XXIII-E	-1.96	-2.89	-2.57	-4.29	1.16	-0.13	-5.94	6.29	0.471
XXIV	1.68	-1.26	-1.46		0.46		-1.18	1.21	0.109
XXV	-0.70	-1.57	-2.03		0.94		-4.87	5.09	0.156
XXVI	-1.33	-1.45	-3.69	3.83	1.29	2.91	-4.04	4.23	0.357

TABLE S4. Errors of PBE+MBD-optimized structures using tight settings w.r.t. experimental structures. This table shows the relative error in % for cell lengths (a,b,c), angles (α,β,γ), cell volume, and density. In addition the $RMSD_{20}$ is shown in Å.

Exp. str.	a	b	c	α	β	γ	Volume	Density	$RMSD_{20}$
XXII	2.48	1.21	2.53		1.66		5.15	-4.92	0.152
XXIII-A	-1.16	-0.81	0.05		-1.19		-1.73	1.78	0.159
XXIII-B	1.94	-0.22	-3.21	2.04	-0.29	-1.66	-2.49	2.54	0.219
XXIII-C	-1.59	-1.23	-0.45	2.12	1.69	0.80	-2.72	2.80	0.220
XXIII-D	-1.90	1.37	1.00		2.44		-1.81	1.87	0.397
XXIII-E	-0.66	-1.70	-2.39	-2.70	1.26	-0.36	-3.24	3.33	0.460
XXIV	4.14	-1.02	-0.98		0.26		2.01	-1.91	0.138
XXV	-0.10	-1.02	-1.11		0.74		-2.71	2.72	0.116
XXVI	-0.96	-0.24	-2.03	2.47	0.99	1.30	-1.87	1.93	0.225

TABLE S5. Errors of the thermally-expanded structures (corresponding to 300 K within the QHA) calculated with PBE+TS and light settings w.r.t. experimental structures. This table shows the relative error in % for cell lengths (a,b,c), angles (α,β,γ), cell volume, and density. In addition the $RMSD_{20}$ is shown in Å.[34]

Exp. str.	a	b	c	α	β	γ	Volume	Density	$RMSD_{20}$
XXIII-A	-0.46	-0.73	0.28		-1.48		-0.70	0.74	0.193
XXIII-B	2.84	0.75	-3.72	3.97	1.56	-1.49	-0.76	0.72	0.293
XXIII-C	-0.69	-0.75	-0.36	2.03	2.06	0.23	-1.37	1.43	0.244
XXIII-D	-2.34	2.13	1.50		2.07		-0.66	0.67	0.408
XXIII-E	0.35	-2.42	-1.49	-3.16	0.56	-1.02	-1.70	1.70	0.479

PHONON BAND STRUCTURES

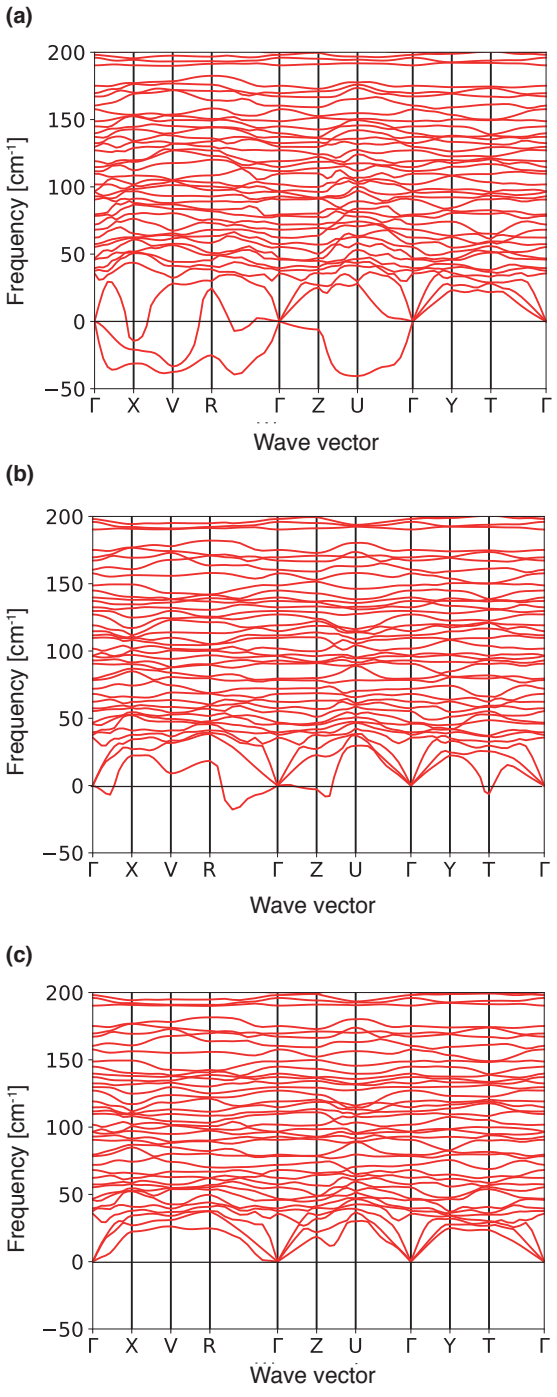

FIG. S1. Low-frequency phonon band structure plot along several high-symmetry lines for structure XXIII-N18 calculated using the unit cell (a), a supercell with a minimum length of 10 Å (b), and a supercell with a minimum length of 14 Å (c) in every direction.

PHONON DENSITIES OF STATE

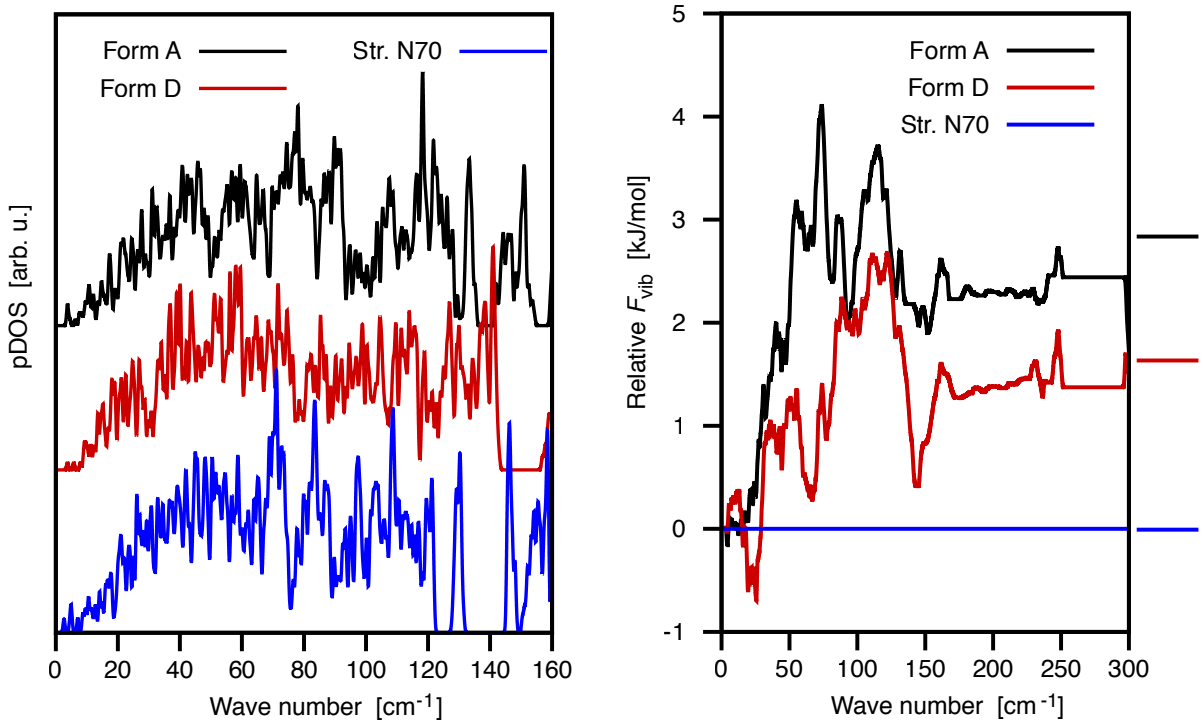

FIG. S2. Low frequency part of the phonon density of states (pDOS) for three structures of system XXIII (left) and the corresponding cumulative relative vibrational free energies at 300 K w.r.t. the wave number. (right). The vibrational free energy of structure N70 is always set to zero and the vibrational free energy is evaluated based on the pDOS up to the shown wave number. The right plot shows the low-frequency part up to 300 wave numbers. The final relative vibrational free energies after taking into account all modes are indicated with the three lines outside of the right plot. It can be seen that the relative vibrational free energies are essentially determined by low-frequency modes up to about 200 wave numbers.