Intermolecular Interactions in Molecular Organic Crystals upon Relaxation of Lattice Parameters

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Supplementary Information

Table S1. CSD reference codes of the molecules from the benchmark set X23.

Molecule	Code	Details of Structure
1,4-Cyclohexanedione	CYHEXO	133 K
Adamantane	ADAMAN08	Highest T structure at 200 K
Anthracene	ANTCEN09	RT
Benzene	BENZEN01	218 K
CO_2	CCDC 1597008	150 K
Hexamine	HXMTAM09	RT
Naphthalene	NAPHTA23	239 K
Pyrazine	PYRAZI01	RT
Pyrazole	PYRZOL05	RT
Triazine	TRIZIN	RT
Trioxane	TROXAN11	RT
Acetic Acid	ACETAC07	278 K
Cytosine	CYTSIN01	RT
Imidazole	IMAZOL04	RT
Uracil	URACIL	RT
Ammonia	ICSD 84461	160 K
Cyanamide	CYANAM01	108 K
Ethylcarbamate	ECARBM01	RT
Formamide	FORMAM02	RT
Oxalic Acid (alpha)	OXALAC03	RT
Oxalic Acid (beta)	OXALAC04	RT
Succinic Acid	SUCACB11	RT
Urea	UREAXX02	RT

Table S2. Calculated lattice energies for the benchmark set X23 with PBE-D3/ def2-TZVP are compared to experimental lattice energies; absolute and relative deviations from experiment are given.

	PBE-D3 def2-TZVP (kJ/ mol)	Deviation (kJ/ mol)	Rel. deviation (%)
1,4-Cyclohexanedione	-100.11	-11.51	12.99
Adamantane	-79.33	-9.93	14.31
Anthracene	-112.90	-0.20	0.18
Benzene	-58.41	-3.11	5.62
CO_2	-27.27	1.13	-3.98
Hexamine	-99.19	-12.99	15.07
Naphthalene	-83.94	-0.84	1.01
Pyrazine	-70.00	-8.70	14.19
Pyrazole	-86.28	-8.58	11.04
Triazine	-65.08	-3.38	5.48
Trioxane	-70.89	-4.49	6.76
Acetic Acid	-82.60	-9.80	13.46
Cytosine	-170.14	-7.34	4.51
Imidazole	-97.48	-10.68	12.30
Uracil	-146.20	-10.50	7.74
Ammonia	-50.74	-13.54	36.40
Cyanamide	-96.00	-16.30	20.45
Ethylcarbamate	-97.75	-11.45	13.27
Formamide	-89.47	-10.27	12.97
Oxalic Acid (alpha)	-102.60	-6.30	6.54
Oxalic Acid (beta)	-105.19	-9.09	9.46
Succinic Acid	-145.24	-14.94	11.47
Urea	-117.58	-15.08	14.71

Table S3. Experimental unit cell parameters and volumes of the X23 benchmark set.

	Volume in bohr^3	Vector in bohr		Angle in °	
1,4-Cyclohexanedione	1886.4684	a	12.5666	α	90.00
		b	11.7351	β	99.82
		c	12.9824	γ	90.00
Adamantane	2652.5437	a	12.5458	α	90.00
		b	12.5458	β	90.00
		c	16.8525	γ	90.00
Anthracene	3080.3599	a	15.9008	α	90.00
		b	11.3200	β	125.29
		c	20.9670	γ	90.00
Benzene	3199.1322	a	13.9650	α	90.00
		b	17.8011	β	90.00
		c	12.8690	γ	90.00
CO2	1200.3991	a	10.6278	α	90.00
		b	10.6278	β	90.00
		c	10.6278	γ	90.00
Hexamine	2269.3457	a	13.1412	α	90.00
		b	13.1412	β	90.00

		c	13.1412	γ	90.00
Naphthalene	2299.4269	a	15.2784	α	90.00
		b	11.2211	β	124.70
		c	16.3139	γ	90.00
Pyrazine	1374.2079	a	17.6216	α	90.00
		b	11.0548	β	90.00
		c	7.0543	γ	90.00
Pyrazole	4712.0669	a	15.4768	α	90.00
		b	23.7877	β	90.00
		c	12.7990	γ	90.00
Triazine	3960.007	a	18.2301	α	90.00
		b	18.2301	β	90.00
		c	13.7590	γ	120.00
Trioxane	4160.5825	a	17.6122	α	90.00
		b	17.6122	β	90.00
		c	15.4881	γ	120.00
Acetic Acid	2006.0422	a	24.8517	α	90.00
		b	7.4134	β	90.00
		c	10.8885	γ	90.00
Cytosine	3188.0265	a	24.6495	α	90.00
		b	17.9447	β	90.00
		c	7.2074	γ	90.00
Imidazole	2353.0843	a	14.3279	α	90.00
		b	10.1497	β	119.00
		c	18.5004	γ	90.00
Uracil	3126.865	a	22.5594	α	90.00
		b	23.3871	β	120.90
		c	6.9069	γ	90.00
Ammonia	911.3156	a	9.6952	α	90.00
		b	9.6952	β	90.00
		c	9.6952	γ	90.00
Cyanamide	2804.928	a	12.9559	α	90.00
		b	12.5250	β	90.00
		c	17.2852	γ	90.00
Ethylcarbamate	1678.7774	a	9.5450	α	101.37
		b	13.2488	β	104.58
		c	14.2541	γ	76.65
Formamide	1512.1077	a	6.8105	α	90.00
		b	17.0849	β	100.50
		c	13.2167	γ	90.00
Oxalic Acid (alpha)	2109.4437	a	12.3739	α	90.00
		b	14.8229	β	90.00
		c	11.5008	γ	90.00
Oxalic Acid (beta)	1058.5669	a	10.0722	α	90.00
		b	11.3666	β	115.83
		c	10.2725	γ	90.00
Succinic Acid	1646.0025	a	10.3292	α	90.00
		b	16.5161	β	91.70
		c	9.6527	γ	90.00
Urea	978.8969	a	10.5163	α	90.00
		b	10.5163	β	90.00
		c	8.8514	γ	90.00

Table S4. PBE calculated unit cell parameters for crystals from the X23 benchmark set.

PBED3/def2-TZVP													
Optimized Unit Cell					**Deviations**								
Volume in bohr^3	Vector in bohr		Angle in °		Volume in bohr^3	Vol %		Vector in bohr	Vector %		Angle in °	Angle %
1884.85	a	12.5402	α	90,008	-1.61	-0.09	a	-0.0264	-0.2101	α	0.0080	0.0089
	b	11.9266	β	99,521			b	0.1915	1.6318	β	-0.2990	-0.2995
	c	12.7785	γ	90,03			c	-0.2039	-1.5704	γ	0.0300	0.0333
2562.18	a	12.4370	α	90,036	-90.36	-3.41	a	-0.1089	-0.8678	α	0.0360	0.0400

	b	12.4312	β	89,99			b	-0.1147	-0.9140	β	-0.0100	-0.0111
	c	16.5724	γ	90,112			c	-0.2801	-1.6621	γ	0.1120	0.1244
3104.74	a	15.9162	α	90,189	24.38	0.79	a	0.0154	0.0967	α	0.1890	0.2100
	b	11.3582	β	125,023			b	0.0382	0.3378	β	-0.2700	-0.2155
	c	20.9721	γ	90,085			c	0.0051	0.0244	γ	0.0850	0.0944
3156.81	a	13.8387	α	89,891	-42.32	-1.32	a	-0.1263	-0.9044	α	-0.1090	-0.1211
	b	17.7900	β	90,244			b	-0.0112	-0.0627	β	0.2440	0.2711
	c	12.8228	γ	89,985			c	-0.0462	-0.3587	γ	-0.0150	-0.0167
1267.96	a	10.8234	α	90,235	67.56	5.63	a	0.1957	1.8412	α	0.2350	0.2611
	b	10.8239	β	90,24			b	0.1962	1.8460	β	0.2400	0.2667
	c	10.8235	γ	90,238			c	0.1957	1.8415	γ	0.2380	0.2644
2253.66	a	13.1108	α	89,966	-15.68	-0.69	a	-0.0303	-0.2308	α	-0.0340	-0.0378
	b	13.1108	β	89,966			b	-0.0303	-0.2309	β	-0.0340	-0.0378
	c	13.1108	γ	89,966			c	-0.0303	-0.2309	γ	-0.0340	-0.0378
2339.17	a	15.3350	α	90,217	39.74	1.73	a	0.0566	0.3708	α	0.2170	0.2411
	b	11.2973	β	124,286			b	0.0762	0.6788	β	-0.4140	-0.3320
	c	16.3419	γ	89,934			c	0.0280	0.1718	γ	-0.0660	-0.0733
1349.68	a	17.6501	α	90,098	-24.53	-1.79	a	0.0285	0.1618	α	0.0980	0.1089
	b	10.7131	β	90,026			b	-0.3418	-3.0917	β	0.0260	0.0289
	c	7.1379	γ	89,989			c	0.0836	1.1846	γ	-0.0110	-0.0122
4775.56	a	15.4601	α	89,887	63.49	1.35	a	-0.0167	-0.1077	α	-0.1130	-0.1256
	b	23.8282	β	90,04			b	0.0404	0.1699	β	0.0400	0.0444
	c	12.9635	γ	89,974			c	0.1644	1.2848	γ	-0.0260	-0.0289
3766.83	a	18.1327	α	89,334	-193.18	-4.88	a	-0.0974	-0.5341	α	-0.6660	-0.7400
	b	18.1809	β	89,562			b	-0.0492	-0.2696	β	-0.4380	-0.4867
	c	13.2033	γ	120,053			c	-0.5558	-4.0392	γ	0.0530	0.0442
4264.32	a	17.7881	α	90,194	103.74	2.49	a	0.1759	0.9990	α	0.1940	0.2156
	b	17.9289	β	90,09			b	0.3168	1.7986	β	0.0900	0.1000
	c	15.4120	γ	119,82			c	-0.0761	-0.4917	γ	-0.1800	-0.1500
2001.91	a	24.7623	α	90,057	-4.13	-0.21	a	-0.0893	-0.3594	α	0.0570	0.0633
	b	7.4575	β	89,985			b	0.0441	0.5948	β	-0.0150	-0.0167
	c	10.8409	γ	89,814			c	-0.0477	-0.4376	γ	-0.1860	-0.2067
3189.88	a	24.5093	α	89,838	1.86	0.06	a	-0.1402	-0.5688	α	-0.1620	-0.1800
	b	17.8841	β	89,869			b	-0.0607	-0.3381	β	-0.1310	-0.1456
	c	7.2775	γ	89,791			c	0.0701	0.9733	γ	-0.2090	-0.2322
2366.83	a	14.2404	α	90,236	13.75	0.58	a	-0.0876	-0.6111	α	0.2360	0.2622
	b	10.1926	β	117,745			b	0.0429	0.4224	β	-1.2550	-1.0546
	c	18.4251	γ	90,018			c	-0.0753	-0.4069	γ	0.0180	0.0200
3103.96	a	22.6436	α	89,265	-22.91	-0.73	a	0.0841	0.3729	α	-0.7350	-0.8167
	b	23.2013	β	122,247			b	-0.1858	-0.7945	β	1.3470	1.1141
	c	6.9865	γ	90,084			c	0.0795	1.1516	γ	0.0840	0.0933
847.89	a	9.4651	α	89,856	-63.43	-6.96	a	-0.2301	-2.3734	α	-0.1440	-0.1600
	b	9.4649	β	89,862			b	-0.2303	-2.3755	β	-0.1380	-0.1533
	c	9.4646	γ	89,854			c	-0.2306	-2.3784	γ	-0.1460	-0.1622
2853.83	a	13.1743	α	89,961	48.90	1.74	a	0.2184	1.6859	α	-0.0390	-0.0433
	b	12.9641	β	90,034			b	0.4391	3.5054	β	0.0340	0.0378
	c	16.7093	γ	90,087			c	-0.5759	-3.3318	γ	0.0870	0.0967
1632.20	a	9.5075	α	101,006	-46.57	-2.77	a	-0.0375	-0.3924	α	-0.3640	-0.3591

	b	13.1625	β	106,78			b	-0.0863	-0.6515	β	2.2000	2.1037
	c	14.1834	γ	75,579			c	-0.0708	-0.4965	γ	-1.0710	-1.3973
1507.40	a	6.8726	α	89,706	-4.71	-0.31	a	0.0621	0.9116	α	-0.2940	-0.3267
	b	16.8495	β	100,835			b	-0.2354	-1.3780	β	0.3350	0.3333
	c	13.2540	γ	89,715			c	0.0373	0.2821	γ	-0.2850	-0.3167
2118.15	a	12.6123	α	90,02	8.71	0.41	a	0.2384	1.9269	α	0.0200	0.0222
	b	14.4116	β	89,793			b	-0.4114	-2.7752	β	-0.2070	-0.2300
	c	11.6535	γ	89,802			c	0.1527	1.3278	γ	-0.1980	-0.2200
1055.08	a	9.9701	α	89,908	-3.49	-0.33	a	-0.1021	-1.0135	α	-0.0920	-0.1022
	b	11.4521	β	115,58			b	0.0854	0.7515	β	-0.2500	-0.2158
	c	10.2448	γ	90,087			c	-0.0277	-0.2700	γ	0.0870	0.0967
1639.02	a	10.4583	α	89,863	-6.98	-0.42	a	0.1291	1.2501	α	-0.1370	-0.1522
	b	16.3947	β	91,421			b	-0.1214	-0.7350	β	-0.2790	-0.3043
	c	9.5621	γ	90,031			c	-0.0906	-0.9381	γ	0.0310	0.0344
979.04	a	10.5130	α	90,079	0.15	0.01	a	-0.0033	-0.0309	α	0.0790	0.0878
	b	10.5079	β	89,949			b	-0.0084	-0.0799	β	-0.0510	-0.0567
	c	8.8626	γ	89,999			c	0.0112	0.1260	γ	-0.0010	-0.0011

Table S5. B97D calculated unit cell parameters for crystals from the X23 benchmark set.

B97D3/def2TZVP												
Optimized Unit Cell					**Deviations**							
Volume in bohr^3	Vector in bohr		Angles in °		Volume in bohr^3	Vol %		Vector in bohr	Vector %		Angle in °	Angle %
1790.53	a	12.4761	α	90,03	-95.94	-5.09	a	-0.0905	-0.7204	α	0.032	0.036
	b	11.5101	β	100,03			b	-0.2251	-1.9178	β	0.210	0.210
	c	12.6623	γ	90,01			c	-0.3200	-2.4650	γ	0.007	0.008
2472.51	a	12.2620	α	89,96	-180.04	-6.79	a	-0.2838	-2.2620	α	-0.036	-0.040
	b	12.2508	β	90,06			b	-0.2950	-2.3515	β	0.062	0.069
	c	16.4593	γ	90,02			c	-0.3932	-2.3333	γ	0.019	0.021
2907.20	a	15.4818	α	90,477	-173.16	-5.62	a	-0.4190	-2.6353	α	0.477	0.530
	b	11.1796	β	126,421			b	-0.1403	-1.2397	β	1.128	0.900
	c	20.8749	γ	89,576			c	-0.0921	-0.4391	γ	-0.424	-0.471
2929.17	a	13.5308	α	90,068	-269.96	-8.44	a	-0.4342	-3.1095	α	0.068	0.076
	b	17.4733	β	90,024			b	-0.3279	-1.8418	β	0.024	0.027
	c	12.3894	γ	90,175			c	-0.4795	-3.7264	γ	0.175	0.194
1267.63	a	10.8226	α	90,26	67.23	5.60	a	0.1948	1.8330	α	0.256	0.284
	b	10.8230	β	90,26			b	0.1952	1.8369	β	0.262	0.291
	c	10.8225	γ	90,26			c	0.1947	1.8324	γ	0.259	0.288
2159.99	a	12.9268	α	89,531	-109.35	-4.82	a	-0.2143	-1.6310	α	-0.469	-0.521
	b	12.9270	β	89,532			b	-0.2141	-1.6294	β	-0.468	-0.520
	c	12.9272	γ	89,533			c	-0.2139	-1.6279	γ	-0.467	-0.519
2170.55	a	14.9354	α	90,388	-128.88	-5.60	a	-0.3430	-2.2448	α	0.388	0.431
	b	10.9933	β	125,452			b	-0.2278	-2.0305	β	0.752	0.603
	c	16.2290	γ	89,676			c	-0.0849	-0.5203	γ	-0.324	-0.360
1280.02	a	17.7241	α	90,20	-94.19	-6.85	a	0.1025	0.5817	α	0.200	0.222
	b	10.6371	β	90,03			b	-0.4178	-3.7792	β	0.034	0.038
	c	6.7894	γ	89,99			c	-0.2649	-3.7549	γ	-0.015	-0.017
4576.80	a	15.3075	α	90,01	-135.26	-2.87	a	-0.1692	-1.0935	α	0.014	0.016
	b	23.6507	β	89,87			b	-0.1370	-0.5759	β	-0.134	-0.149
	c	12.6419	γ	90,00			c	-0.1571	-1.2276	γ	0.001	0.001
3643.88	a	18.0568	α	89,382	-316.13	-7.98	a	-0.1733	-0.9505	α	-0.618	-0.687
	b	18.0424	β	89,567			b	-0.1877	-1.0298	β	-0.433	-0.481
	c	12.9264	γ	120,07			c	-0.8326	-6.0513	γ	0.070	0.058
4011.20	a	17.4832	α	90,132	-149.39	-3.59	a	-0.1290	-0.7324	α	0.132	0.147
	b	17.4489	β	89,731			b	-0.1633	-0.9269	β	-0.269	-0.299
	c	15.1714	γ	119,924			c	-0.3167	-2.0448	γ	-0.076	-0.063
1985.42	a	24.8296	α	90,06	-20.63	-1.03	a	-0.0220	-0.0886	α	0.057	0.063
	b	7.3477	β	90,01			b	-0.0656	-0.8851	β	0.008	0.009
	c	10.8825	γ	90,17			c	-0.0060	-0.0553	γ	0.171	0.190
3043.01	a	24.7005	α	90,11	-145.02	-4.55	a	0.0510	0.2069	α	0.112	0.124
	b	17.8534	β	90,06			b	-0.0914	-0.5092	β	0.059	0.066
	c	6.9005	γ	89,97			c	-0.3069	-4.2582	γ	-0.032	-0.036
2243.09	a	14.0754	α	89,93	-110.00	-4.67	a	-0.2525	-1.7626	α	-0.075	-0.083

	b	9.8950	β	119,51			b	-0.2548	-2.5100	β	0.511	0.429
	c	18.5064	γ	90,10			c	0.0060	0.0323	γ	0.097	0.108
3037.16	a	22.9329	α	88,53	-89.70	-2.87	a	0.3735	1.6556	α	-1.474	-1.638
	b	23.1387	β	122,42			b	-0.2484	-1.0623	β	1.521	1.258
	c	6.7836	γ	90,02			c	-0.1233	-1.7856	γ	0.021	0.023
859.05	a	9.5064	α	89,97	-52.26	-5.74	a	-0.1888	-1.9475	α	-0.034	-0.038
	b	9.5064	β	89,97			b	-0.1888	-1.9472	β	-0.028	-0.031
	c	9.5058	γ	89,96			c	-0.1894	-1.9535	γ	-0.037	-0.041
2701.64	a	12.5546	α	89,95	-103.29	-3.68	a	-0.4013	-3.0973	α	-0.046	-0.051
	b	12.4867	β	90,10			b	-0.0384	-0.3063	β	0.104	0.116
	c	17.2337	γ	89,90			c	-0.0515	-0.2982	γ	-0.100	-0.111
1591.87	a	9.6145	α	99,60	-86.91	-5.18	a	0.0695	0.7281	α	-1.768	-1.744
	b	12.9243	β	107,38			b	-0.3245	-2.4494	β	2.801	2.678
	c	13.9387	γ	75,43			c	-0.3154	-2.2127	γ	-1.222	-1.594
1452.01	a	6.6068	α	90,26	-60.10	-3.97	a	-0.2038	-2.9920	α	0.258	0.287
	b	16.8962	β	103,88			b	-0.1888	-1.1049	β	3.379	3.362
	c	13.3988	γ	90,09			c	0.1822	1.3783	γ	0.091	0.101
2117.39	a	12.5401	α	90,028	7.95	0.38	a	0.1662	1.3431	α	0.028	0.031
	b	14.6488	β	89,955			b	-0.1742	-1.1750	β	-0.045	-0.050
	c	11.5266	γ	89,845			c	0.0258	0.2246	γ	-0.155	-0.172
1058.02	a	10.0664	α	90,01	-0.55	-0.05	a	-0.0058	-0.0576	α	0.007	0.008
	b	11.3657	β	115,81			b	-0.0009	-0.0081	β	-0.018	-0.016
	c	10.2723	γ	89,99			c	-0.0002	-0.0020	γ	-0.006	-0.007
1586.64	a	10.3432	α	89,81	-59.36	-3.61	a	0.0140	0.1353	α	-0.191	-0.212
	b	16.3110	β	93,51			b	-0.2052	-1.2422	β	1.811	1.975
	c	9.4225	γ	90,00			c	-0.2302	-2.3850	γ	-0.003	-0.003
978.50	a	10.4881	α	89,98	-0.40	-0.04	a	-0.0282	-0.2681	α	-0.023	-0.026
	b	10.4861	β	90,01			b	-0.0301	-0.2866	β	0.008	0.009
	c	8.8971	γ	90,01			c	0.0457	0.5160	γ	0.008	0.009

Table S6. Comparison of calculated unit cell volumes with back-corrected values V_{el}^{ref} from reference [1].

		B97-D		**PBE-D3**		**PBE-D3**	
Compound	V^{ref}_{el}/ a.u.^{3}	V_{el}/ a.u.^{3}	Deviation/ %	V_{el}/ a.u.^{3}	Deviation/ %	V_{el}/ a.u.^{3} [1]	Deviation/ %
1,4-Cyclohexanedione	1791.7	1790.5303	-0.06	1884.8543	5.2	1863.21391	3.99
Adamantane	2413.2	2472.5069	2.46	2562.1811	6.2	2549.51907	5.65
Anthracene	2977.4	2907.2003	-2.36	3104.7397	4.3	3036.07367	1.97
Benzene	2998.3	2929.1701	-2.31	3156.8134	5.3	3083.98681	2.86
CO2	1112.1	1267.6283	13.98	1267.9625	14.0	1257.88871	13.11
Hexamine	2170.3	2159.9947	-0.47	2253.6632	3.8	2252.59255	3.79
Naphtalene	2224.9	2170.5483	-2.44	2339.1691	5.1	2279.58587	2.46
Pyrazine	1279.5	1280.019	0.04	1349.6755	5.5	1325.37201	3.59
Pyrazole	4470.8	4576.8038	2.37	4775.5572	6.8	4752.17399	6.29
Triazine	3563.1	3643.8761	2.27	3766.8293	5.7	3755.44565	5.40
Trioxane	3918.8	4011.1956	2.36	4264.3192	8.8	4154.94678	6.03
Acetic Acid	1948.9	1985.417	1.87	2001.9105	2.7	2008.30301	3.05
Cytosine	2971.3	3043.0062	2.41	3189.8817	7.4	3148.09595	5.95
Imidazole	2270.1	2243.0877	-1.19	2366.8298	4.3	2334.24735	2.82
Uracil	2982.8	3037.1646	1.82	3103.9581	4.1	3086.68614	3.48
Ammonia	819.9	859.0514	4.77	847.8864	3.4	827.345258	0.91
Cyanamide	2752.6	2701.6364	-1.85	2853.8317	3.7	2791.10929	1.40
Ethylcarbamate	1560.2	1591.8717	2.03	1632.2042	4.6	1631.74619	4.58
Formamide	1430.0	1452.0081	1.54	1507.4024	5.4	1503.52792	5.14
Oxalic Acid (alpha)	1978.6	2117.3929	7.01	2118.1529	7.1	2122.34979	7.26
Oxalic Acid (beta)	1015.6	1058.016	4.17	1055.077	3.9	1070.95997	5.45
Succinic Acid	1574.4	1586.6411	0.78	1639.0217	4.1	1652.666017	4.97

Urea	950.2	978.4968	2.98	979.0429	3.0	970.409854	2.13
		MD	**1.83**		**5.4**		**4.45**
		MAD	**1.52**		**1.08**		**0.93**

References

1. Dolgonos, G.A.; Hoja, J.; Boese, A.D. Revised values for the x23 benchmark set of molecular crystals. *Physical Chemistry Chemical Physics* **2019**, *21*, 24333-24344.