

Assessing the performance of density functional theory in optimizing molecular crystal structure parameters

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Supplementary Information

Compound details and computational parameters applied to Class I and Class II data sets

Table S1 Class I (hydrogen bond interaction) compound identification and computational parameter setup

CSD Reference	Compound name	Unit cell dimensions ($a/\text{\AA}$, $\angle/^\circ$)	Plane-wave basis set energy cut-off (E_{cut})	Monkhorst-Pack grid (k-point settings)	No. k-points, and actual k-point spacing (\AA^{-1})
ACEMID03	Acetamide	$a = b = c = 7.914$, $\mathbf{a} = \mathbf{b} = \mathbf{g} = 93.3415$.	660	$2 \times 2 \times 2$	2 k-points 0.063412 ×0.063412 ×0.063412
ALOXAN11	2,4,5,6-pyrimidinetetrone	$a = b = 5.481$, $c = 13.853$, $\mathbf{a} = \mathbf{b} = \mathbf{g} = 90$.	520	$3 \times 3 \times 2$	3 k-points 0.057068 ×0.057068 ×0.036093
BZAMID02	Benzamide	$a = 5.529$, $b = 5.033$, $c = 21.343$, $\mathbf{a} = \mathbf{g} = 90.0$, $\mathbf{b} = 88.73$.	600	$3 \times 3 \times 1$	4 k-points 0.060303 ×0.06623 ×0.046865
CBOHAZ02	1,3-diaminourea	$a = 3.618$, $b = 8.789$, $c = 12.487$, $\mathbf{a} = \mathbf{g} = 90.0$, $\mathbf{b} = 106.43$.	620	$4 \times 2 \times 2$	4 k-points 0.072041 ×0.056889 ×0.041746
FACETA01	Monofluoracetamide	$a = 5.0974$, $b = 5.1531$, $c = 6.6501$, $\mathbf{a} = 102.52$, $\mathbf{b} = 101.33$, $\mathbf{g} = 99.54$.	620	$3 \times 3 \times 2$	9 k-points 0.06833 ×0.067889 ×0.079365
FORAMO01	N-hydroxy-methaneimidamide	$a = 8.187$, $b = 7.111$, $c = 4.7609$, $\mathbf{a} = \mathbf{b} = \mathbf{g} = 90.0$.	600	$2 \times 2 \times 3$	2 k-points 0.061072 ×0.070314 ×0.070015
GLOXIM11	Glyoxime	$a = 3.745$, $b = 4.398$, $c = 10.852$, $\mathbf{a} = \mathbf{g} = 90.0$, $\mathbf{b} = 92.41$.	620	$4 \times 3 \times 2$	8 k-points 0.066815 ×0.075792 ×0.046115
GUSRIV	2-(3-dimethylamino-1-oxoprop-2-enyl)phenol	$a = 8.881$, $b = 10.100$, $c = 11.435$,	620	$2 \times 2 \times 2$	2 k-points 0.059798 ×0.049506

		$\mathbf{a} = \mathbf{g} = 90.0$, $\mathbf{b} = 109.69.$			$\times 0.046439$
JUQSUJ01	Methyl α -D-xylofuranoside	$a = 6.2238$, $b = 8.1389$, $c = 7.3637$, $\mathbf{a} = \mathbf{g} = 90.0$, $\mathbf{b} = 101.15.$	620	$3 \times 2 \times 2$	3 k-points 0.054588 $\times 0.061433$ $\times 0.069206$
MALNAC07	Perdeuteromalonic acid	$a = 10.663$, $b = 5.142$, $c = 11.234$, $\mathbf{a} = 103.39$, $\mathbf{b} = 136.81$, $\mathbf{g} = 85.19.$	680	$2 \times 3 \times 2$	6 k-points 0.069077 $\times 0.067187$ $\times 0.067161$
MELAMI06	1,3,-triazine-2,4,6-triamine	$a = 10.4330$, $b = 7.4580$, $c = 7.2380$, $\mathbf{a} = \mathbf{g} = 90.0$, $\mathbf{b} = 113.30.$	480	$2 \times 2 \times 2$	2 k-points 0.05218 $\times 0.067042$ $\times 0.075214$
NALCYS02	N-aceyl-L-cysteine	$a = 5.766$, $b = 6.433$, $c = 5.014$, $\mathbf{a} = 102.8$, $\mathbf{b} = 102.77$, $\mathbf{g} = 95.81.$	600	$3 \times 3 \times 3$	14 k-points 0.06003 $\times 0.053812$ $\times 0.070429$
RIWQET01	2-(methylbenzylamino)-3,5-dinitropyridine	$a = 8.352$, $b = 8.570$, $c = 8.909$, $\mathbf{a} = \mathbf{g} = 90.0$, $\mathbf{b} = 93.98.$	460	$2 \times 2 \times 2$	2 k-points 0.060011 $\times 0.058343$ $\times 0.056259$
SUBRAC01	Octane1,8-dioic acid	$a = 8.710$, $b = 5.0885$, $c = 9.815$, $\mathbf{a} = \mathbf{g} = 90.0$, $\mathbf{b} = 95.07.$	620	$2 \times 3 \times 2$	4 k-points 0.057631 $\times 0.065507$ $\times 0.051143$
TACETA09	3,4-diacetylhexa-2,4-diene-2,5-diol	$a = 9.0859$, $b = 9.2413$, $c = 11.465$, $\mathbf{a} = \mathbf{b} = \mathbf{g} = 90.0.$	600	$2 \times 2 \times 2$	1 k-point 0.05503 $\times 0.054105$ $\times 0.043611$
TRAZOL02	1,2,4-triazole	$a = 9.748$, $b = 9.331$, $c = 6.927$, $\mathbf{a} = \mathbf{b} = \mathbf{g} = 90.0.$	420	$2 \times 2 \times 2$	1 k-point 0.051293 $\times 0.053585$ $\times 0.072181$
UREAXX12	urea	$a = b = 5.565$, $c = 4.684$, $\mathbf{a} = \mathbf{b} = \mathbf{g} = 90.0.$	520	$3 \times 3 \times 3$	6 k-points 0.059898 $\times 0.059898$ $\times 0.071164$

Table S2 Class II (dispersion interaction) compound identification and computational parameter setup

CSD Reference	Compound name	Unit cell dimensions	Plane-wave basis set energy cut-off (E_{cut})	Monkhorst-Pack grid (k-point settings)	No. k-points, and actual k-point spacing (\AA^{-1})
ACETYL05	Dideutero-acetylene	$a = 6.19$, $b = 6.00$, $c = 5.546$, $\alpha = \beta = ? = 90.0$.	460	$2 \times 3 \times 2$	2 k-points 0.08082×0.055546 $\times 0.090155$
GIPVUW02	2,5-Diaza-1,6-dioxa-6a-thiapentalene	$a = 6.76$, $b = 6.92$, $c = 10.90$, $\alpha = \beta = 90.0$, $\gamma = 125.40$	640	$2 \times 2 \times 2$	2 k-points 0.079846 $\times 0.072202$ $\times 0.04952$
ANTCEN16	Decadeutero-anthracene	$a = 8.37$, $b = 6.00$, $c = 11.12$, $\alpha = ? = 90.0$, $\beta = 125.40$	500	$2 \times 2 \times 2$	2 k-points 0.073286 $\times 0.083333$ $\times 0.055162$
HXMTAM10	Hexamethylenetetramine	$a = b = c = 5.9993$, $\alpha = \beta = ? = 109.471$	420	$3 \times 3 \times 3$	4 k-points 0.068049 $\times 0.068049$ $\times 0.068049$
NBONAN01	exo,exo-2,3-Norborn-5-enedicarboxylic anhydride	$a = 7.362$, $b = 7.968$, $c = 12.500$, $\alpha = \beta = ? = 90.0$.	620	$2 \times 2 \times 1$	1 k-point 0.067916 $\times 0.062751 \times 0.08$
NURWOM03	2,6-Dimethylpyrazine	$a = 7.287$, $b = 10.725$, $c = 7.452$ $\alpha = ? = 90.0$, $\beta = 90.37$.	500	$2 \times 2 \times 2$	2 k-points 0.068617×0.04662 $\times 0.067097$
BENZEN06	Hexadeutero-benzene	$a = 7.360$, $b = 9.375$, $c = 6.703$, $\alpha = \beta = ? = 90.0$.	480	$2 \times 2 \times 2$	2 k-points 0.078406 $\times 0.078406$ $\times 0.069979$
OCHTET13*	1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane	$a = 6.521$, $b = 10.761$, $c = 7.306$ $\alpha = ? = 90.0$, $\beta = 102.06$.	640	$2 \times 2 \times 2$	2 k-points 0.078406 $\times 0.046464$ $\times 0.069979$
NAPHTA14*	Perdeuteronaphthalene	$a = 8.096$, $b = 5.941$ $c = 8.648$ $\alpha = ? = 90.0$, $\beta = 124.63$	500	$2 \times 2 \times 2$	2 k-points 0.075056 $\times 0.084161$ $\times 0.070265$
POCTUW	Trichlorofluoromethane	$a = 15.511$, $b = 5.879$, $c = 9.526$, $\alpha = \beta = ? = 90.0$	620	$1 \times 2 \times 2$	1 k-points 0.06447×0.085051 $\times 0.052487$
TFMETH03*	Tetrafluoromethane	$a = b = 4.73845$, $c = 8.4800$, $\alpha = \beta = 117.027$,	640	$4 \times 4 \times 2$	10 k-points 0.067358 $\times 0.067358$

		? = 54.2387			$\times 0.068573$
ZZZUEE04*	Strychnine	$a = 11.326,$ $b = 11.765,$ $c = 11.994,$ $\alpha = \beta = \gamma = 90.0.$	580	$1 \times 1 \times 1$	1 k-point 0.084993 $\times 0.12081 \times 0.083625$
BIPHEN08	Decadeutero-biphenyl	$a = 7.780,$ $b = 5.565,$ $c = 9.440,$ $\alpha = \gamma = 90.0,$ $\beta = 93.90.$	500	$2 \times 2 \times 2$	2 k-points 0.064417 $\times 0.089847$ $\times 0.053089$

* X-ray data collection.

Figure S1 Convergence graphs with respect to (a) Plane wave basis set energy cut-off and (b) Monkhorst Pack k-point setting grids for model system NURWOM3 (2,6-Dimethylpyrazine)

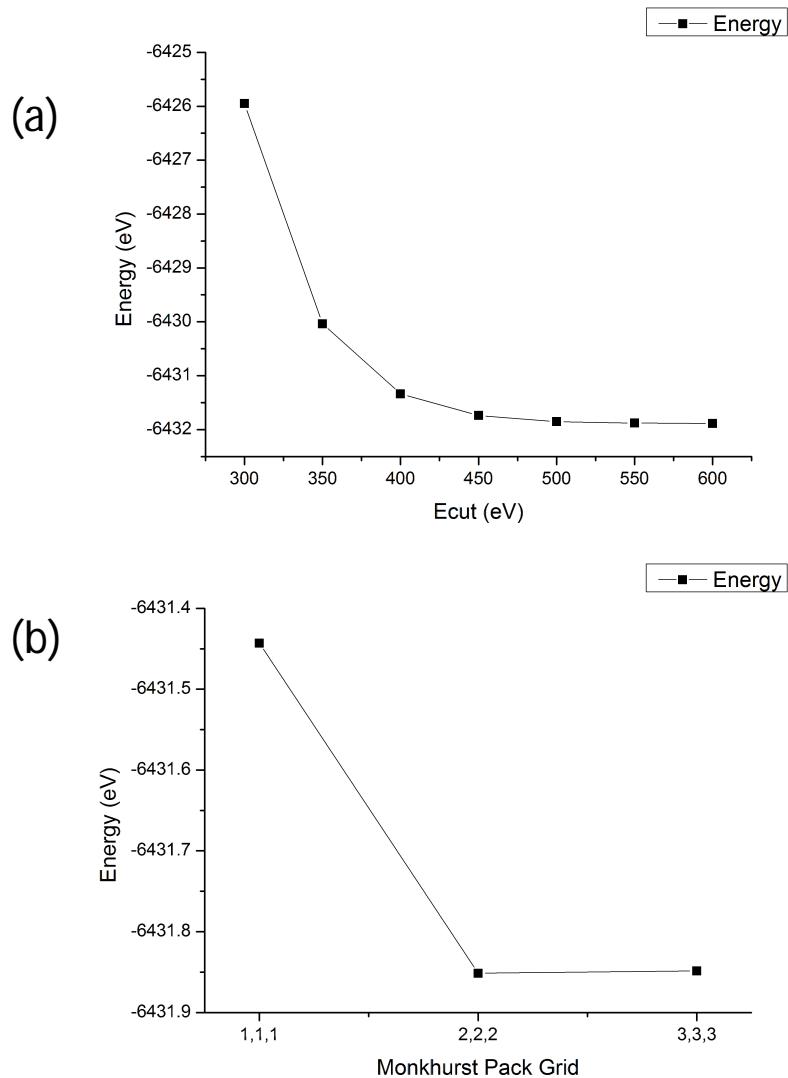


Table S3 Class I calculated crystal packing similarity (CPS) scores

CSD Reference	PBE		PW91		PBEsol		PBE-TS		PW91-OBS		PBE-G06	
	Fix cell	Opt cell										
ACEMID03	0.008	0.078	0.008	0.071	0.122	0.039	0.008	0.02	0.009	0.223	0.008	0.065
ALOXAN11	0.009	0.319	0.009	0.384	0.007	0.099	0.009	0.091	0.009	0.052	0.011	0.047
BZAMID02	0.005	0.671	0.005	0.732	0.056	0.298	0.005	0.027	0.053	0.465	0.007	0.15
CBOHAZ02	0.02	0.288	0.022	0.35	0.032	0.118	0.021	0.047	0.072	0.252	0.022	0.083
FACETA01	0.013	0.405	0.013	0.463	0.056	0.183	0.014	0.06	0.038	0.226	0.015	0.09
FORAMO01	0.038	0.411	0.041	0.422	0.11	0.257	0.035	0.112	0.089	0.239	0.034	0.083
GLOXIM11	0.056	0.469	0.057	0.572	0.086	0.204	0.051	0.108	0.056	0.135	0.054	0.09
GUSRIV	0.011	0.574	0.011	0.618	0.018	0.117	0.011	0.015	0.098	0.446	0.011	0.131
JUQSUJ01	0.012	0.513	0.012	0.461	0.073	0.234	0.027	0.067	0.057	0.451	0.011	0.092
MALNAC07	0.047	0.475	0.044	0.474	0.093	0.262	0.045	0.081	0.05	0.117	0.038	0.053
MELAMI06	0.013	0.38	0.023	0.428	0.04	0.214	0.013	0.058	0.045	0.261	0.03	0.101
NALCYS02	0.015	0.506	0.015	0.596	0.067	0.174	0.021	0.066	0.057	0.253	0.016	0.05
RIWQET01	0.01	0.922	0.01	0.781	0.016	0.653	0.014	0.121	0.108	0.3	0.01	0.012
SUBRAC01	0.014	0.746	0.02	0.878	0.045	0.308	0.021	0.057	0.195	0.691	0.011	0.167
TACETA09	0.007	0.483	0.159	0.667	0.022	0.111	0.006	0.3	0.007	0.48	0.005	0.114
TRAZOL02	0.007	0.601	0.062	0.679	0.11	0.294	0.007	0.043	0.008	0.13	0.008	0.054
UREAXX12	0.011	0.179	0.012	0.18	0.016	0.037	0.011	0.02	0.013	0.232	0.01	0.09

Table S4 Class II calculated crystal packing similarity (CPS) scores

CSD Reference	PBE		PW91		PBEsol		PBE-TS		PW91-OBS		PBE-G06		PBE-MBD Opt cell
	Fix cell	Opt cell											
ACETYLO5	0.045	0.277	0.044	0.321	0.045	0.13	0.045	0.092	0.044	0.428	0.045	0.207	
GIPVUW02	0.065	0.482	0.107	0.697	0.104	0.221	0.071	0.161	0.107	0.149	0.038	0.128	0.126
ANTCEN16	0.017	0.846	0.018	1.013	0.021	0.249	0.017	0.037	0.016	0.457	0.013	0.209	
HXMTAM10	0.004	0.379	0.005	0.294	0.005	0.065	0.005	0.014	0.006	0.461	0.007	0.142	
NBONAN01	0.009	0.328	0.011	0.389	0.007	0.099	0.019	0.036	0.197	0.334	0.01	0.086	
NURWOM03	0.006	0.56	0.007	0.713	0.006	0.121	0.006	0.094	0.012	0.579	0.007	0.179	0.061
BENZEN06	0.002	0.544	0.002	0.657	0.004	0.001	0.001	0.001	0.001	0.177	0.001	0.177	0.002
OCHTET13*	0.045	0.478	0.014	0.53	0.053	0.18	0.051	0.18	0.038	0.111	0.035	0.091	
NAPHTA14*	0.007	0.53	0.008	0.609	0.01	0.156	0.007	0.018	0.007	0.462	0.006	0.235	
POCTUW	0.042	0.418	0.044	0.46	0.048	0.109	0.027	0.108	0.046	0.215	0.044	0.029	
TFMETH03*	0.012	0.452	0.012	0.448	0.008	0.408	0.012	0.11	0.0012	0.248	0.013	0.027	
ZZZUEE04*	0.013	0.527	0.012	0.579	0.018	0.018	0.014	0.016	0.108	0.614	0.012	0.125	
BIPHEN08	0.016	0.76	0.016	0.96	0.018	0.187	0.016	0.033	0.015	0.511	0.014	0.226	

Table S5 Class I calculated unit cell volume

CSD reference	Exp	PBE	PW91	PBEsol	PBE-TS	PW1-OBS	PBE-G06
ACEMID03	492.95	514.77	513.12	482.98	487.40	432.87	474.60
ALOXAN11	472.63	556.31	574.05	489.47	495.93	485.43	484.11
BZAMID02	593.78	751.62	778.63	644.40	587.87	489.96	557.74
CBOHAZ02	380.86	429.26	439.19	374.41	379.86	332.40	367.31
CYCACHZ01	440.93	512.61	515.06	513.30	432.77	403.45	432.77
FACETA01	163.20	198.23	202.52	172.03	166.43	146.18	156.92
FORAMO01	277.17	319.00	320.60	282.11	277.21	241.37	264.94
GLOXIM11	178.58	219.65	224.56	182.81	179.88	165.30	171.72
GUSRIV	965.72	1196.91	1236.93	1007.56	964.40	803.41	921.26
JUQSUJ01	365.97	427.58	435.36	368.84	360.48	301.35	350.63
MALNAC07	406.75	508.84	531.44	444.36	414.96	388.70	404.88
MELAMIO6	517.25	614.97	621.89	533.17	511.85	466.21	493.30
NALCYS02	174.66	212.58	218.84	182.78	178.86	157.71	171.78
RIWQET01	636.14	966.94	924.36	772.31	659.94	587.12	637.03
SUBRAC01	433.31	551.57	573.75	474.10	428.98	344.90	410.09
TACETA09	962.66	1173.92	798.97	1006.44	962.40	798.95	919.03
TRAZOL02	630.07	809.13	842.43	702.69	626.24	581.45	611.73
UREAXX12	145.06	158.71	158.56	142.64	146.52	128.13	138.79

Table S6 Class II calculated unit cell volume

Compound name	Exp	PBE	PW91	PBEsol	PBE-TS	PW1-OBS	PBE-G06	PBE-MBD
ACETYL05	102.97	116.70	122.16	98.38	97.46	81.94	91.17	--
GIPVUW02	472.81	602.23	644.53	521.76	501.32	497.82	483.38	501.07
ANTCEN16	455.21	589.18	618.08	489.67	450.81	379.83	417.31	--
HXMTAM0	166.22	198.65	191.07	171.50	167.32	131.79	155.01	--
NBONAN01	733.26	848.87	872.33	766.46	733.21	638.82	705.77	--
NURWOM03	582.38	726.27	766.00	606.35	569.12	455.85	539.99	567.41
BENZEN06	462.51	611.90	646.53	464.53	462.59	419.49	419.49	462.45
OCHTET13	501.37	599.88	610.74	538.08	530.35	512.54	513.15	--
NAPTHA14	342.26	428.65	442.14	360.64	339.73	280.06	312.43	--
POCTUW	868.65	1068.84	1094.13	908.66	919.81	974.57	865.51	--
TFMETH03	132.85	175.80	175.43	171.27	141.69	155.22	132.69	--
ZZZUEE04	1598.21	1912.46	1945.04	1602.34	1594.79	1311.79	1533.40	--
BIPHEN08	407.76	523.29	555.47	435.36	403.34	334.03	375.83	--

Table S7 Class I Calculated unit cell shape (longest unit cell length/shortest unit cell length)

CSD reference	Exp	PBE	PW91	PBESol	PBE-TS	PW1-OBS	PBE-G06
ACEMID03	N/A*	N/A	N/A	N/A	N/A	N/A	N/A
ALOXAN11	2.37168	2.39099	2.2571	2.30719	2.36505	2.36842	2.36534
BZAMID02	4.24061	4.60626	4.73255	4.44463	4.24788	4.17854	4.18371
CBOHAZ02	3.45135	3.11559	3.04153	3.30618	3.40327	3.55498	3.43368
CYCACHZ01	1.19746	1.03682	1.02763	1.03549	1.21263	1.22968	1.21263
FACETA01	1.30461	1.44519	1.47488	1.35321	1.32359	1.24933	1.28204
FORAMO01	1.71963	1.66774	1.65294	1.66673	1.73194	1.74956	1.74956
GLOXIM11	2.89773	2.5002	2.42932	2.74596	2.83812	2.95354	2.91327
GUSRIV	1.28767	1.36867	1.38381	1.30614	1.28654	1.24172	1.27943
JUQSUJ01	1.30771	1.33271	1.33717	1.3232	1.31828	1.36036	1.32021
MALNAC07	2.18475	2.03743	1.97872	2.06516	2.1675	2.21135	2.17622
MELAMI06	1.44142	1.52401	1.52538	1.48092	1.46506	1.4727	1.44087
NALCYS02	1.28301	1.2298	1.22039	1.26029	1.27852	1.27086	1.29305
RIWQET01	1.03956	1.11296	1.10652	1.07743	1.05061	1.07323	1.03903
SUBRAC01	1.92886	1.8774	1.86757	1.90031	1.93833	1.98062	1.93375
TACETA09	1.26185	1.26351	1.39322	1.25705	1.26255	1.39351	1.24822
TRAZOL02	1.40725	1.14369	1.10828	1.24477	1.38032	1.42842	1.4029
UREAXX12	1.18809	1.23019	1.23249	1.20054	1.1884	1.13511	1.16232

* cubic system

Table S8 Class II Calculated unit cell shape (longest unit cell length/shortest unit cell length)

Compound name	Exp	PBE	PW91	PBESol	PBE-TS	PW1-OBS	PBE-G06	PBE-MBD
ACETYL05	1.51457	1.41136	1.39018	1.43384	1.49479	1.53593	1.49921	
GIPVUW02	1.61239	1.50555	1.39738	1.56752	1.59515	1.59985	1.63769	1.56989
ANTCEN16	1.85333	1.79328	1.78265	1.83934	1.84945	1.86919	1.86973	--
HXMTAM0	1.69791	1.68118	1.68294	1.70683	1.69826	1.69752	1.70896	--
NBONAN01	1.4718	1.36712	1.33663	1.43243	1.47304	1.61442	1.50553	1.46
NURWOM03	1.39863	1.35887	1.35314	1.39897	1.39868	1.4146	1.4146	1.3986
BENZEN06	1.65023	1.72423	1.72605	1.68541	1.70585	1.69002	1.67073	--
OCHTET13	1.45565	1.43221	1.43104	1.45371	1.45652	1.42499	1.46469	--
NAPTHA14	2.63848	2.65302	2.6539	2.69468	2.63819	2.70609	2.63169	--
POCTUW	1.78961	1.78086	1.78052	1.78318	1.77666	1.77652	1.78191	--
TFMETH03	1.05898	1.08093	1.08239	1.05841	1.05817	1.04522	1.04353	--
ZZZUEE04	1.69632	1.65127	1.63731	1.68732	1.69994	1.67136	1.70974	--
BIPHEN08	1.51457	1.41136	1.39018	1.43384	1.49479	1.53593	1.49921	