Supporting Information

Dimorphs of 4'-Amino-4-Hydroxy-2'-Methylbiphenyl: Assessment of Likelihood of Polymorphism in Flexible Molecules

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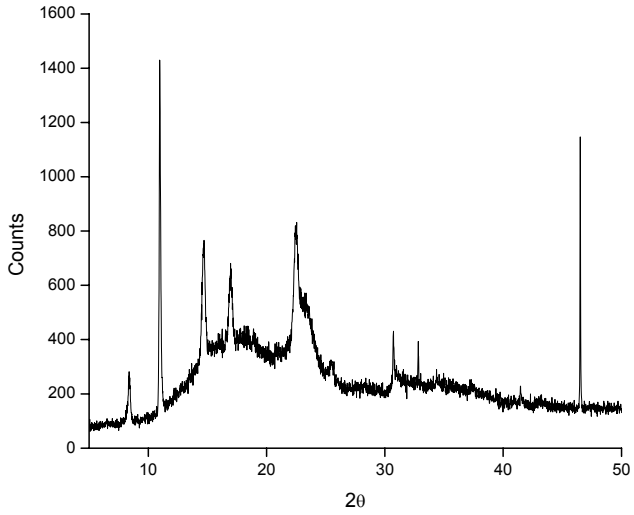
Powder X Ray

PXRD data of compound **3** were collected on an INEL XRG3000 instrument (λ = 1.788965 A, Co-Kα1). The base line in not satisfactory. But the powder pattern gives a hint that the compound has limited crystallinity and we did not get a single crystal for further work.



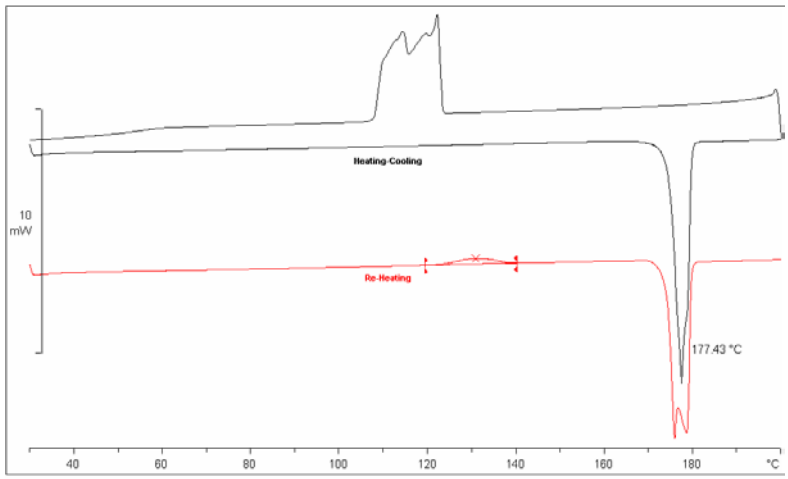
The powder pattern of compound, **3**

Thermal analysis

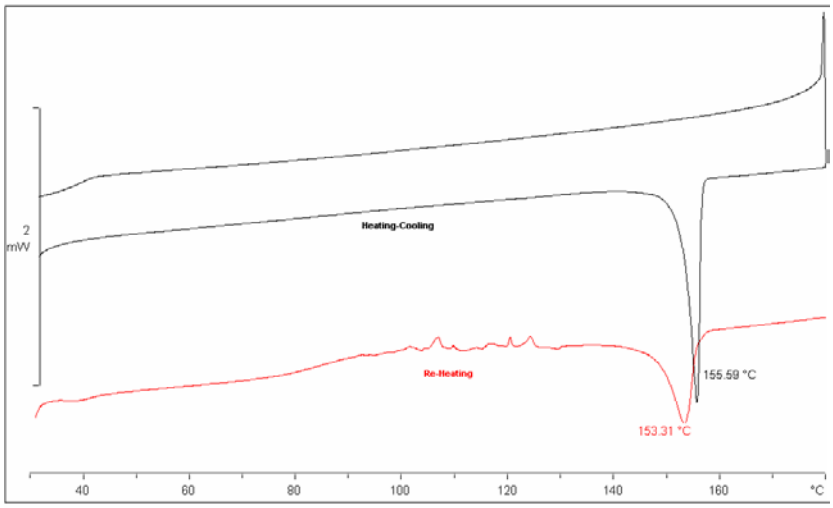
We started these experiment with the hope that we would get some characteristic polymorphic behaviour of the compound **2** and as well as compound **3.** But there were no such observations.

DSC, A Mettler Toledo Differential Scanning Calorimeter was used. N_2 was used as the inert gas to flush through the DSC furnace (purge rate 150ml/min) and this prevents condensation. Samples were analyzed using closed aluminum pans at a heating rate of 5˚C min^{-1}. Crude **2** was heated from 30ºC to 200˚C (1st step) then cooled to 30ºC (2nd step) and the melt was further heated to 200˚C (3rd step). Compound **3** was heated from

30ºC to 180˚C (1st step) then cooled to 30ºC (2nd step) and the melt was further heated to 180˚C (3rd step). Compound **3** does not crystallise during cooling (see HSM picture) and even for the compound **2**, the crystallisation is not sharp. Partial decompostion occours in both cases.



(a)



(b)

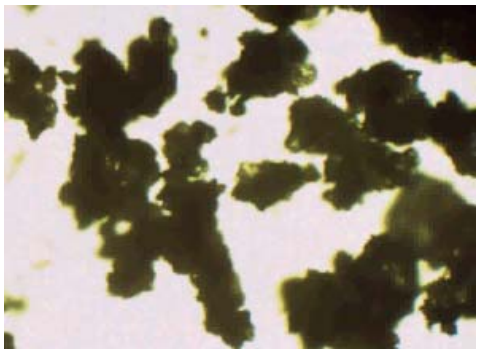
DSC plots of compound, **2** (a) and **3** (b).

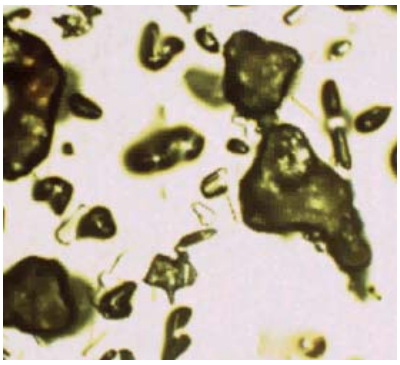
Hot stage microscopy (HSM)**,** A Kofler hot stage microscope was used. The temperature and heating rate were monitored with a digital thermometer. Pictures were taken with a

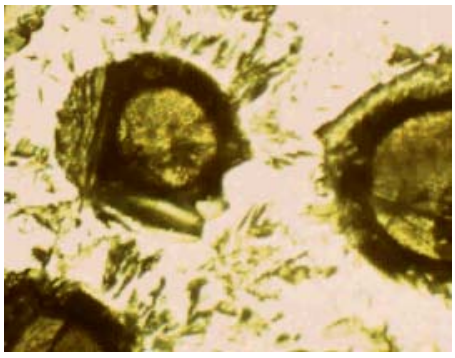
digital camera attached to the microscope and processed with the Motic software.

Samples were loaded in a glass plate, placed on the hot bench and heated at a rate of ~10˚C min^{-1}. Heating–cooling–heating cycles were performed for each case.

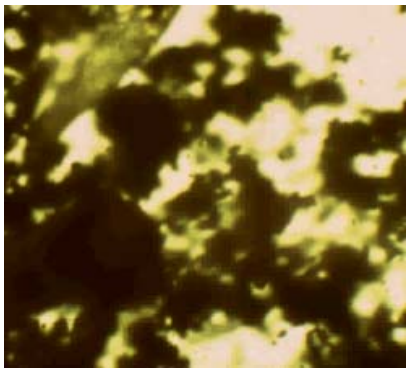
2

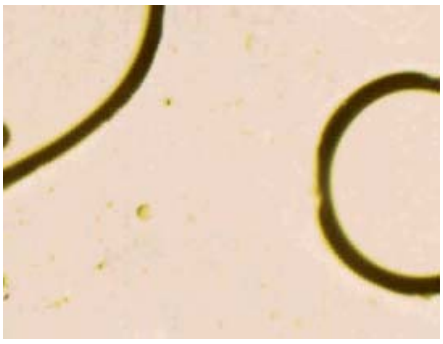


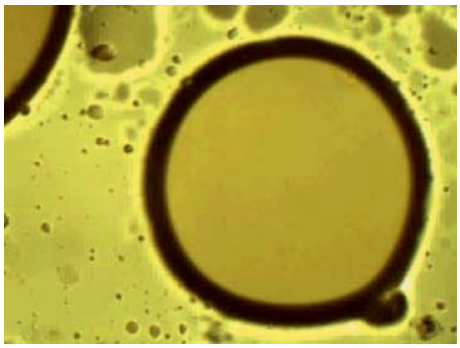




3 **~50 ºC** **~178ºC** **~110 º C**







~50ºC **~155ºC** **~90ºC**

HSM pictures: crude sample, melting and crystallization.

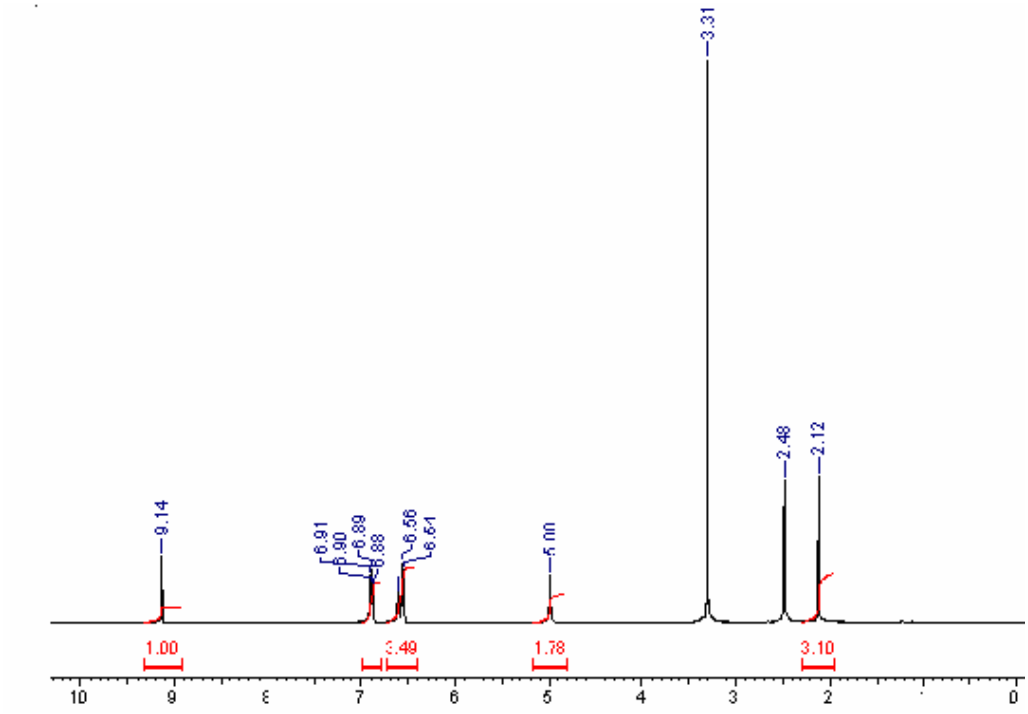


Figure S1 NMR spectrum of compound, **3**.

Table S1 Intermolecular interactions for dimorphs of **2**

Form	Interations	d (A°)	D (A°)	θ (deg)
I	N−H…O	2.223	3.254 (2)	158.3
	N−H…O	2.072	3.154 (2)	177.5
	O−H…N	1.778	2.751 (2)	169.9
	O−H…N	1.806	2.776 (2)	168.7
	C−H…O	2.476	3.470 (2)	152.0
II	N−H…O	2.164	3.167 (2)	172.6
	O−H…O	1.709	2.688 (2)	173.3
	O−H…N	1.783	2.783 (2)	174.8
	N−H…O	2.167	3.156 (2)	166.2
	N−H…N	2.073	3.061 (2)	165.8

All C–H, O–H and N–H distances are neutron normalised to 1.083, 0.983 and 1.009 A°.

Table S2 Evaluation of force fields.

		Experimental			Predicted			
	FF	**Reduced Cell Parameters (Å, º)**	**V (Å^3)**	**Energy kcal mol^{-1}**	**Reduced Cell Parameters (Å, º)**		**V (Å^3)**	**Energy kcal mol^{-1}**
1 (*Pna*2$_1$)	DRE	4.968, 8.700, 21.472	927.98	−108.016	1st *P*2$_1$	5.518, 7.821, 21.255, 90	452.77	−117.632
					2nd *P*2$_1$	5.363, 8.053, 10.510, 95.02	452.19	−117.608
					7th *Pna*2$_1$	**5.518, 7.821, 21.255**	**917.22**	**−116.729**
	COM	5.352, 7.850, 20.808	874.26	−108.587	**1st *Pna*2$_1$**	**5.307, 7.773, 21.249**	**876.54**	**−110.010**
					2nd *P*2$_1$2$_1$2$_1$	5.397, 7.563, 21.302,	869.43	−109.989
					3rd *Pna*2$_1$	5.318, 7.743, 21.246	874.90	−109.950
	cff	5.279, 8.785, 20.371	944.67	−115.600	1st *P*–1	4.155, 6.571, 18.987, 93.47, 90.94, 90.81	517.25	−158.710
					2nd *P*–1	3.760, 12.717, 13.308, 107.44, 90.26, 98.50	599.66	−158.678
					83th *Pna*2$_1$	3.845, 13.013, 23.023	1151.93	−161.081

Table S3 Crystal and gas phase torsion angles for selected biphenyls.

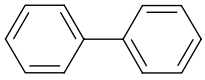
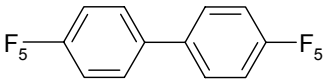
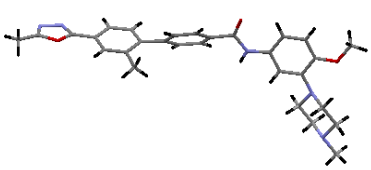
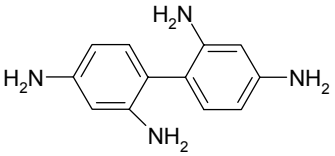
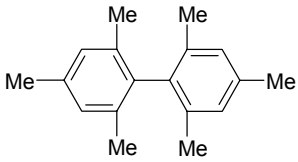
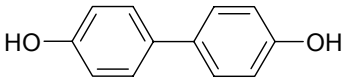
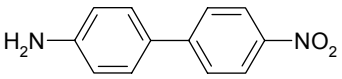
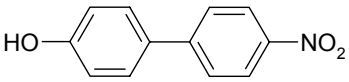
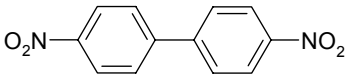
CSD REFCODEs	Structures	Torsion Angle	
		Solid state	ab initio
BIPHEN		0.11	38.48
DECFDP01		58.87	54.14
QIMYUG		47.56	50.25
BUWCAX		68.56	63.64
ZZZMBS01		89.36	89.97
DOHDPH02		0.30	40.47
KEFLEM01		1.58	33.16
NEHFAH		26.32	35.60
DNTDPH		25.93	38.32

Table S4 Ten lowest lattice energy crystal structures for compounds **1-4**.

Compound **1**						
Torsion angle	**Rank**	**Space group**	**Lattice energy kcal mol^{-1}**	**Average**	**Re–minimized lattice energy kcal mol^{-1}**	**Average**
0	1	$P2_12_12_1$	–129.301	–128.346	–82.439	–81.585
	2	$P2_12_12_1$	–129.197		–82.314	
	3	$P2_1$	–128.722		–82.275	
	4	$P2_1$	–128.703		–82.494	
	5	$P2_1/c$	–128.212		–80.597	
	6	*Pbca*	–128.173		–79.185	
	7	$P2_1$	–128.164		–81.870	
	8	$P2_1$	–127.797		–85.056	
	9	$P2_1/c$	–127.647		–79.508	
	10	*Pbca*	–127.544		–80.106	
15	1	$Pna2_1$	–112.279	–111.517	–81.358	–79.128
	2	$P2_12_12_1$	–112.243		–80.717	
	3	$Pna2_1$	–112.175		–81.199	
	4	$P2_12_12_1$	–111.763		–80.726	
	5	$P2_1$	–111.722		–80.337	
	6	$P2_12_12_1$	–111.299		–79.666	
	7	$P2_1$	–111.193		–80.502	
	8	*Pbca*	–111.163		–78.718	
	9	$P2_1$	–110.878		–80.441	
	10	$P2_1/c$	–110.452		–67.613	
30	1	*Pbca*	–121.008	–119.924	–77.632	–74.091
	2	*Pbca*	–120.844		–72.770	
	3	$P2_12_12_1$	–119.999		–71.149	
	4	*Pbca*	–119.876		–78.357	
	5	$Pna2_1$	–119.731		–76.754	
	6	*Pbca*	–119.669		–71.644	
	7	*P*–1	–119.605		–70.915	
	8	*Pbca*	–119.545		–75.000	
	9	$P2_1/c$	–119.517		–72.594	
	10	$P2_12_12_1$	–119.446		–77.632	
45	1	*Pbca*	–130.693	–129.836	–74.542	–73.677
	2	$P2_1/c$	–130.631		–71.674	

	3	$P2_1/c$	–130.106		–72.842	
	4	$P2_1/c$	–130.073		–72.388	
	5	$P2_1/c$	–129.867		–76.338	
	6	$P2_12_12_1$	–129.797		–72.103	
	7	P–1	–129.763		–73.479	
	8	$Pna2_1$	–129.490		–79.723	
	9	$P2_1$	–129.006		–70.880	
	10	$Pbca$	–128.932		–72.803	
	1	$C2/c$	–125.465		–74.079	
	2	$P2_1/c$	–125.387		–72.315	
	3	$C2/c$	–125.327		–74.951	
	4	$Pbca$	–125.325		–75.161	
60	5	$P2_1/c$	–124.801	–124.866	–73.488	–74.976
	6	$P2_1/c$	–124.763		–76.545	
	7	$Pna2_1$	–124.735		–80.504	
	8	$P2_1/c$	–124.688		–76.404	
	9	$P2_12_12_1$	–124.191		–71.489	
	10	$Pbca$	–123.974		–74.825	
	1	P–1	–112.163		–72.601	
	2	$Pbca$	–112.125		–72.149	
	3	$C2/c$	–112.112		–71.371	
	4	$P2_1/c$	–112.107		–72.861	
75	5	$C2/c$	–112.071	–111.843	–71.908	–71.381
	6	$P2_1/c$	–111.925		–70.381	
	7	$P2_1/c$	–111.694		–72.241	
	8	$P2_1/c$	–111.553		–72.537	
	9	$Pbca$	–111.482		–65.013	
	10	P–1	–111.194		–72.748	
	1	$Pbca$	–106.082		–65.609	
	2	$Pbca$	–105.814		–66.260	
	3	P–1	–105.744		–69.056	
	4	P–1	–105.544		–68.927	
90	5	$P2_1/c$	–105.395	–105.327	–68.994	–67.116
	6	$P2_12_12_1$	–105.294		–65.413	
	7	$P2_12_12_1$	–105.263		–65.095	
	8	$Pbca$	–104.733		–67.674	
	9	P–1	–104.731		–69.130	
	10	$Pbca$	–104.669		–64.997	

Compound **2**

Torsion angle	Rank	Space group	Lattice energy kcal mol^{-1}	Average	Re–minimized lattice energy kcal mol^{-1}	Average
0	1	$Pna2_1$	–148.937	–147.762	–57.479	–59.271
	2	*Pbca*	–148.259		–56.035	
	3	*Pbca*	–148.001		–55.303	
	4	$P2_1/c$	–147.725		–60.129	
	5	$P2_1$	–147.624		–65.386	
	6	$P2_1$	–147.527		–62.174	
	7	$P2_1$	–147.463		–61.210	
	8	$P2_1/c$	–147.437		–57.833	
	9	$P2_1$	–147.334		–57.433	
	10	$P2_12_12_1$	–147.315		–59.730	
15	1	*Pbca*	–148.922	–147.75	–59.626	–60.471
	2	*Pbca*	–148.477		–67.396	
	3	$P2_1$	–148.143		–63.573	
	4	$P2_1/c$	–148.130		–63.796	
	5	$P2_1/c$	–147.476		–61.061	
	6	P 21/c	–147.425		–62.160	
	7	$P2_12_12_1$	–147.400		–59.064	
	8	*Pbca*	–147.252		–56.263	
	9	$P2_12_12_1$	–147.153		–56.092	
	10	$P2_1/c$	–147.125		–55.680	
30	1	*Pbca*	–151.887	–151.246	–70.103	–63.512
	2	$P2_1/c$	–151.880		–61.554	
	3	*Pbca*	–151.851		–68.048	
	4	$P2_1/c$	–151.333		–64.326	
	5	$P2_1/c$	–151.133		–60.061	
	6	*P*–1	–151.051		–64.554	
	7	*C*2/*c*	–150.919		–64.880	
	8	$Pna2_1$	–150.858		–61.050	
	9	$P2_1/c$	–150.843		–58.188	
	10	*Pbca*	–150.708		–62.350	
45	1	*Pbca*	–153.711	–151.947	–69.477	–64.455
	2	$P2_1/c$	–152.344		–62.183	
	3	$P2_1/c$	–152.197		–63.852	
	4	*C*2/*c*	–152.008		–60.832	
	5	*Pbca*	–151.941		–64.471	

	6	*P*–1	–151.568		–69.223	
	7	*P*–1	–151.483		–62.306	
	8	*Pbca*	–151.444		–58.880	
	9	*Pbca*	–151.405		–66.414	
	10	$P2_1/c$	–151.372		–66.914	
	1	*P*–1	–147.748		–61.737	
	2	*Pbca*	–147.637		–65.411	
	3	$P2_12_12_1$	–147.529		–67.822	
	4	P b c a	–147.201		–57.949	
60	5	$P2_12_12_1$	–147.169	–147.140	–66.448	–64.260
	6	*C*2/*c*	–146.928		–60.941	
	7	$Pna2_1$	–146.842		–65.755	
	8	*Pbca*	–146.829		–62.796	
	9	$P2_1$	–146.763		–66.607	
	10	$P2_12_12_1$	–146.756		–67.136	
	1	*P*–1	–144.348		–67.874	
	2	*P*–1	–144.215		–62.546	
	3	$P2_1/c$	–144.162		–66.392	
	4	*C*2/*c*	–143.786		–61.557	
75	5	*C*2/*c*	–143.325	–143.315	–63.047	–63.389
	6	*Pbca*	–142.999		–64.177	
	7	$P2_1/c$	–142.776		–63.344	
	8	*C*2/*c*	–142.686		–61.956	
	9	*P*–1	–142.503		–62.629	
	10	*C*2/*c*	–142.346		–60.364	
	1	*P*–1	–142.574		–60.479	
	2	*C*2/*c*	–141.300		–59.304	
	3	$P2_1/c$	–141.144		–58.959	
	4	*C*2/*c*	–141.126		–61.806	
90	5	$P2_1/c$	–141.113	–141.170	–61.310	–60.484
	6	*P*–1	–141.069		–59.565	
	7	*C*2/*c*	–140.901		–59.615	
	8	$P2_12_12_1$	–140.889		–60.293	
	9	*Pbca*	–140.864		–64.321	
	10	*Pbca*	–140.715		–59.184	

Compound **3**

Torsion angle	Rank	Space group	Lattice energy kcal mol^{-1}	Average	Re–minimized lattice energy kcal mol^{-1}	Average
0	1	$P2_1$	–139.489	–138.010	–64.866	–61.314
	2	$Pna2_1$	–138.618		–63.118	
	3	$Pbca$	–138.199		–52.954	
	4	$P2_1/c$	–138.109		–62.076	
	5	$P2_1/c$	–137.789		–63.047	
	6	$C2/c$	–137.709		–62.012	
	7	$C2/c$	–137.677		–61.130	
	8	$P2_12_12_1$	–137.617		–57.357	
	9	$P2_1/c$	–137.451		–61.061	
	10	$P2_12_12_1$	–137.440		–65.517	
15	1	$P2_1$	–138.279	–137.530	–64.702	–61.829
	2	$P2_1/c$	–137.800		–55.710	
	3	$P2_1/c$	–137.758		–57.904	
	4	$P2_1/c$	–137.658		–65.251	
	5	$P2_1/c$	–137.550		–60.855	
	6	$P2_1/c$	–137.413		–64.151	
	7	$P2_12_12_1$	–137.387		–62.498	
	8	$P2_1/c$	–137.346		–64.135	
	9	$P2_1/c$	–137.174		–60.932	
	10	P–1	–136.934		–62.148	
30	1	$P2_1/c$	–144.535	–143.574	–69.243	–65.049
	2	P–1	–144.485		–67.843	
	3	$Pna2_1$	–143.666		–64.861	
	4	$P2_1$	–143.617		–65.610	
	5	$P2_12_12_1$	–143.511		–64.693	
	6	$P2_1/c$	–143.414		–57.154	
	7	$Pna2_1$	–143.194		–65.000	
	8	$P2_1/c$	–143.153		–66.240	
	9	$Pna2_1$	–143.111		–65.879	
	10	$P2_1/c$	–143.055		–63.969	
45	1	$P2_1/c$	–148.192	–146.880	–71.052	–67.213
	2	P–1	–148.001		–69.067	
	3	P–1	–147.237		–67.794	

	4	$P2_1/c$	–147.119		–66.4308	
	5	$Pna2_1$	–147.002		–64.727	
	6	$Pna2_1$	–146.878		–66.428	
	7	$Pna2_1$	–146.353		–66.522	
	8	$P2_1$	–146.151		–65.128	
	9	*Pbca*	–145.987		–68.452	
	10	$P2_1/c$	–145.884		–66.526	
	1	$P2_1$	–141.063		–66.333	
	2	$P2_1/c$	–140.910		–68.542	
	3	$Pna2_1$	–140.412		–64.134	
	4	*P*–1	–140.255		–63.929	
60	5	$P2_12_12_1$	–140.220	–140.233	–64.411	–65.653
	6	*P*–1	–140.198		–66.409	
	7	*P*–1	–140.086		–66.315	
	8	*P*–1	–140.048		–63.335	
	9	$P2_1/c$	–139.589		–64.86	
	10	*Pbca*	–139.545		–68.266	
	1	*P*–1	–136.242		–65.886	
	2	*P*–1	–136.241		–67.327	
	3	$P2_1$	–136.067		–64.965	
	4	$P2_12_12_1$	–136.052		–62.903	
75	5	*P*–1	–135.682	–135.629	–67.974	–65.444
	6	$P2_1/c$	–135.411		–64.732	
	7	$P2_12_12_1$	–135.290		–68.823	
	8	*P*–1	–135.225		–66.195	
	9	*P*–1	–135.200		–60.033	
	10	$P2_1/c$	–134.880		–65.601	
	1	*P*–1	–135.517		–66.843	
	2	*P*–1	–135.208		–66.850	
	3	$P2_12_12_1$	–134.760		–63.294	
	4	$P2_12_12_1$	–134.714		–67.885	
90	5	$P2_12_12_1$	–134.266	–134.017	–67.463	–63.912
	6	*P*–1	–133.374		–62.714	
	7	$P2_1$	–133.127		–62.095	
	8	$P2_1/c$	–133.102		–57.011	
	9	$P2_1$	–133.069		–60.901	
	10	$P2_1$	–133.029		–64.067	

Compound **4**

Torsion angle	Rank	Space group	Lattice energy kcal mol^{-1}	Average	Re–minimized lattice energy kcal mol^{-1}	Average
0	1	$P2_1$	–180.905	–180.455	–52.970	–50.934
	2	$P2_1/c$	–180.897		–52.409	
	3	*Pbca*	–180.784		–52.517	
	4	$P2_12_12_1$	–180.661		–48.222	
	5	$P2_12_12_1$	–180.632		–50.181	
	6	$P2_1/c$	–180.257		–51.472	
	7	$P2_1$	–180.181		–50.776	
	8	*Pbca*	–180.136		–49.917	
	9	$P2_12_12_1$	–180.084		–50.981	
	10	$P2_1/c$	–180.015		–49.901	
15	1	$P2_1$	–180.345	–179.738	–58.426	–56.105
	2	$P2_1/c$	–180.222		–55.122	
	3	$P2_1/c$	–179.879		–57.708	
	4	$P2_1/c$	–179.859		–59.127	
	5	*Pbca*	–179.745		–57.551	
	6	$P2_1$	–179.712		–57.487	
	7	$P2_1/c$	–179.560		–55.510	
	8	$P2_1/c$	–179.497		–56.119	
	9	$P2_12_12_1$	–179.310		–54.726	
	10	*Pbca*	–179.246		–49.273	
30	1	*Pbca*	–173.675	–172.508	–61.754	–61.202
	2	*Pbca*	–172.819		–58.503	
	3	$P2_1$	–172.634		–62.521	
	4	$P2_1/c$	–172.606		–58.265	
	5	*Pbca*	–172.427		–62.632	
	6	*Pbca*	–172.421		–65.564	
	7	*Pbca*	–172.413		–67.366	
	8	*C*2/*c*	–172.048		–57.835	
	9	$P2_1$	–172.030		–59.962	
	10	$P2_12_12_1$	–172.011		–57.614	
45	1	*Pbca*	–169.471	–168.615	–70.015	–63.153
	2	$P2_1/c$	–169.340		–67.295	
	3	*Pbca*	–168.606		–67.926	
	4	P 21/c	–168.564		–58.211	
	5	$P2_12_12_1$	–168.555		–59.170	
	6	*Pbca*	–168.477		–61.819	

	7	$P2_1/c$	–168.462		–61.339	
	8	$P2_1/c$	–168.401		–64.186	
	9	$C2/c$	–168.162		–59.644	
	10	$P2_1$	–168.115		–61.921	
	1	$Pbca$	–168.048		–71.817	
	2	$P2_1/c$	–167.729		–68.685	
	3	$Pna2_1$	–167.655		–66.067	
	4	$P2_12_12_1$	–167.425		–59.020	
	5	$P2_1$	–167.371	–167.196	–65.025	–65.326
60	6	$P2_1/c$	–167.059		–60.048	
	7	$P2_1/c$	–166.853		–64.847	
	8	$P2_1/c$	–166.641		–67.662	
	9	$Pbca$	–166.619		–64.617	
	10	$P2_12_12_1$	–166.558		–65.470	
	1	$P2_12_12_1$	–171.376		–66.277	
	2	$P2_12_12_1$	–171.36		–66.645	
	3	$P2_1$	–171.352		–68.240	
	4	$C2/c$	–171.294		–66.327	
	5	$P2_12_12_1$	–171.266	–171.092	–65.738	–66.608
75	6	$Pbca$	–171.033		–66.754	
	7	$P2_1$	–170.882		–64.981	
	8	$P2_1/c$	–170.855		–69.027	
	9	$P2_1/c$	–170.793		–64.128	
	10	$Pbca$	–170.711		–67.961	
	1	$P2_1$	–172.839		–67.703	
	2	$P2_12_12_1$	–172.106		–64.697	
	3	$P2_1/c$	–171.483		–66.483	
	4	$P2_12_12_1$	–171.371		–66.912	
	5	$P2_1$	–171.323	–171.468	–66.613	–65.439
90	6	$C2/c$	–171.293		–65.593	
	7	$P2_1/c$	–171.263		–59.967	
	8	$Pbca$	–171.085		–63.626	
	9	$P2_12_12_1$	–170.967		–66.328	
	10	P 21/c	–170.947		–66.463	