Supplementary Material (ESI) for Chemical Communications

Synthon evolution and unit cell evolution during crystallisation. A study of symmetry-independent molecules (Z´>1) in crystals of some hydroxy compounds

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Supplementary Material (ESI)
(17 pages)

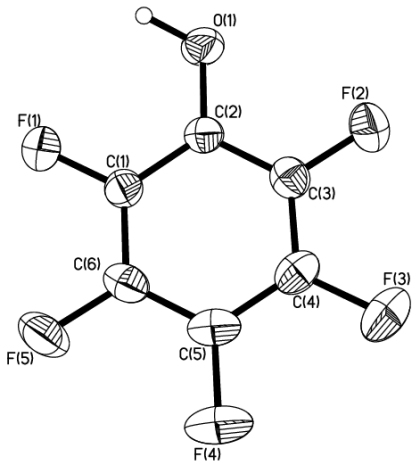


Fig.1 ORTEP diagram of pentafluorophenol (**1-L**).

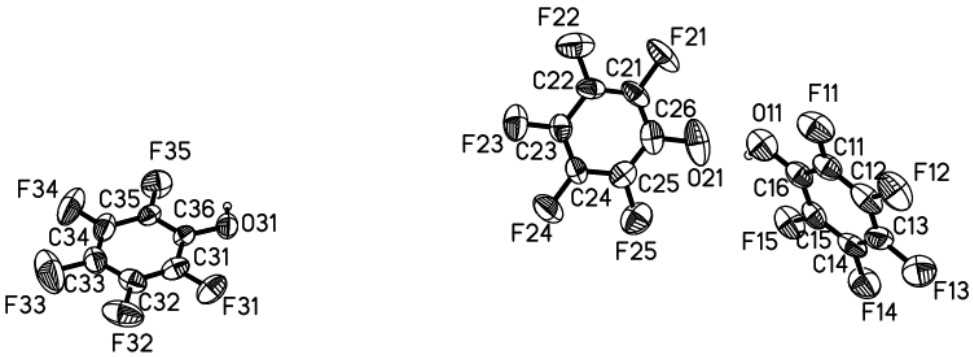


Fig.2 ORTEP diagram of pentafluorophenol (**1-H**)

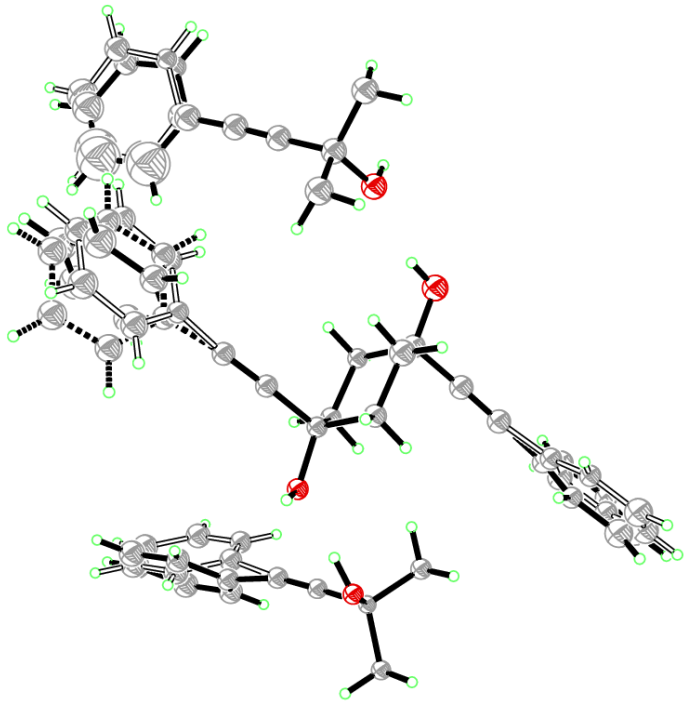


Fig.3 ORTEP diagram of *trans*-1,4-bis(phenylethynyl)cyclohexane-1,4-diol (**2-L**).

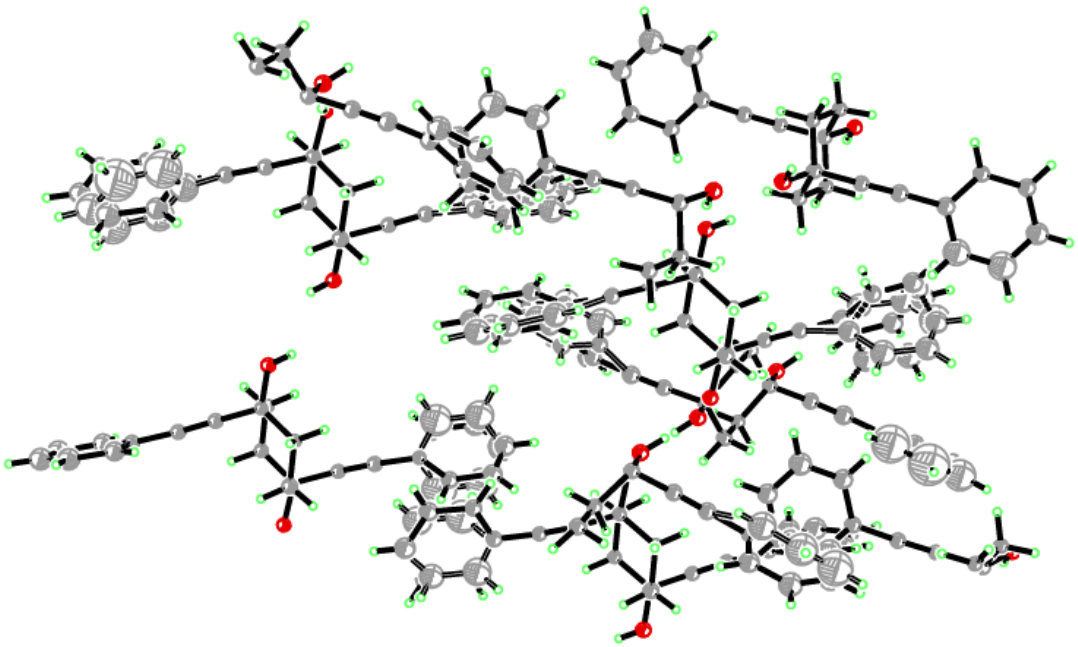


Fig.4 ORTEP diagram of *trans*-1,4-bis(phenylethynyl)cyclohexane-1,4-diol (**2-H**).

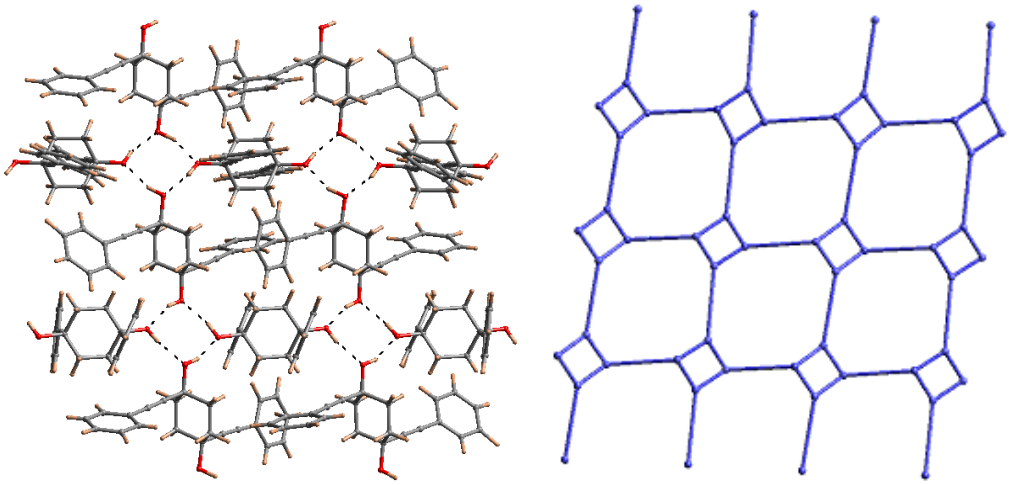


Fig. 5 High Z' form **2-H** of *trans*-1,4-bis(phenylethynyl)cyclohexane-1,4-diol. Notice the $(O–H\cdots O)_4$ square synthon and the 4.8^2 network.

Fig. 6 Conformational variations in the symmetry independent molecules in **2-L** and **2-H**.

Crystallisation of polymorphs

Low Z' form **1-L**: Semi-solid pentafluorophenol was liquefied by warming, and then filled in a 0.3 mm. diameter quartz capillary and sealed by flame sealing. The filled capillary was mounted on the goniometer and cooled to 261K. The solid which resulted was melted at 303K by slowly increasing the temperature. The mass was then cooled down to 283K and this resulted in solidification. The capillary surface was gently pressed by hand; this treatment increases both the temperature and the pressure within the capillary. This is sufficient to melt the solid. Cooling then to 277K resulted in a crystal, which was used for data collection. Data was, however, collected at 269K.

High Z' form **1-H**: Pentafluorophenol and pentafluoroaniline were mixed in 1:1 ratio, and the procedure above was repeated except that the various temperatures in the heat-cool cycles were slightly different. The liquid inside the capillary was initially solidified at 301K. It was then melted at 298K and crystals (which were shown in the X-ray analysis to be **1-H**) were finally grown at 294K. Data were collected at 292K.

The dimorphs of **2**, namely **2-L** ($P\bar{1}$, $Z'=2$) and **2-H** ($P\bar{1}$, $Z'=8$) were obtained concomitantly from acetone in the University of Durham, and large crystals of **2-H** suitable for neutron diffraction analysis were also obtained in this experiment. However, crystallization of the same synthetic sample in Hyderabad gave only **2-L**. The higher Z′ polymorph **2-H** could never be obtained despite using more than five solvents and different crystallization conditions, and unit cells for approximately 25 crystals from different batches were determined: all the crystals were found to be **2-L**. However, **2-H** was obtained in Hyderabad by melt cooling. Approximately 4 mg of **2-L** were heated in the hot bench attached to the Kofler hot stage microscope and melting occurred normally at 456K. When the melt was cooled at the rate of 5°C min^{-1} crystallisation was observed at 369K. A single crystal from the cooled melt was studied on the diffractometer and found to be the high Z′ polymorph **2-H**. IR and NMR data of the melt confirms that there was no solid-state reaction or decomposition during heating. Once this metastable polymorph (**2-H**) crystallises it remains as such for a sufficiently long time.

Thermal analysis for compound 2

Thermochemical data provides valuable information about the stability of a polymorph and the interconversion of one polymorph into another. Since crystals of **2-H** and **2-L** were obtained concomitantly from acetone we tried to understand the stability of these two polymorphs via DSC (Mettler Toledo Star) and HSM experiments.

DSC

A Mettler Toledo Star 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}. When crystals of **2-L** were heated, DSC showed that melting occurs normally at 456K (fig. 7). When the melt was cooled, a crystallisation exotherm was observed at 389K (fig 8). When the cooled melt was reheated, a solid state phase transformation was observed at 389K (fig 9). A single crystal from the cooled melt was studied on the diffractometer and found to be the high Z′ polymorph **2-H**.

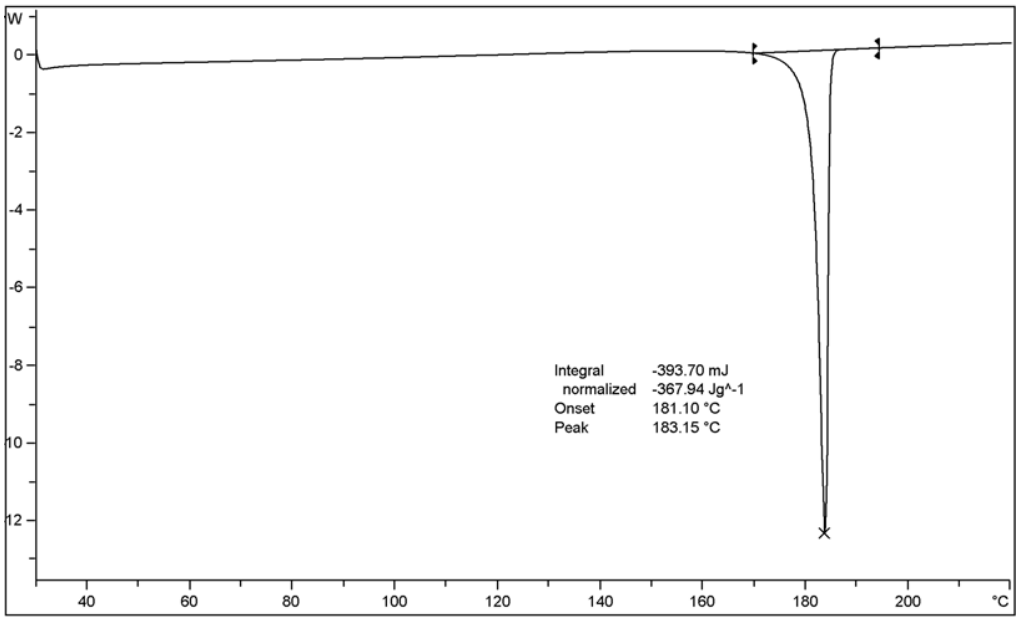


Fig. 7. Melting endotherm of the low Z′ polymorph **2-L**.

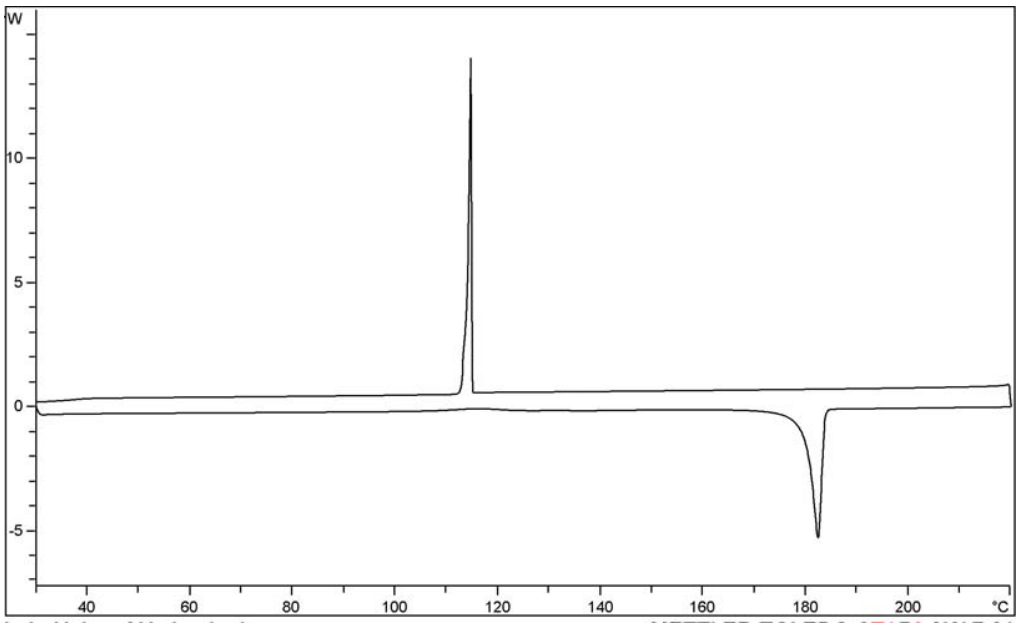


Fig 8 Crystallisation exotherm of the high Z′ polymorph **2-H** from the melt obtained by heating the low Z′ polymorph **2-L** of compound **2** to its melting temperature of 456K. Note that the crystallisation occurs at 389K.

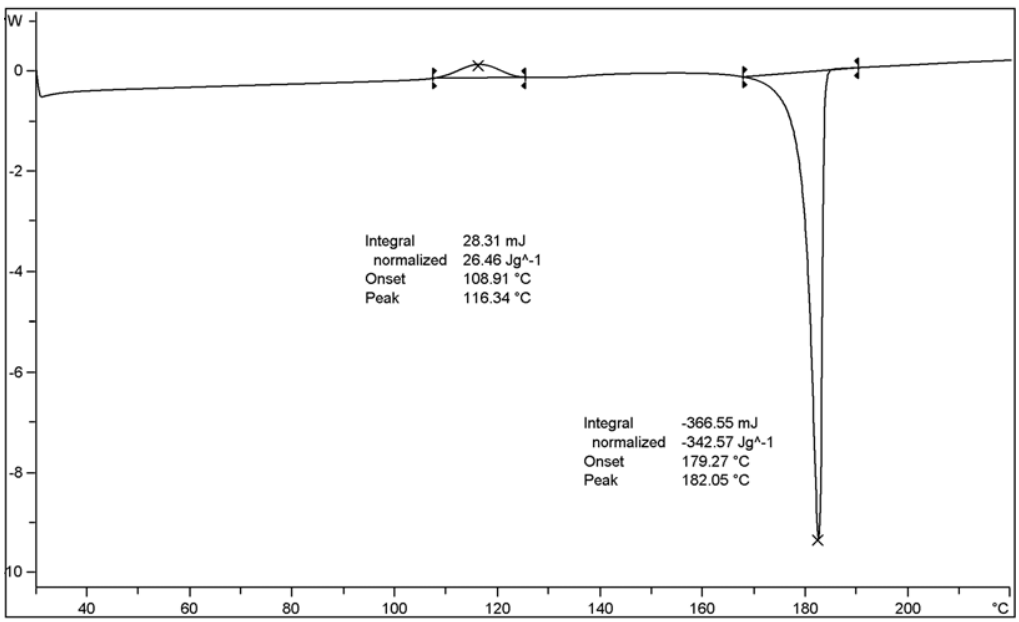
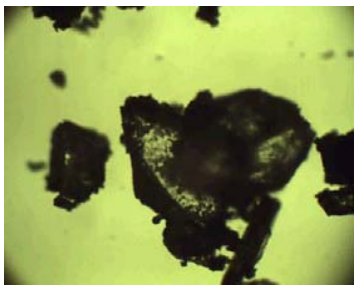


Fig 9. Exotherm showing the phase transformation **2-H→2-L** at 389K. The **2-H** material was obtained by melt cooling as indicated in Fig. 8.

Hot stage microscopy, HSM, for compound 2

A Kofler hot stage microscope (Wagner and Munz) was used. The temperature and heating rate were monitored by a digital thermometer. Pictures were taken by a digital camera attached to the microscope and processed with the Motic software. Samples were loaded on a glass slide, placed on the hot bench and heated at a rate of 5°C min^{-1}. The figures below represent the full heating and cooling cycles sequentially. The numbers refer to the temperature in °C.



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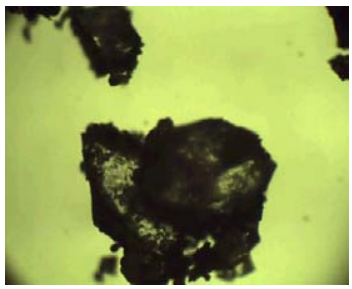

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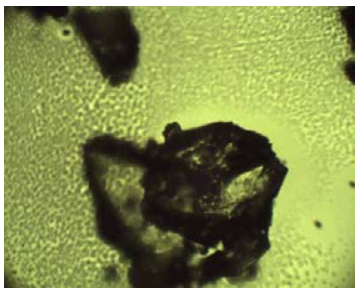

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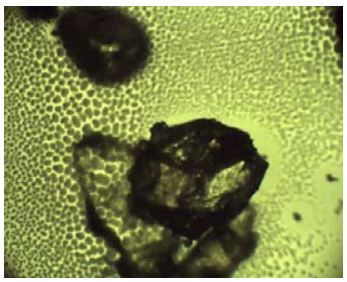

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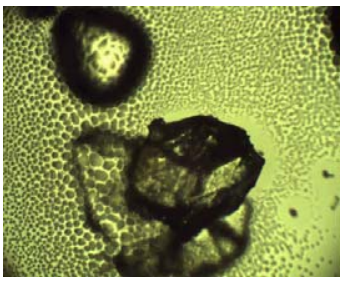

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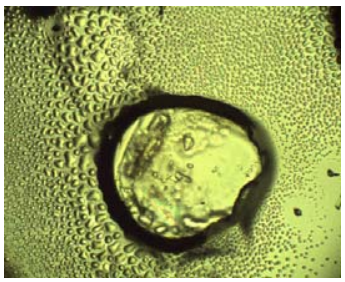

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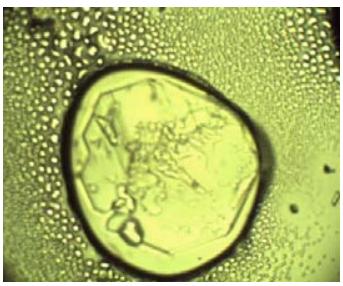

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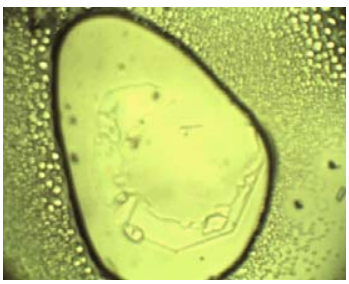

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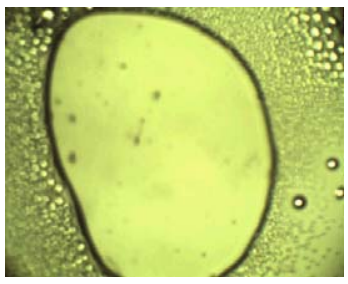

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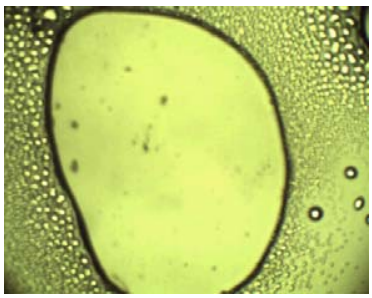

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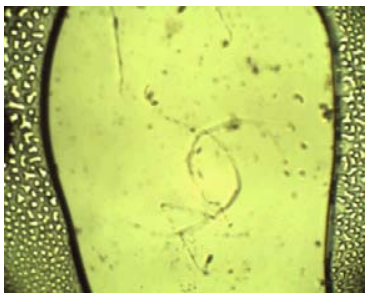

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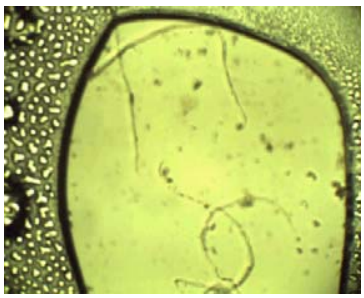

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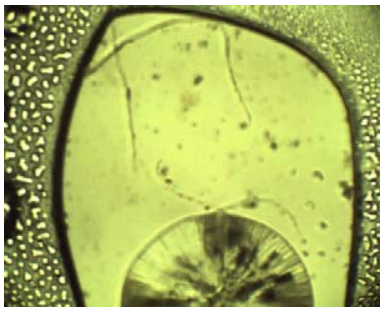

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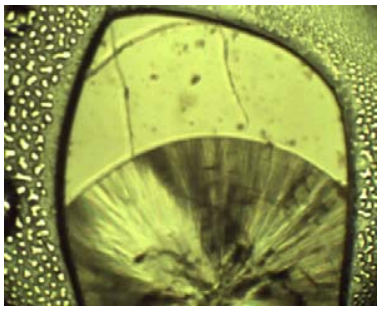

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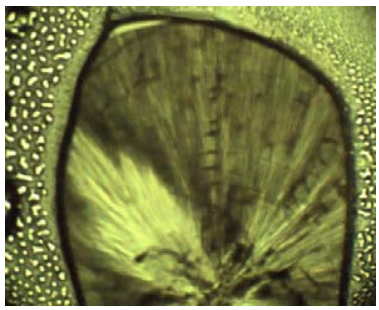

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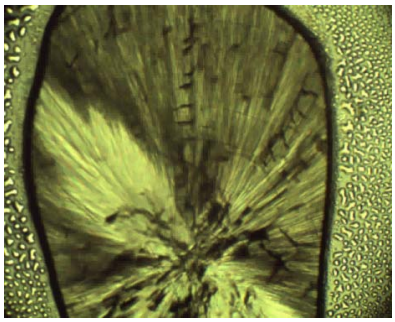

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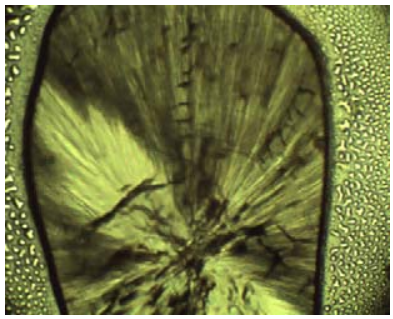

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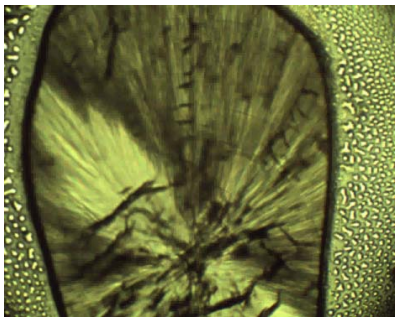

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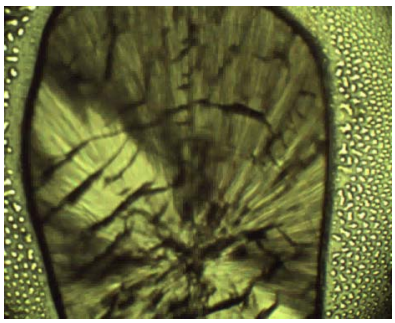

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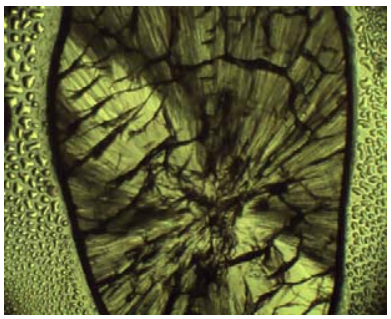

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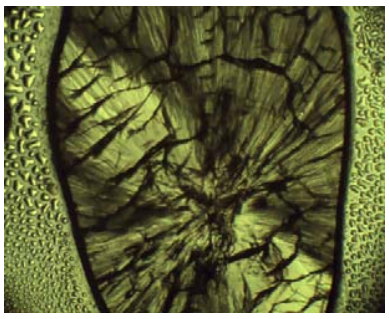

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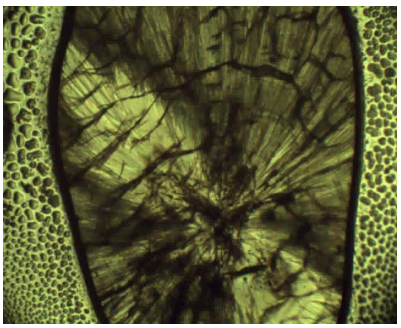

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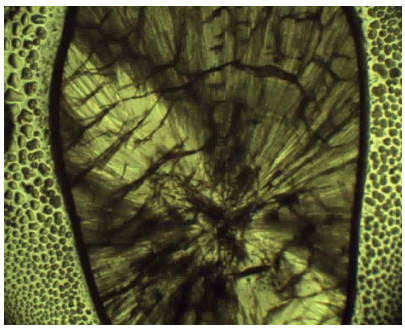

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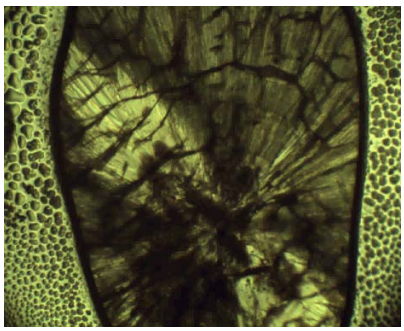

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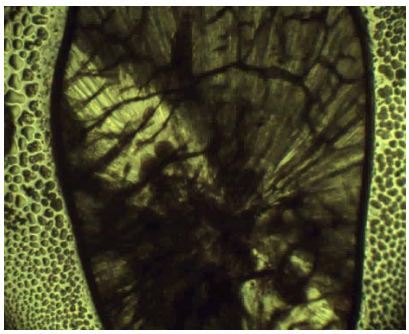

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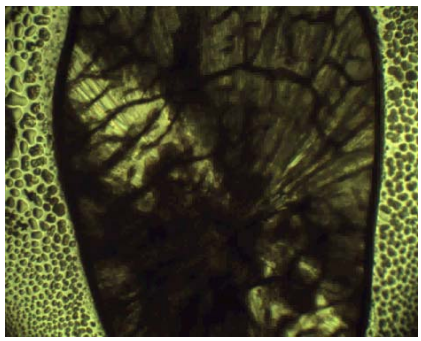

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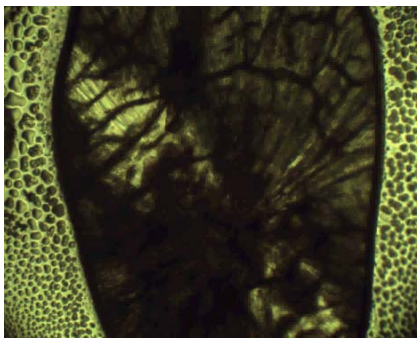

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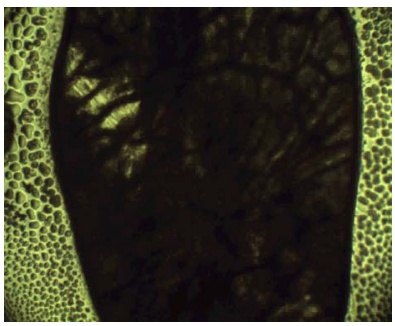

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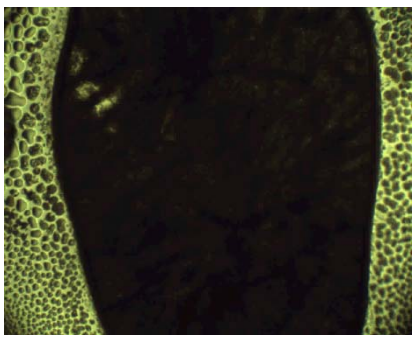

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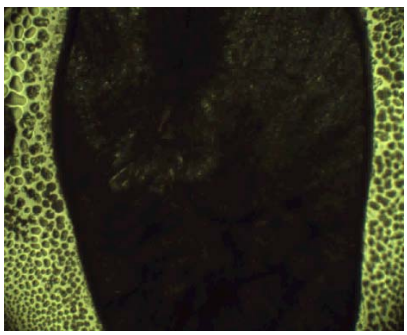

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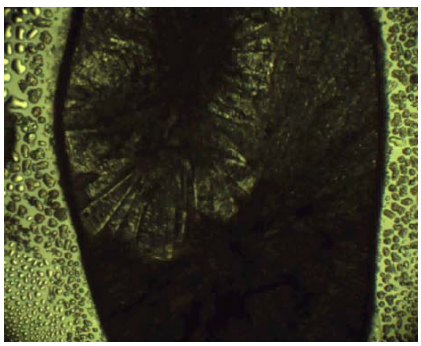

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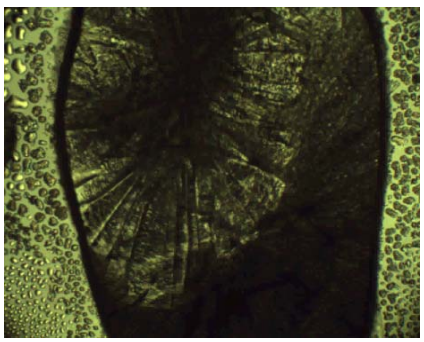

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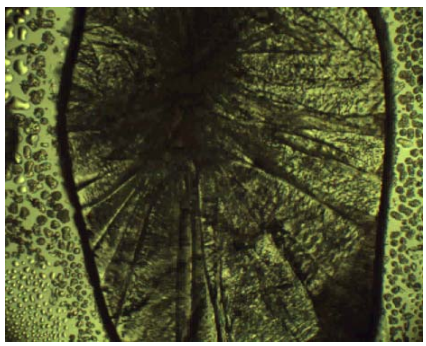

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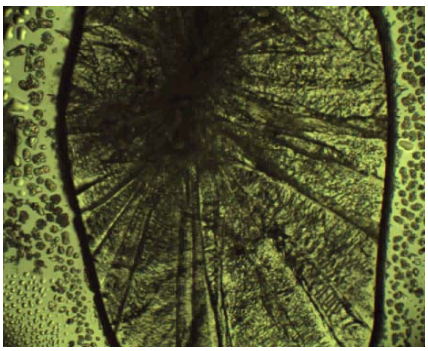

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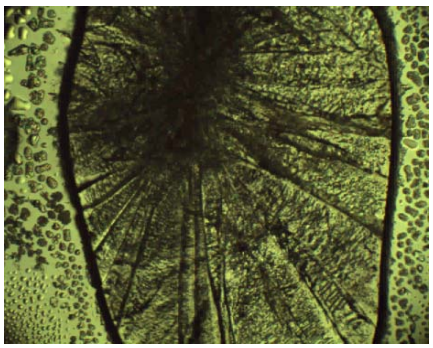

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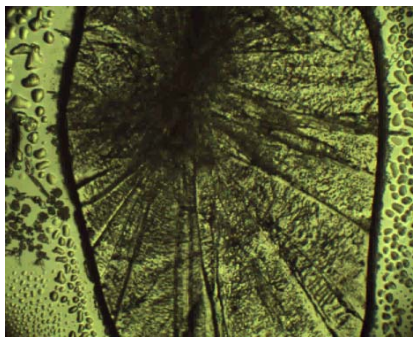

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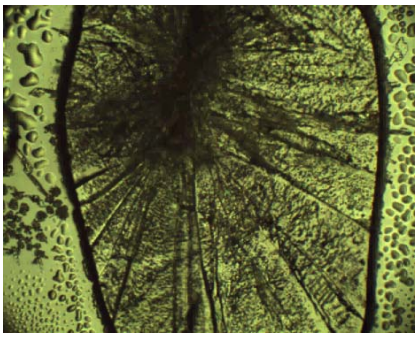

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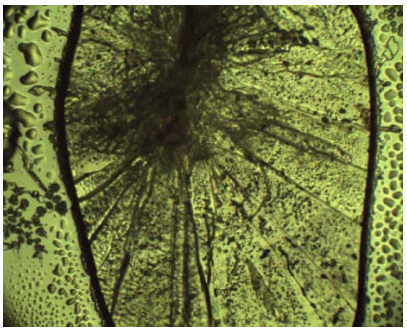

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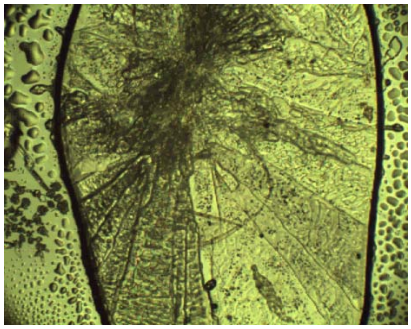

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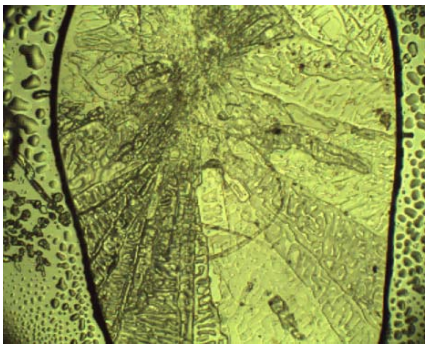

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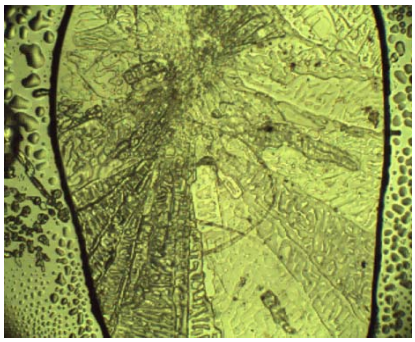

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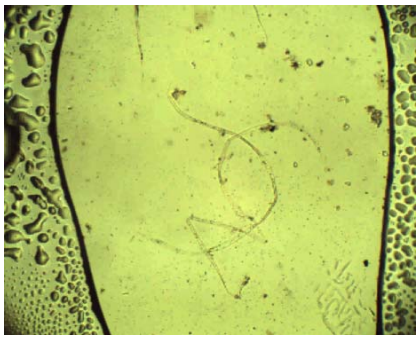

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Thermal analysis for compound 1

The sample was cooled from room temperature to 223K. DSC scans were then recorded during heating from 223K to 323K and then during cooling from 323K to 223K. These traces show no evidence of Form **1-H**. However, there appears to be a third (enantiotropic) polymorph with a melting point around 270K.

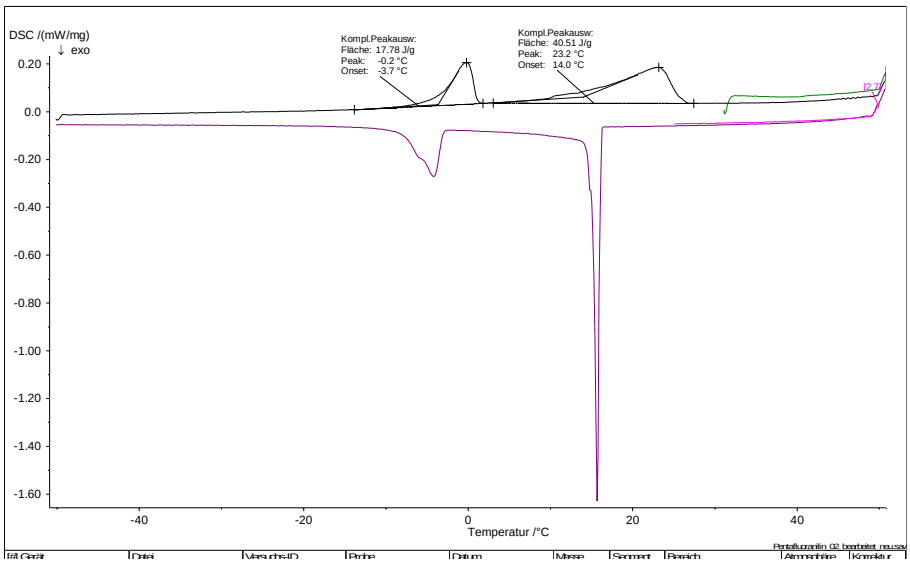

Fig 10 Melting endotherm (270K, 287K) and crystallisation exotherm (273K, 296K) of pentafluorophenol.

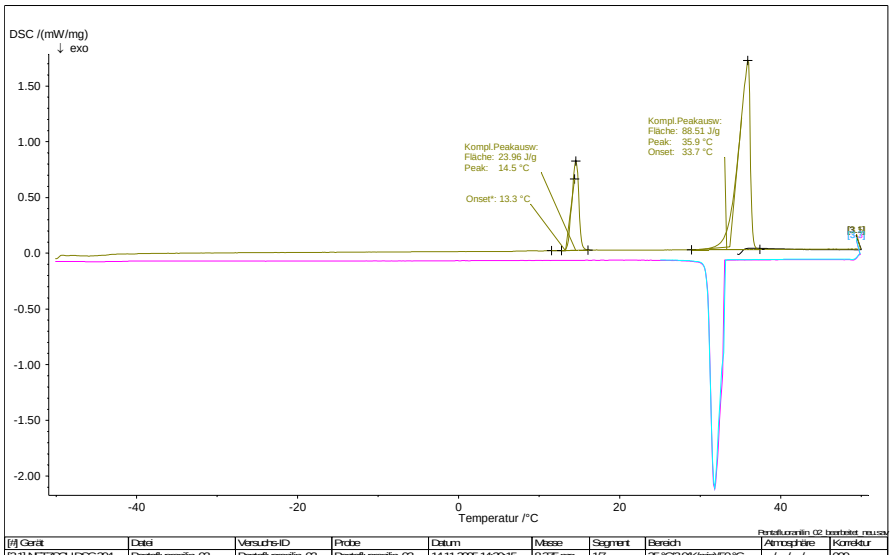

Fig 11 Melting endotherm (306K) and crystallisation exotherm (309K, 288K) of pentafluoroaniline.

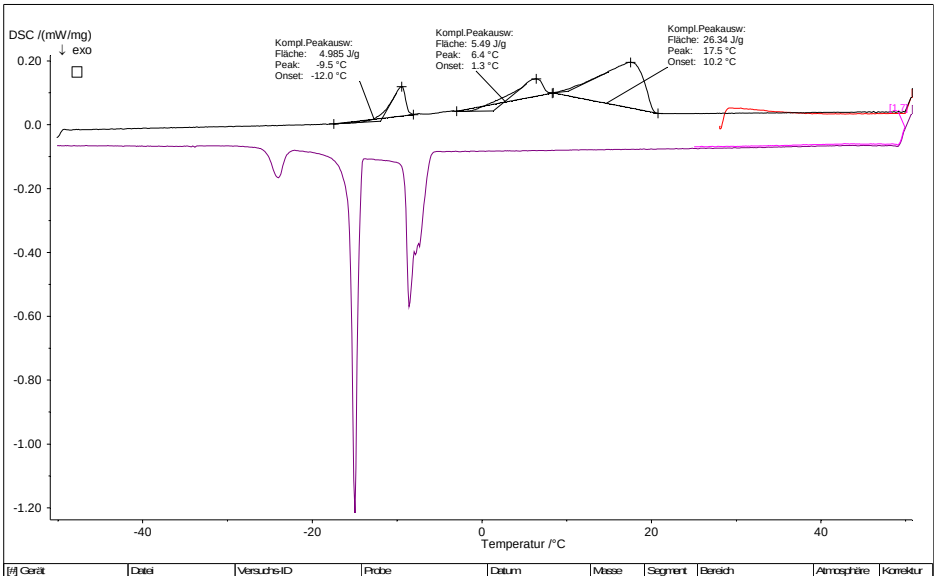

Fig 12 DSC traces of the 1:1 mixture of pentafluorophenol and pentafluoroaniline.

Table 1. Lattice energy of polymorphs with different Z´. Compounds were chosen where the synthon or 1D structures are similar in the polymorphs. The Dreiding 2.21 force field was used to calculate the energy (SP = single point, GO = geometry optimized).

Sl. No.	Refcode	Z´	Z	Space group	Lattice energy (kJ mol^{-1})	
					SP energy	GO energy
1	BOCPRO	1	4	$P2_12_12_1$	–181.09	–198.42
	BOCPRO01	4	8	$P2_1$	–177.91	–191.22
2	CBMZPN10	1	4	$P\bar{1}$	–168.15	–171.31
	CBMZPN11	4	8	$P2_1/c$	–157.72	–160.99
3	CYACAC	2	4	$P2_1/c$	–78.03	–86.57
	CYACAC01	3	12	$P\bar{1}$	–62.58	–80.20
4	DETBAA02	0.5	4	$C2/c$	–168.74	–174.10
	DETBAA01	1	18	$R\bar{3}$	–151.41	–154.13
	DETBAA06	2	18	$R3$	–150.28	–152.50
	DETBAA03	4	8	$P2_1$	–152.87	–160.24
5	FACRIK	1	4	$P2_1$/a	–66.89	–136.17
	FACRIK08	4	8	$P2_1$	–51.40	–135.50
6	FAKROY01	2	8	Cc	–84.22	–98.58
	FAKROY	4	4	$P1$	–61.45	–89.37
7	HUKHUQ01	2	8	$P2_1$/c	–218.72	–223.66
	HUKHUQ	6	24	$P2_1$/n	–211.48	–213.44
8	MELXEG01	2	8	$P2_12_12_1$	–193.02	–194.48
	MELXEG	3	6	$P2_1$	–190.42	–192.22
9	MHNPRY	1	4	$P2_12_12_1$	–193.94	–201.31
	MHNPRY01	3	12	$P2_12_12_1$	–187.24	–196.49
10	THIOUR01	0.5	4	$Pnma$	–69.11	–74.72
	THIOUR11	1	4	$P2_1ma$	–71.99	–75.31
	THIOUR19	1.5	12	$Pbnm$	–67.77	–71.99
	THIOUR05	4.5	36	$Pbnm$	–64.05	–70.07
11	UHENUQ01	3	24	Cc	–119.39	–121.98
	UHENUQ	6	12	$P\bar{1}$	–116.92	–120.03
12	BENZIL	0.5	3	$P3_12_1$	–165.47	–168.28
	BENZIL03	3	6	$P2_1$	–167.02	–168.95

Sl. No.	Refcode	Z´	Z	Space group	Lattice energy (kJ mol^{-1})	
					SP energy	GO energy
13	PULHUZ	2	8	*Cc*	–253.13	–255.43
	PULHUZ01	4	4	*P*1	–253.34	–255.60
14	CLEOZP01	1	9	*R*3	–240.18	–294.76
	CLEOZP10	3	3	*P*1	–246.69	–264.10
15	FABFUJ	1	4	$P2_12_12_1$	–112.32	–133.67
	FABFUJ01	2	8	$P2_12_12_1$	–131.62	–143.97
	FABFUJ02	3	12	$P2_1/c$	–126.94	–130.08
16	TAHLET20	2	8	*P*2c	–133.44	–139.75
	TAHLET21	4	8	$P2_1/c$	–151.23	–154.85
17	ZZZVTY12	1	6	$P\bar{3}$	–139.54	–148.67

The validation of the force field was done by considering the unit cell parameters before and after minimization. Only those cases were considered where the variation of each of the cell parameters in all polymorphs was less than 5%. This procedure removed one of the 18 sets of compounds (Ref. Code: FAKRIS, FAKRIS01) obtained in the CSD searches, leaving 17 sets of compounds. These calculations are shown in the next table.

Refcode	Cell parameters (before minimization)						Cell parameters (after minimization)					
BOCPRO	16.968	14.490	6.664	90	90	90	16.773	14.703	6.562	90	90	90
BOCPRO01	14.667	16.600	15.502	90	117.84	90	14.480	16.514	15.509	90	117.30	90
CBMZPN10	7.537	11.156	13.912	90	92.86	90	7.531	11.003	13.640	90	93.19	90
CBMZPN11	5.170	20.574	22.245	84.12	88.01	85.19	5.210	20.324	22.547	84.12	86.27	85.69
CYACAC	5.536	7.793	9.936	86.24	84.89	69.77	5.478	7.828	9.835	85.26	83.80	72.84
CYACAC01	11.629	7.761	13.758	90	108.92	90	11.984	7.591	14.110	90	109.78	90
DETBAA02	7.120	14.162	9.81	90	89.14	90	6.689	14.674	9.674	90	8728	90
DETBAA01	26.921	26.921	6.828	90	90	120	26.510	26.510	6.861	90	90	120
DETBAA06	26.800	26.800	6.828	90	90	120	26.410	26.410	6.826	90	90	120
DETBAA03	12.585	22.083	6.788	90	90.92	90	12.387	21.733	6.625	90	90.05	90
FACRIK	8.193	11.712	6.128	90	99.44	90	8.061	11.174	6.365	90	99.62	90
FACRIK08	11.875	14.995	6.651	90	90.49	90	12.039	14.794	6.741	90	91.33	90
FAKROY01	29.574	7.075	7.281	90	104.69	90	29.663	7.027	7.021	90	100.20	90
FAKROY	7.075	7.281	15.194	75.69	76.71	89.92	6.822	7.004	16.306	73.84	78.68	90.16
HUKHUQ01	9.475	9.490	36.087	90	95.63	90	9.524	9.561	36.269	90	95.51	90
HUKHUQ	28.386	9.579	38.379	90	109.41	90	28.359	9.617	38.373	90	109.13	90
MELXEG01	10.058	10.485	34.977	90	90	90	9.988	10.483	34.882	90	90	90
MELXEG	10.555	10.119	26.487	90	99.20	90	10.566	10.054	26.516	90	98.97	90
MHNPRY	18.140	11.810	8.560	90	90	90	18.223	11.596	8.759	90	90	90
MHNPRY01	20.266	19.262	14.384	90	90	90	20.659	19.249	14.505	90	90	90
THIOUR01	7.655	8.537	5.520	90	90	90	6.959	7.957	5.590	90	90	90
THIOUR11	7.487	8.536	5.474	90	90	90	7.196	8.222	5.633	90	90	90
THIOUR19	5.503	7.138	24.788	90	90	90	5.456	7.216	24.159	90	90	90
THIOUR05	5.467	7.545	76.867	90	90	90	5.561	7.164	72.737	90	90	90

UHENUQ01	41.086	7.386	23.391	90	117.70	90	40.844	7.196	23.680	90	117.03	90
UHENUQ	13.782	13.798	18.944	94.30	95.13	119.43	13.760	13.864	18.815	95.43	93.48	118.48
BENZIL	8.376	8.376	13.700	90	90	120	8.385	8.385	13.651	89.93	90.03	119.99
BENZIL03	14.380	8.373	13.359	90	88.82	90	14.410	8.398	13.515	90	88.98	90
PULHUZ	11.827	11.828	23.211	90	102.89	90	11.731	11.766	22.839	90	103.83	90
PULHUZ01	8.363	8.370	23.387	98.90	101.59	90	8.327	8.379	22.894	99.78	100.74	90.12
CLEOZP01	17.097	17.097	10.761	90	90	120	17.018	17.018	10.176	90	90	120
CLEOZP10	10.500	10.490	10.761	110.0	110.0	108.9	10.575	10.518	10.260	108.08	110.23	108.90
FABFUJ	13.566	8.271	7.340	90	90	90	13.131	8.817	7.298	90	90	90
FABFUJ01	13.572	8.248	14.508	90	90	90	13.545	8.439	14.381	90	90	90
FABFUJ02	13.543	8.290	22.591	90	104.97	90	13.290	8.774	22.289	90	102.55	90
TAHLET20	18.499	6.214	26.450	90	103.16	90	19.165	6.168	26.769-	90	105.10	90
TAHLET21	18.499	6.214	26.450	90	103.16	90	18.802	6.051	26.831	90	104.33	90
ZZZVTY12	13.998	13.998	13.202	90	90	120	13.901	13.901	13.603	90	90	120
ZZZVTY03	13.208	13.559	13.969	117.67	92.67	91.43	13.607	13.060	13.733	114.03	96.97	92.89
ZZZVTY04	14.156	21.319	13.065	99.92	92.68	106.15	14.013	20.454	13.436	100.54	94.13	103.8
FAKRIS	9.196	9.697	9.940	68.01	67.18	77.00	9.155	9.658	9.714	69.11	66.69	72.40
FAKRIS01	31.430	5.492	17.726	90	98.60	90	24.954	7.534	17.134	90	76.14	90