

Supporting Information

Specific energy contributions from competing hydrogen-bonded structures in six polymorphs of phenobarbital

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Contents

1.	Preparation of polymorphs V and VI	3
2.	Thermal ellipsoid plots for forms V and VI	4
3.	Structural features of forms I , II and III	5
4.	IR spectroscopy	7
4.1.	Experimental.....	7
4.2.	Results	7
5.	PIXEL calculations	8
5.1.	Overview	8
5.2.	Form I	9
5.3.	Form II	10
5.4.	Form III	12
5.5.	Form V	12
5.6.	Form VI	13
5.7.	Form X	14
6.	Intramolecular energy penalties	15
7.	<i>XPac</i> comparisons with theoretical structures	16
7.1.	Method.....	16
7.2.	Form V	16
7.3.	Form X	17
8.	Structure model for polymorph X	18
9.	References	19

1. Preparation of polymorphs V and VI

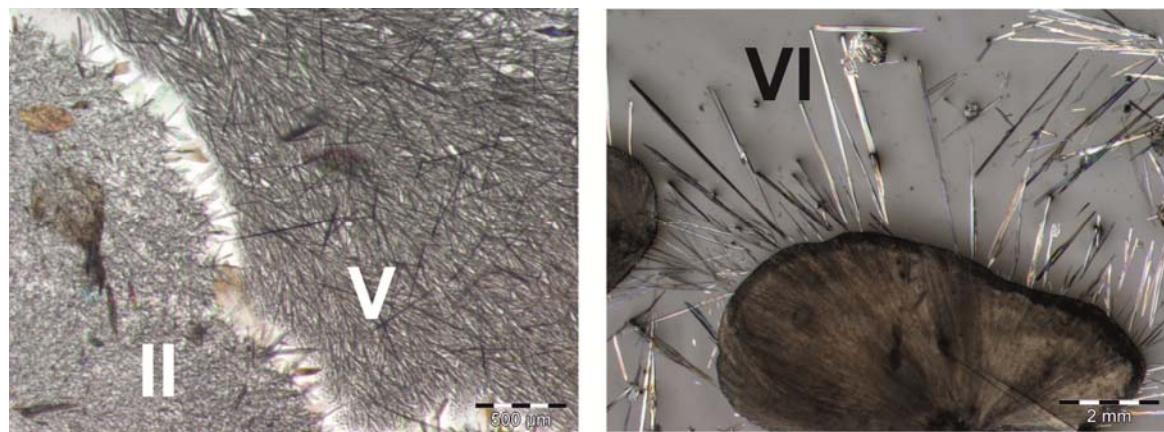


Fig. S1. Left: Pbtl forms **II** and **V** produced by sublimation at 135 °C. The two phases are separated by a transformation frontier (scale bar = 500 μm). Right: Polycrystalline aggregate and prismatic single crystals of polymorph **VI** in paraffin oil after crystallization at 100 °C (scale bar = 2 mm).

2. Thermal ellipsoid plots for forms V and VI

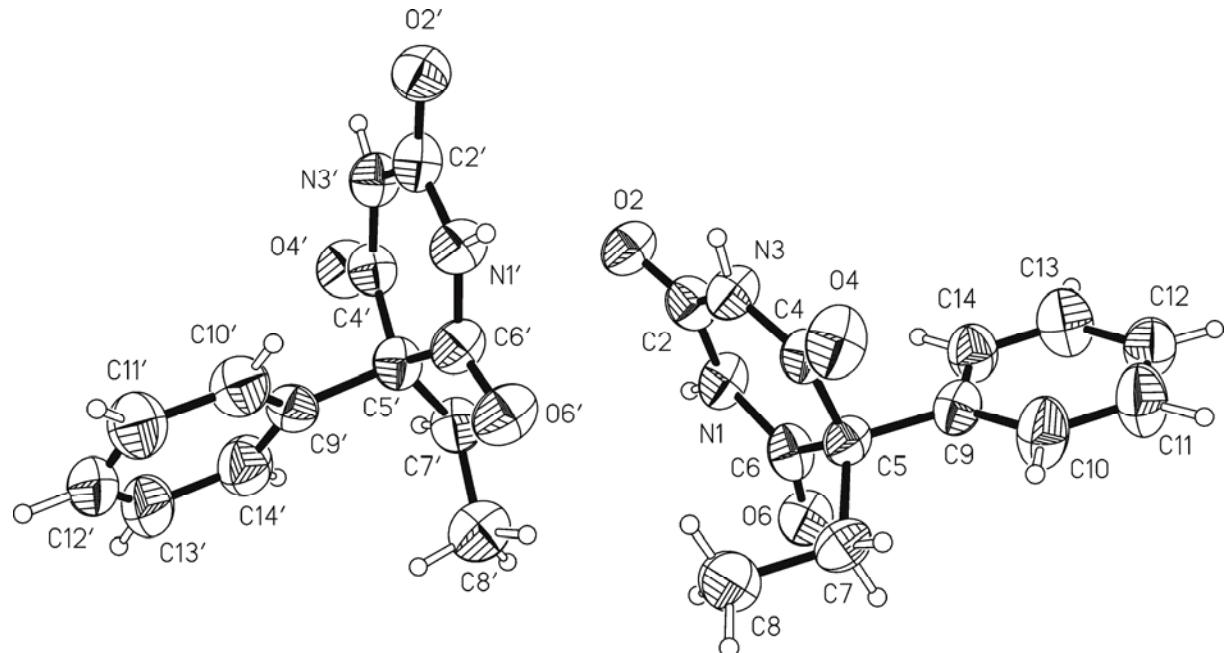


Fig. S2. Asymmetric unit of form V of PbtI with thermal ellipsoids drawn at the 50% probability level.

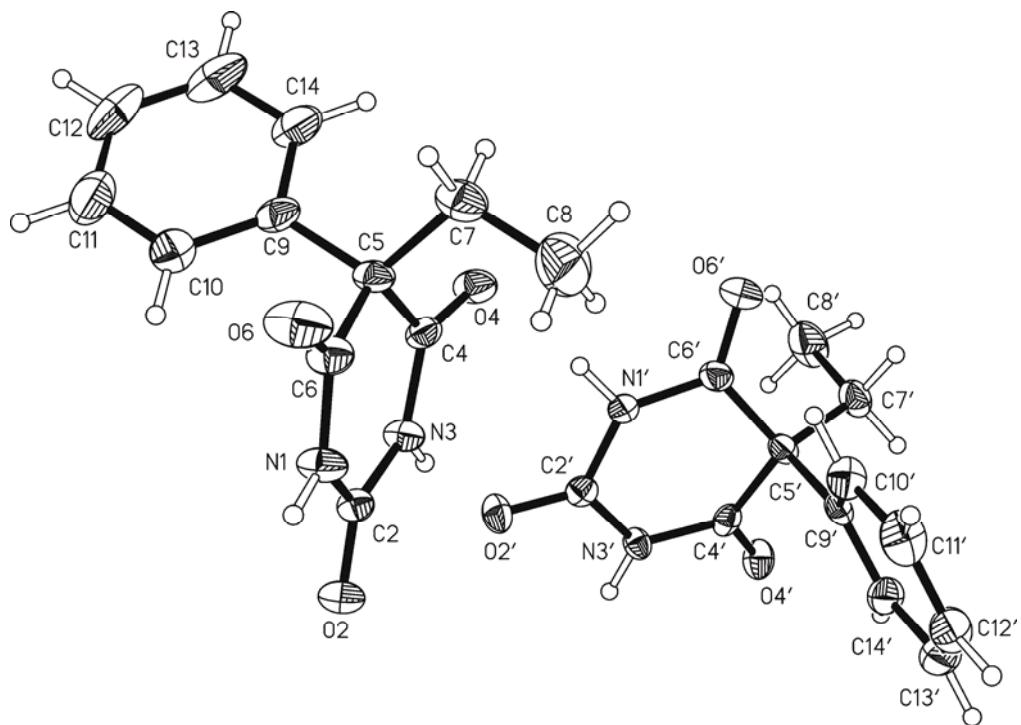


Fig. S3. Asymmetric unit of form VI of PbtI with thermal ellipsoids drawn at the 50% probability level.

3. Structural features of forms I, II and III

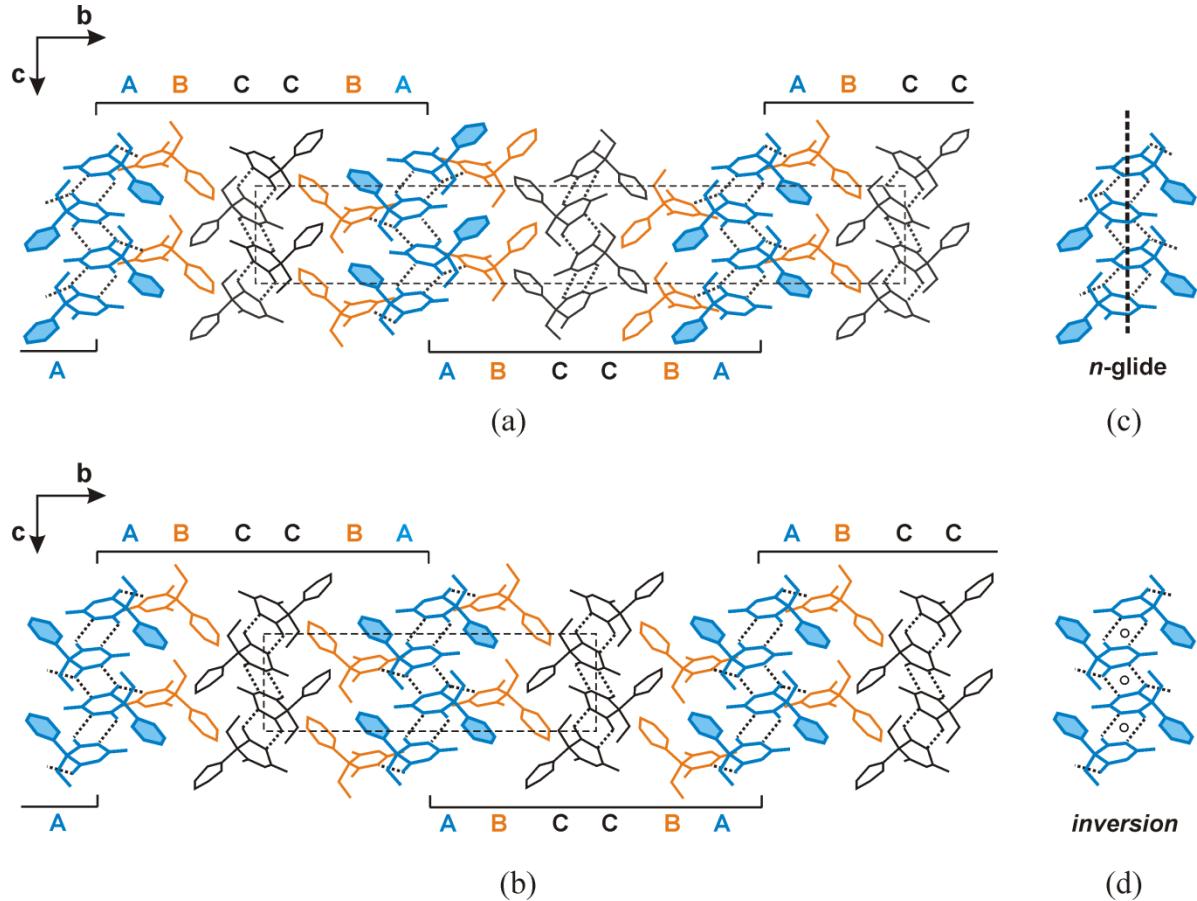


Fig. S4. Illustration of the close packing relationship between polymorphs **I** (a) and **II** (b) of PbtI, both containing three symmetry-independent molecules, labelled A – C. In each structure, BAAB sequences correspond with a N–H···O bonded **L-3** layer topology and the CC sequences with a **C-2** chain (see Fig. 1). The only fundamental difference between the two forms is the symmetry of **C-2** chains composed of C-type molecules, which in form **I** is a glide symmetry (c) and an inversion symmetry in form **II** (d). For more details, see ref. [1].

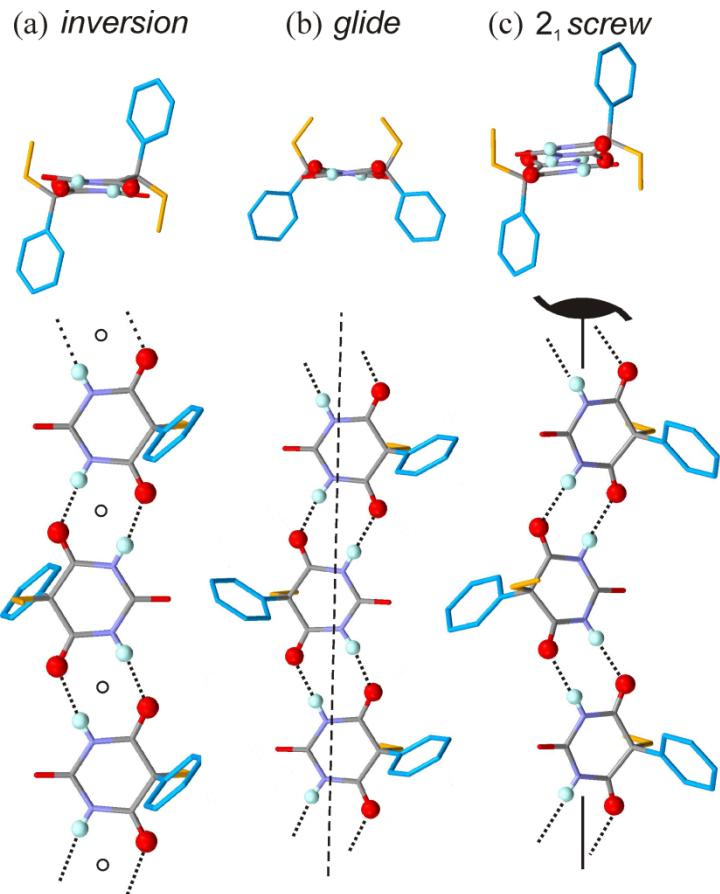


Fig. S5. **C-2** chains of different symmetry in polymorphs of PbtI: **(a)** inversion (**I**: molecule B; **II**: molecules B and C); **(b)** glide plane (**I**: molecule C); **(c)** 2_1 axis (**III**). Each **C-2** chain is viewed parallel (top) and perpendicular to its direction of translation.

4. IR spectroscopy

4.1. Experimental

FT-IR spectra were recorded with a Bruker IFS 25 spectrometer connected with the IR microscope I (Bruker). The samples were prepared on ZnSe discs and measured in transmission mode (15x Cassegrain objective, spectral range 4000 to 600 cm^{-1} , resolution 4 cm^{-1} , 64 interferograms per spectrum).

4.2. Results

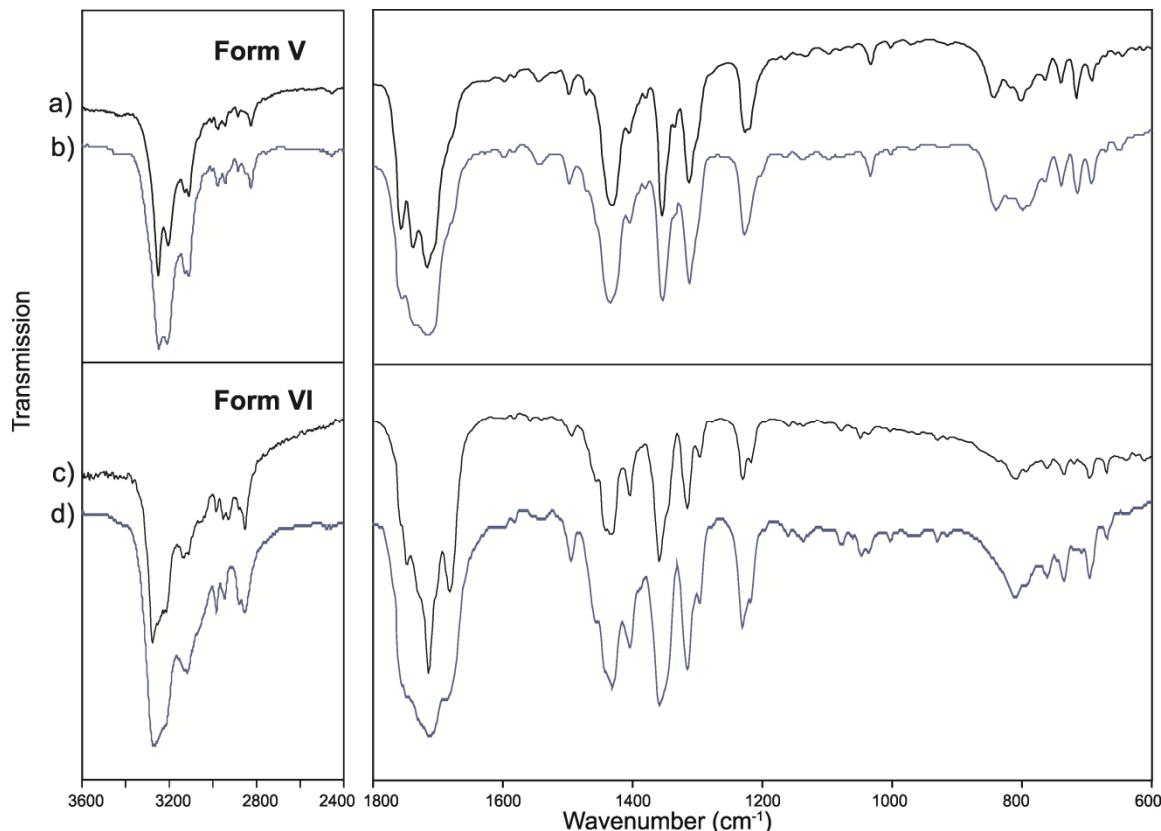


Fig. S6. Comparison of IR spectra for polymorphs **V** (a) and **VI** (c) of PbI obtained in this study (a, c) with reference spectra (b, d) recorded in a previous study [1].

5. PIXEL calculations

5.1. Overview

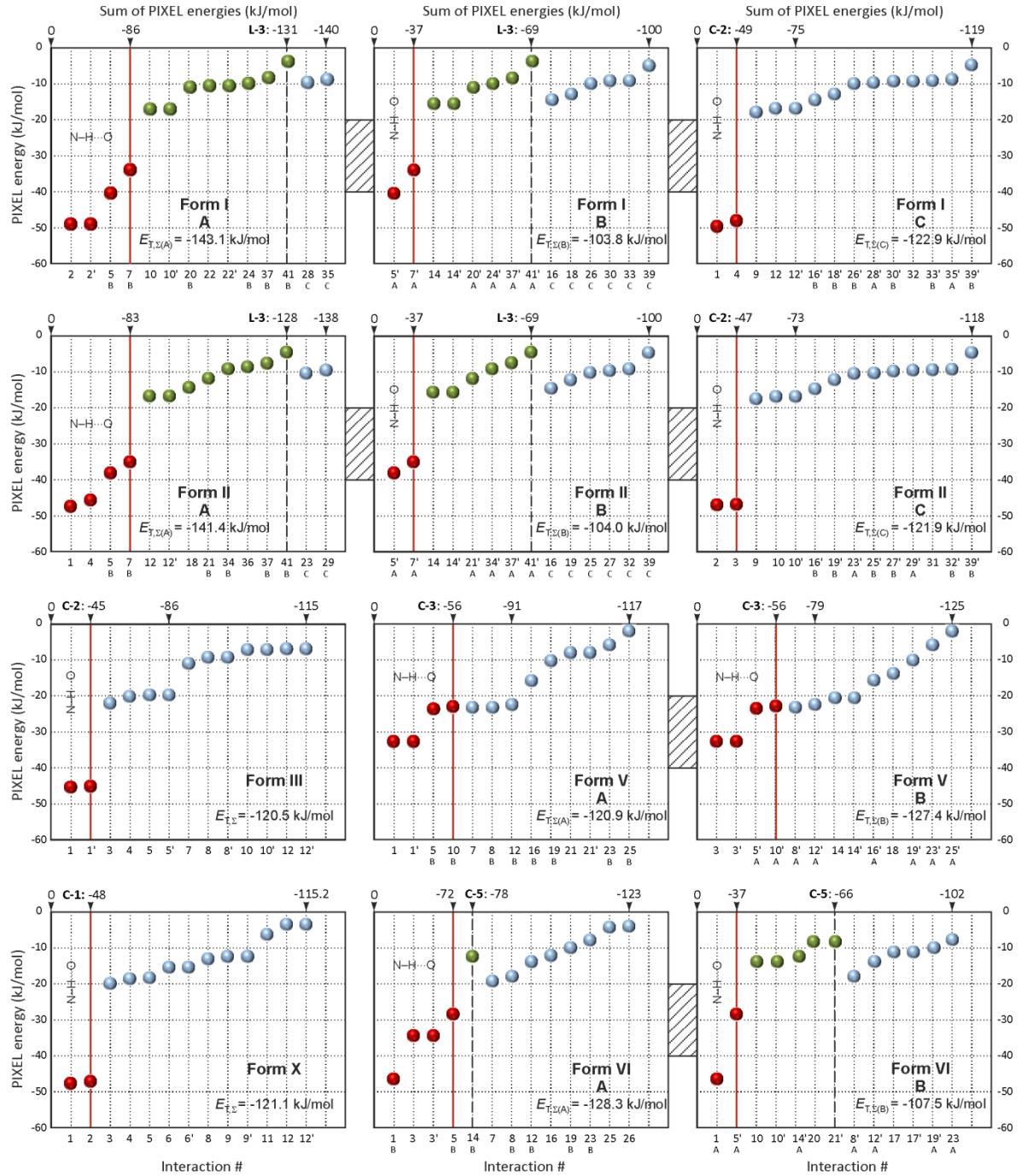


Fig. S7. PIXEL interaction energies for polymorphs of PbtI. Red balls indicate H-bond interactions and green balls non-H bond interactions within the same instance of an HBS. All other interactions are represented by grey balls.

5.2. Form I

$E_{T,\Sigma} = -123.3 \text{ kJ mol}^{-1}$ ($E_{T,\text{Cry}}$ not calculated)

$E_{T,\Sigma(A)} = -143.1 \text{ kJ mol}^{-1}$

$E_{T,\Sigma(B)} = -103.8 \text{ kJ mol}^{-1}$

$E_{T,\Sigma(C)} = -122.9 \text{ kJ mol}^{-1}$

Table S1. Pairwise interaction energies (kJ mol^{-1}) for polymorph I of PbtI (molecule A).

#	Type	Mol.	Symmetry operation	d (Å)	E_C	E_P	E_D	E_R	E_T
2	L-3_t	A	$-1/2+x, 1/2-y, -1/2+z$	7.019	-60.2	-22.1	-19.8	52.8	-49.2
2'	L-3_t	A	$1/2+x, 1/2-y, 1/2+z$	7.019	-60.2	-22.1	-19.8	52.8	-49.2
5	L-3_o	B	x, y, z	6.352	-27.3	-8.9	-29.3	24.9	-40.5
7	L-3_o	B	$x-1, y, z$	6.806	-31.0	-9.9	-23.4	30.3	-34.0
10	L-3_n	A	$x, y, z-1$	6.803	-5.9	-2.7	-20.8	12.1	-17.2
10'	L-3_n	A	$x, y, z+1$	6.803	-5.9	-2.7	-20.8	12.1	-17.2
20	L-3_n	B	$-1/2+x, 1/2-y, -1/2+z$	7.794	-3.8	-2.8	-13.1	8.6	-11.1
22	L-3_n	A	$-1/2+x, 1/2-y, 1/2+z$	7.389	-1.2	-1.1	-11.2	2.8	-10.7
22'	L-3_n	A	$1/2+x, 1/2-y, -1/2+z$	7.389	-1.2	-1.1	-11.2	2.8	-10.7
24	L-3_n	B	$-1/2+x, 1/2-y, 1/2+z$	8.208	-2.3	-2.1	-9.8	4.3	-10.0
28	@1a	C	x, y, z	9.011	-2.3	-1.0	-12.5	6.1	-9.7
35	@1c	C	$x, y, z+1$	9.185	-1.2	-0.8	-10.9	4.1	-8.9
37	L-3_n	B	$x, y, z-1$	9.238	-6.3	-2.5	-9.4	9.8	-8.4
41	L-3_n	B	$x-1, y, z-1$	8.980	-0.6	-0.1	-3.3	0.2	-3.8

Table S2. Pairwise interaction energies (kJ mol^{-1}) for polymorph I of PbtI (molecule B).

#	Type	Mol.	Symmetry operation	d (Å)	E_C	E_P	E_D	E_R	E_T
5'	L-3_o	A	x, y, z	6.352	-27.3	-8.9	-29.3	24.9	-40.5
7'	L-3_o	A	$x+1, y, z$	6.806	-31.0	-9.9	-23.4	30.3	-34.0
14	L-3_n	B	$x, y, z-1$	6.803	-3.7	-1.6	-18.8	8.6	-15.5
14'	L-3_n	B	$x, y, z+1$	6.803	-3.7	-1.6	-18.8	8.6	-15.5
16	@1a	C	$x+1, y, z+1$	7.459	-7.4	-3.5	-18.6	15.1	-14.5
18	@1b	C	$x+1, y, z$	8.027	-3.4	-1.5	-14.8	6.8	-12.9
20'	L-3_n	A	$1/2+x, 1/2-y, 1/2+z$	7.794	-3.8	-2.8	-13.1	8.6	-11.1
24'	L-3_n	A	$1/2+x, 1/2-y, -1/2+z$	8.208	-2.3	-2.1	-9.8	4.2	-10.0
26	@1c	C	$x, y, z+1$	8.019	-0.4	-1.6	-13.5	5.5	-10.0
30	@1a	C	x, y, z	7.902	-0.4	-1.8	-15.5	8.4	-9.3
33	@1a	C	$1-x, 1-y, 1-z$	7.993	1.0	-1.0	-12.3	3.2	-9.2
37'	L-3_n	A	$x, y, z+1$	9.238	-6.3	-2.5	-9.4	9.8	-8.4
39	@1b	C	$1-x, 1-y, -z$	10.293	-3.4	-1.5	-5.2	5.3	-4.9
41'	L-3_n	A	$x+1, y, z+1$	8.980	-0.6	-0.1	-3.3	0.2	-3.8

Table S3. Pairwise interaction energies (kJ mol^{-1}) for polymorph **I** of PbtI (molecule C).

#	Type	Mol.	Symmetry operation	d (\AA)	E_C	E_P	E_D	E_R	E_T
1	C-2	C	$-x, 1-y, -z$	6.888	-64.4	-24.2	-20.6	59.4	-49.7
4	C-2	C	$1-x, 1-y, 1-z$	7.125	-67.2	-25.5	-20.7	65.3	-48.1
9	@2	C	$1-x, 1-y, -z$	6.958	-9.5	-3.8	-15.0	10.4	-18.0
12	@2	C	$x, y, z-1$	6.803	-4.3	-1.7	-21.0	10.0	-16.9
12'	@3	C	$x, y, z+1$	6.803	-4.3	-1.7	-21.0	10.0	-16.9
16'	@1	B	$x-1, y, z-1$	7.459	-7.4	-3.5	-18.6	15.1	-14.5
18'	@1	B	$x-1, y, z$	8.027	-3.4	-1.5	-14.8	6.8	-12.9
26'	@1	B	$x, y, z-1$	8.019	-0.4	-1.6	-13.5	5.5	-10.0
28'	@1	A	x, y, z	9.011	-2.3	-1.0	-12.5	6.1	-9.7
30'	@1	B	x, y, z	7.902	-0.4	-1.8	-15.5	8.4	-9.3
32	@3	C	$-x, 1-y, 1-z$	7.776	-1.1	-1.4	-14.0	7.2	-9.3
33'	@1	B	$1-x, 1-y, 1-z$	7.993	1.0	-1.0	-12.3	3.2	-9.2
35'	@1	A	$x, y, z-1$	9.185	-1.2	-0.8	-10.9	4.1	-8.9
39'	@1	B	$1-x, 1-y, -z$	10.293	-3.4	-1.5	-5.2	5.3	-4.9

#9: Two symmetry-related contacts (phenyl)C33-H33...O7 (H···O 2.65 Å, CHO = 134°)

5.3. Form II

$$E_{T,\Sigma} = -122.4 \text{ kJ mol}^{-1} (E_{T,\text{Cry}} \text{ not calculated})$$

$$E_{T,\Sigma(A)} = -141.4 \text{ kJ mol}^{-1}$$

$$E_{T,\Sigma(B)} = -104.0 \text{ kJ mol}^{-1}$$

$$E_{T,\Sigma(C)} = -121.9 \text{ kJ mol}^{-1}$$

Table S4. Pairwise interaction energies (kJ mol^{-1}) for polymorph **II** of PbtI (molecule A).

#	Type	Mol.	Symmetry operation	d (\AA)	E_C	E_P	E_D	E_R	E_T
1	L-3_t	A	$-x+1, -y+1, -z+2$	6.968	-61.9	-23.1	-19.8	57.3	-47.5
4	L-3_t	A	$-x, -y+1, -z+1$	7.118	-61.6	-23.6	-20.8	60.2	-45.7
5	L-3_o	B	$x-1, y, z$	6.326	-25.9	-9.4	-30.2	27.4	-38.2
7	L-3_o	B	x, y, z	6.788	-35.1	-11.6	-24.6	36.2	-35.1
12	L-3_n	A	$x, y, z-1$	6.719	-5.9	-2.6	-22.3	13.9	-16.8
12'	L-3_n	A	$x, y, z+1$	6.719	-5.9	-2.6	-22.3	13.9	-16.8
18	L-3_n	A	$-x, -y+1, -z+2$	6.860	-6.1	-3.1	-13.6	8.2	-14.4
21	L-3_n	B	$-x+1, -y+1, -z+1$	7.914	-4.2	-3.1	-15.7	11.2	-11.9
34	L-3_n	B	$x-1, y, z+1$	9.066	-6.4	-2.5	-10.3	10.0	-9.2
36	L-3_n	A	$-x+1, -y+1, -z+1$	7.967	-0.2	-0.6	-10.5	2.8	-8.6
37	L-3_n	B	$-x+1, -y+1, -z+2$	7.874	-1.6	-1.9	-9.0	5.0	-7.6
41	L-3_n	B	$x, y, z+1$	8.771	-0.5	-0.2	-4.4	0.5	-4.6
23	@1b	C	$x, y, z+1$	8.880	-3.3	-1.6	-15.0	9.3	-10.5
29	@1a	C	x, y, z	9.072	-1.8	-0.9	-11.9	5.0	-9.6

Table S5. Pairwise interaction energies (kJ mol⁻¹) for polymorph **II** of PbtI (molecule B).

#	Type	Mol.	Symmetry operation	<i>d</i> (Å)	<i>E</i> _C	<i>E</i> _P	<i>E</i> _D	<i>E</i> _R	<i>E</i> _T
5'	L-3_o	A	<i>x</i> +1, <i>y</i> , <i>z</i>	6.326	-25.9	-9.4	-30.2	27.4	-38.2
7'	L-3_o	A	<i>x</i> , <i>y</i> , <i>z</i>	6.788	-35.1	-11.6	-24.6	36.2	-35.1
14	L-3_n	B	<i>x</i> , <i>y</i> , <i>z</i> -1	6.719	-4.7	-2.1	-20.2	11.3	-15.7
14'	L-3_n	B	<i>x</i> , <i>y</i> , <i>z</i> +1	6.719	-4.7	-2.1	-20.2	11.3	-15.7
21'	L-3_n	A	- <i>x</i> +1, - <i>y</i> +1, - <i>z</i> +1	7.914	-4.2	-3.1	-15.7	11.2	-11.9
34'	L-3_n	A	<i>x</i> +1, <i>y</i> , <i>z</i> -1	9.066	-6.4	-2.5	-10.3	10.0	-9.2
37'	L-3_n	A	- <i>x</i> +1 - <i>y</i> +1, - <i>z</i> +2	7.874	-1.6	-1.9	-9.0	5.0	-7.6
41'	L-3_n	A	<i>x</i> , <i>y</i> , <i>z</i> -1	8.771	-0.5	-0.2	-4.4	0.5	-4.6
16	@ 1b	C	<i>x</i> , <i>y</i> , <i>z</i>	7.401	-9.1	-4.3	-19.4	18.1	-14.7
19	@ 1a	C	<i>x</i> , <i>y</i> , <i>z</i> +1	8.101	-3.3	-1.5	-14.6	7.0	-12.3
25	@ 1a	C	- <i>x</i> +1, - <i>y</i> +2, - <i>z</i> +1	7.939	0.3	-1.4	-14.0	4.8	-10.3
27	@ 1c	C	<i>x</i> +1, <i>y</i> , <i>z</i>	7.932	-0.3	-1.9	-15.1	7.5	-9.8
32	@ 1a	C	<i>x</i> +1, <i>y</i> , <i>z</i> +1	7.903	-0.6	-2.0	-16.1	9.3	-9.3
39	@ 1b	C	- <i>x</i> +1, - <i>y</i> +2, - <i>z</i> +2	10.283	-3.7	-1.6	-5.4	6.1	-4.7

#16: Contact (phenyl)C35-H35...O5 (H···O 2.40 Å, CHO = 163°)

Table S6. Pairwise interaction energies (kJ mol⁻¹) for polymorph **II** of PbtI (molecule C).

#	Type	Mol.	Symmetry operation	<i>d</i> (Å)	<i>E</i> _C	<i>E</i> _P	<i>E</i> _D	<i>E</i> _R	<i>E</i> _T
2	C-2	C	- <i>x</i> , - <i>y</i> +2, - <i>z</i>	7.093	-71.1	-27.3	-21.4	72.8	-47.0
3	C-2	C	- <i>x</i> +1, - <i>y</i> +2, - <i>z</i> +1	6.864	-67.3	-25.5	-21.2	67.2	-46.8
9	@ 2	C	- <i>x</i> , - <i>y</i> +2, - <i>z</i> +1	6.953	-9.8	-3.8	-15.4	11.3	-17.6
10	@ 3	C	<i>x</i> , <i>y</i> , <i>z</i> -1	6.719	-5.3	-2.2	-23.4	14.0	-16.9
10'	@ 2	C	<i>x</i> , <i>y</i> , <i>z</i> +1	6.719	-5.3	-2.2	-23.4	14.0	-16.9
16'	@ 1	B	<i>x</i> , <i>y</i> , <i>z</i>	7.401	-9.1	-4.3	-19.4	18.1	-14.7
19'	@ 1	B	<i>x</i> , <i>y</i> , <i>z</i> -1	8.101	-3.3	-1.5	-14.6	7.0	-12.3
23'	@ 1	A	<i>x</i> , <i>y</i> , <i>z</i> -1	8.880	-3.3	-1.6	-15.0	9.3	-10.5
25'	@ 1	B	- <i>x</i> +1, - <i>y</i> +2, - <i>z</i> +1	7.939	0.3	-1.4	-14.0	4.8	-10.3
27'	@ 1	B	<i>x</i> -1, <i>y</i> , <i>z</i>	7.932	-0.3	-1.9	-15.1	7.5	-9.8
29'	@ 1	A	<i>x</i> , <i>y</i> , <i>z</i>	9.072	-1.8	-0.9	-11.9	5.0	-9.6
31	@ 3	C	- <i>x</i> +1, - <i>y</i> +2, - <i>z</i>	7.771	-1.3	-1.5	-14.4	7.8	-9.5
32'	@ 1	B	<i>x</i> -1, <i>y</i> , <i>z</i> -1	7.903	-0.6	-2.0	-16.1	9.3	-9.3
39'	@ 1	B	- <i>x</i> +1, - <i>y</i> +1, - <i>z</i> +2	10.283	-3.7	-1.6	-5.4	6.1	-4.7

#9: Two symmetry-related contacts (phenyl)C33-H33...O7 (H···O 2.62 Å, CHO = 134°)

#16': Contact (phenyl)C35-H35...O5 (H···O 2.40 Å, CHO = 163°)

5.4. Form III

$$E_{T,Cry} = -118.3 \text{ kJ mol}^{-1}$$

$$E_{T,\Sigma} = -120.5 \text{ kJ mol}^{-1}$$

Table S7. Pairwise interaction energies (kJ mol⁻¹) for polymorph **III** of PbtI.

#	Type	Symmetry operation	d (Å)	E _C	E _P	E _D	E _R	E _T
1	C-2	2-x, -1/2+y, 1/2-z	7.052	-60.3	-23.8	-21.0	59.7	-45.4
1'	C-2	2-x, 1/2+y, 1/2-z	7.052	-60.3	-23.8	-21.0	59.7	-45.3
3	@ 3	1-x, -y, -z	6.183	-3.9	-2.5	-30.7	15.1	-22.1
4	@ 1	2-x, -y, 1-z	6.807	-13.2	-4.9	-17.3	15.1	-20.2
5	@ 1	x, 1/2-y, 1/2+z	6.313	-4.4	-2.8	-27.0	14.5	-19.7
5'	@ 2	x, 1/2-y, -1/2+z	6.313	-4.4	-2.8	-27.0	14.5	-19.7
7	@ 2	2-x, -y, -z	7.450	-5.1	-2.7	-22.8	19.6	-11.0
8	@ 4	1-x, -1/2+y, 1/2-z	8.393	-1.5	-1.0	-9.1	2.4	-9.2
8'	@ 4	1-x, 1/2+y, 1/2-z	8.393	-1.5	-1.0	-9.1	2.4	-9.2
10	@ 3	x-1, 1/2-y, -1/2+z	9.643	-5.5	-1.5	-5.0	4.9	-7.1
10'	@ 5	x+1, 1/2-y, 1/2+z	9.643	-5.5	-1.5	-5.0	4.9	-7.2
12	@ 4	x-1, y, z	9.546	-1.7	-1.1	-7.9	3.9	-6.8
12'	@ 6	x+1, y, z	9.546	-1.7	-1.1	-7.9	3.9	-6.8

#4: Two symmetry-related contacts (phenyl)C12-H12...O1 (H...O 2.58 Å, CHO = 143°)

#10/10': Two symmetry-related contacts (phenyl)C9-H9...O1 (H...O 2.61 Å, CHO = 151°)

5.5. Form V

$$E_{T,Cry} = -122.2 \text{ kJ mol}^{-1}$$

$$E_{T,\Sigma} = -124.1 \text{ kJ mol}^{-1}$$

$$E_{T,\Sigma(A)} = -120.9 \text{ kJ mol}^{-1}$$

$$E_{T,\Sigma(B)} = -127.4 \text{ kJ mol}^{-1}$$

Table S8. Pairwise interaction energies (kJ mol⁻¹) for polymorph **V** (molecule A).

#	Type	Mol.	Symmetry operation	d (Å)	E _C	E _P	E _D	E _R	E _T
1	C-3	A	x, y-1, z	6.762	-41.8	-16.9	-19.4	45.1	-32.9
1'	C-3	A	x, y+1, z	6.762	-41.8	-16.9	-19.4	45.1	-32.9
5	C-3	B	-x, -y, -z	7.969	-36.9	-15.4	-11.0	39.6	-23.8
7	@ 1	A	2-x, 1-y, 2-z	6.222	-4.4	-3.7	-30.7	15.3	-23.5
8	@ 1	B	x+1, y, z	6.815	-6.8	-3.1	-23.4	9.9	-23.5
10	C-3	B	1-x, 2-y, 2-z	8.172	-29.9	-10.6	-9.5	26.9	-23.2
12	@ 2	B	x, y, z	6.812	-11.7	-5.6	-28.4	23.0	-22.7
16	@ 1	B	x+1, y-1, z	7.784	-4.7	-2.4	-21.9	13.0	-16.0
19	@ 2	B	x, y-1, z	7.781	-4.0	-1.2	-11.0	5.7	-10.5
21	@ 4	A	3/2-x, -1/2+y, 3/2-z	8.527	-4.0	-1.7	-10.8	8.3	-8.3
21'	@ 4	A	3/2-x, 1/2+y, 3/2-z	8.527	-4.0	-1.7	-10.8	8.3	-8.3
23	@ 5	B	3/2-x, -1/2+y, 3/2-z	8.463	-2.2	-0.8	-8.0	4.8	-6.2
25	@ 6	B	1/2-x, 1/2+y, 3/2-z	10.931	0.3	-0.2	-3.5	1.0	-2.4

#12/12': Contact (CH₂)C7'-H7'1···O2 (H···O 2.58 Å, CHO = 143°)

Table S9. Pairwise interaction energies (kJ mol⁻¹) for polymorph **V** (molecule B).

#	Type	Mol.	Symmetry operation	d (Å)	E _C	E _P	E _D	E _R	E _T
3	C-3	B	x, y-1, z	6.762	-35.6	-13.5	-17.4	33.5	-32.9
3'	C-3	B	x, y+1, z	6.762	-35.6	-13.5	-17.4	33.5	-32.9
5'	C-3	A	1-x, 1-y, 2-z	7.969	-36.9	-15.4	-11.0	39.6	-23.7
8'	@1	A	x-1, y, z	6.815	-6.8	-3.1	-23.4	9.9	-23.5
10'	C-3	A	1-x, 2-y, 2-z	8.172	-29.9	-10.6	-9.5	26.9	-23.1
12'	@2	A	x, y, z	6.812	-11.7	-5.6	-28.4	23.0	-22.7
14	@3	B	1/2-x, -1/2+y, 3/2-z	7.628	-5.7	-2.4	-24.9	12.0	-20.9
14'	@3	B	1/2-x, 1/2+y, 3/2-z	7.628	-5.7	-2.4	-24.9	12.0	-20.9
16'	@1	A	x-1, y+1, z	7.784	-4.7	-2.4	-21.9	13.0	-16.0
18	@2	B	1-x, 1-y, 2-z	8.982	-9.0	-1.8	-7.8	4.5	-14.1
19'	@2	A	x, y+1, z	7.781	-4.0	-1.2	-11.0	5.7	-10.5
23'	@5	A	3/2-x, 1/2+y, 3/2-z	8.463	-2.2	-0.8	-8.0	4.8	-6.2
25'	@6	A	1/2-x, 1/2+y, 3/2-z	10.931	0.3	-0.2	-3.5	1.0	-2.4

#12, #12': Single contact (CH₂)C7'-H7'1···O2 (H···O 2.58 Å, CHO = 143°)

5.6. Form VI

$$E_{T,Cry} = -114.9 \text{ kJ mol}^{-1}$$

$$E_{T,\Sigma} = -117.9 \text{ kJ mol}^{-1}$$

$$E_{T,\Sigma(A)} = -128.3 \text{ kJ mol}^{-1}$$

$$E_{T,\Sigma(B)} = -107.5 \text{ kJ mol}^{-1}$$

Table S10. Pairwise interaction energies (kJ mol⁻¹) for polymorph **VI** (molecule A).

#	Type	Mol.	Symmetry operation	d (Å)	E _C	E _P	E _D	E _R	E _T
1	L-5_t	B	x, y, z	7.071	-63.7	-25.1	-22.6	64.9	-46.5
3	L-5_o	A	x, y-1, z	6.900	-27.2	-10.2	-20.7	23.7	-34.4
3'	L-5_o	A	x, y+1, z	6.900	-27.2	-10.2	-20.7	23.7	-34.4
5	L-5_o	B	3/2-x, 1/2+y, 1/2-z	7.028	-36.0	-15.0	-16.8	39.4	-28.4
7	@1	A	1-x, 1-y, -z	6.717	-3.2	-2.6	-24.5	11.2	-19.2
8	@1	B	-1/2+x, 1/2-y, -1/2+z	6.948	-4.2	-2.4	-23.0	11.6	-17.9
12	@1	B	-1/2+x, -1/2-y, -1/2+z	8.419	-6.4	-2.4	-16.4	11.3	-13.9
14	L-5_n	B	x, y+1, z	7.750	-6.2	-2.6	-12.8	9.1	-12.4
16	@1	A	1-x, -y, -z	7.593	-0.2	-0.7	-12.8	1.6	-12.1
19	@2	B	2-x, -y, -z	7.394	-1.3	-1.4	-13.6	6.3	-10.0
23	@2	B	2-x, 1-y, -z	8.926	-5.1	-1.2	-4.7	3.1	-7.8
25	@2	A	2-x, -y, -z	9.513	-0.6	-0.1	-4.3	0.7	-4.3
26	@2	A	2-x, 1-y, -z	8.829	-0.7	-0.8	-7.2	4.8	-4.0

Table S11. Pairwise interaction energies (kJ mol^{-1}) for polymorph **VI** (molecule B).

#	Type	Mol.	Symmetry operation	d (Å)	E_C	E_P	E_D	E_R	E_T
1'	L-5_t	A	x, y, z	7.071	-63.7	-25.1	-22.6	64.9	-46.5
5'	L-5_o	A	$3/2-x, -1/2+y, 1/2-z$	7.028	-36.0	-15.0	-16.8	39.4	-28.4
8'	@1	A	$1/2+x, 1/2-y, 1/2+z$	6.948	-4.2	-2.4	-23.0	11.6	-17.9
10	L-5_n	B	$x, y-1, z$	6.900	-7.5	-3.1	-26.3	22.9	-13.9
10'	L-5_n	B	$x, y+1, z$	6.900	-7.5	-3.1	-26.3	22.9	-13.9
12'	@1	A	$1/2+x, -1/2-y, 1/2+z$	8.419	-6.4	-2.4	-16.4	11.3	-13.9
14'	L-5_n	A	$x, y-1, z$	7.750	-6.2	-2.6	-12.8	9.1	-12.4
17	@3	B	$5/2-x, -1/2+y, 1/2-z$	8.569	-6.8	-3.6	-20.6	19.9	-11.1
17'	@3	B	$1/2-x, 1/2+y, 1/2-z$	8.569	-6.8	-3.6	-20.6	19.9	-11.1
19'	@2	A	$2-x, -y, -z$	7.394	-1.3	-1.4	-13.6	6.3	-10.0
20	L-5_n	B	$3/2-x, -1/2+y, 1/2-z$	7.711	-5.6	-3.0	-12.2	12.4	-8.3
21'	L-5_n	B	$3/2-x, 1/2+y, 1/2-z$	7.711	-5.6	-3.0	-12.2	12.4	-8.3
23'	@2	A	$2-x, 1-y, -z$	8.926	-5.1	-1.2	-4.7	3.1	-7.8

5.7. Form X

$$E_{T,\text{Cry}} = -118.3 \text{ kJ mol}^{-1}$$

$$E_{T,\Sigma} = -121.1 \text{ kJ mol}^{-1}$$

Table S12. Pairwise interaction energies (kJ mol^{-1}) for polymorph **X**.

#	Type	Symmetry operation	d (Å)	E_C	E_P	E_D	E_R	E_T
1	C-1	$2-x, y, 1/2-z$	6.272	-68.7	-28.9	-22.9	72.8	-47.7
2	C-1	$2-x, y, 3/2-z$	8.001	-67.4	-24.6	-19.2	64.0	-47.2
3	@1	$3/2-x, 1/2-y, 1-z$	6.675	-9.8	-2.9	-15.1	8.0	-19.7
4	@1	$3/2-x, 1/2-y, -z$	7.942	-6.0	-1.8	-18.0	7.5	-18.3
5	@3	$1-x, y, 1/2-z$	6.597	-9.5	-4.1	-19.9	15.4	-18.1
6	@2	$x, 1-y, -1/2+z$	7.316	-4.1	-1.9	-13.0	3.9	-15.1
6'	@2	$x, 1-y, 1/2+z$	7.316	-4.1	-1.9	-13.0	3.9	-15.1
8	@2	$2-x, 1-y, 1-z$	7.256	-9.1	-5.0	-21.4	22.7	-12.8
9	@1	$-1/2+x, 1/2-y, -1/2+z$	7.857	-5.3	-3.4	-20.1	16.7	-12.1
9'	@4	$1/2+x, 1/2-y, 1/2+z$	7.857	-5.3	-3.4	-20.1	16.7	-12.1
11	@5	$1-x, 1-y, -z$	8.680	1.2	-0.7	-10.6	4.2	-5.9
12	@6	$3/2-x, -1/2+y, 1/2-z$	10.406	0.6	-0.2	-4.5	0.9	-3.1
12'	@7	$3/2-x, 1/2+y, 1/2-z$	10.406	0.6	-0.2	-4.5	0.9	-3.1

#3: Two symmetry-related contacts (phenyl)C9–H9…O3 (H…O 2.68 Å, CHO = 140°)

#5: Two symmetry-related contacts (CH₂)C5–H4…O3 (H…O 2.56 Å, CHO = 155°)#8: Two symmetry-related contacts (CH₃)C6–H7…O1 (H…O 2.51 Å, CHO = 170°)

6. Intramolecular energy penalties

Table S13. Intramolecular energy penalties (ΔE_{intra}) of the experimental geometries with respect to the global conformational energy minimum, calculated at the MP2/6-31G(d,p) level of theory.

Polymorph	Molecule ^a	$\phi^b / {}^\circ$	$\omega^b / {}^\circ$	$\Delta E_{\text{intra}} / \text{kJ mol}^{-1}$
I	A	1.1	34.1	8.9
	B	1.1	48.1	6.9
	C	-2.2	44.3	6.0
	crystal	-	-	7.3
II	A	0.8	39.5	8.7
	B	2.4	46.2	8.2
	C	-1.0	46.5	5.5
	crystal	-	-	7.5
III	A, crystal	-0.4	52.5	3.9
V	A	-3.1	30.9	8.5
	B	-129.3	31.3	17.6
	crystal	-	-	13.1
VI	A	-0.6	76.7	0.3
	B	0.7	42.3	7.1
	crystal	-	-	3.7
X (Nbtl-Pbtl)	A, crystal	-6.9	18.3	8.0

^aSymmetry-independent molecules are denoted by letters (A, B, C) and “crystal” indicates the average ΔE_{intra} value of all geometries in a polymorph. ^bDihedral angles are defined in Fig. 15.

7. XPac comparisons with theoretical structures

7.1. Method

XPac comparison was carried out

7.2. Form V

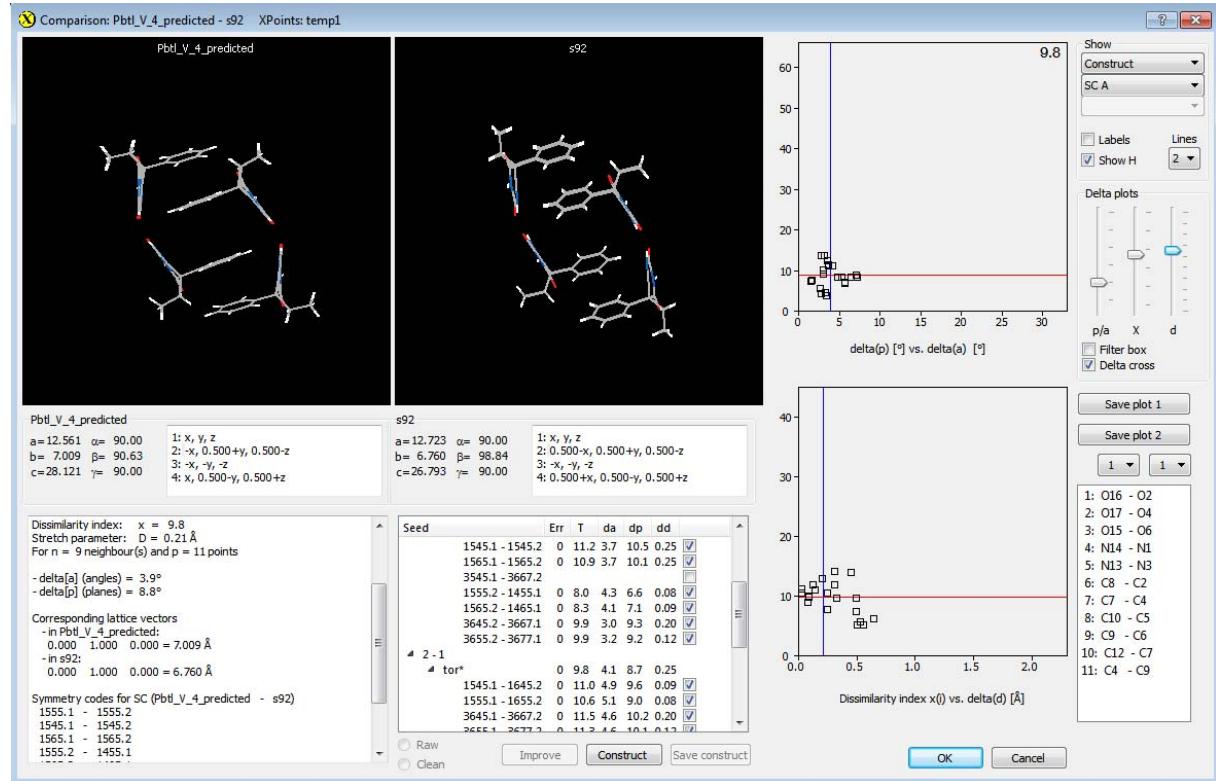


Fig. S8. Screenshot showing a summary of an XPac comparison [2] between the experimental crystal structure of form V (“s92”) and the theoretical candidate structure #4 for form V (“PbtI_V_4_predicted”) reported by Day *et al.* [3]. The 11 matching atomic positions listed in the bottom right panel (the complete pyrimidinetrione unit and the first C atom of each of the phenyl and ethyl substituents at ring atom C5) were used to generate geometrical parameters for the XPac calculations, which were therefore largely unaffected by any differences in molecular geometry. A stack of centrosymmetric molecule pairs propagating along the respective b axis (one-dimensional supramolecular construct) was identified as the closest common structure fragment. The XPac dissimilarity index [4] for this common structure fragment of 9.8 indicates significant geometrical differences.

7.3. Form X

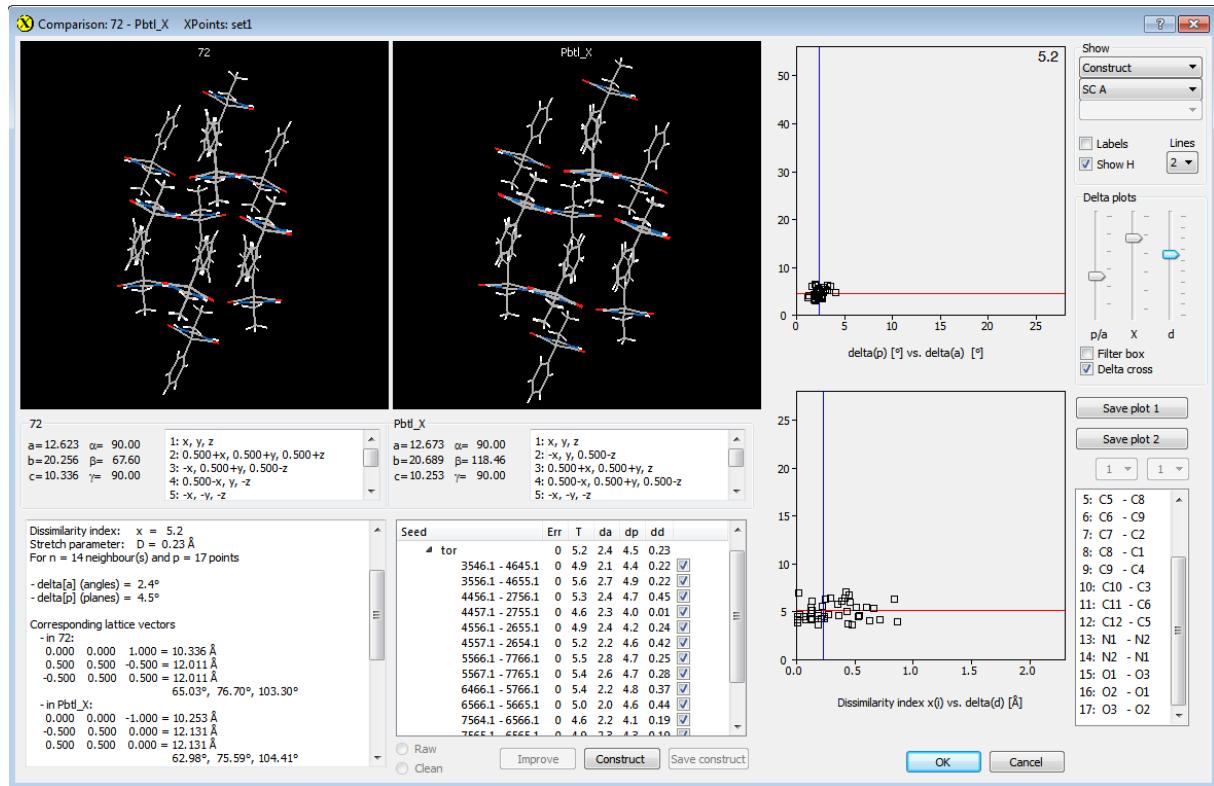


Fig. S9. Screenshot showing a summary of an *XPac* comparison [2] between the model for polymorph **X** and the theoretical candidate structure #72 reported by Day *et al.* [3]. All 17 matching non-H atomic positions were used to generate geometrical parameters for the *XPac* calculations. The two structures are isostructural with an *XPac* dissimilarity index [4] of 5.2 for the complete molecule shells.

Relationship between unit cells

A transformation of #72 with the matrix **(101 010 001)** leads to a *C2/c* structure whose lattice parameters correspond directly with those of polymorph **X**.

Predicted structure #72 [3]:

$a = 12.623 \text{ \AA}$, $b = 20.256 \text{ \AA}$, $c = 10.336 \text{ \AA}$; $\beta = 67.60^\circ$; space group *I2/a*.

Transformed structure #72:

$a' = 12.913 \text{ \AA}$, $b' = 20.256 \text{ \AA}$, $c' = 10.336 \text{ \AA}$; $\beta = 115.34^\circ$; space group *C2/c*.

PbtI polymorph **X**:

$a = 12.673 \text{ \AA}$, $b = 20.689 \text{ \AA}$, $c = 10.253 \text{ \AA}$; $\beta = 118.46^\circ$; space group *C2/c*.

8. Structure model for polymorph X

The following structure model for polymorph X of Pbtl was derived from that of the co-crystal of Pbtl with pentobarbital (CSD refcode LATMEA).

```
_symmetry_cell_setting monoclinic
_symmetry_space_group_name_H-M 'C 2/c'
_symmetry_Int_Tables_number 15
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 -x,y,1/2-z
3 1/2+x,1/2+y,z
4 1/2-x,1/2+y,1/2-z
5 -x,-y,-z
6 x,-y,-1/2+z
7 -1/2-x,-1/2-y,-z
8 -1/2+x,-1/2-y,-1/2+z
_cell_length_a 12.6733(11)
_cell_length_b 20.6887(19)
_cell_length_c 10.2529(7)
_cell_angle_alpha 90
_cell_angle_beta 118.458(9)
_cell_angle_gamma 90
_cell_formula_units_Z 4
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
O1 O 1.0648(2) 0.42427(17) 0.6420(2)
O2 O 0.8417(2) 0.43034(18) 0.1480(2)
O3 O 0.6670(2) 0.3995(2) 0.4608(3)
N1 N 0.8648(2) 0.4116(2) 0.5488(3)
H1 H 0.87360 0.41130 0.63930
N2 N 0.9512(2) 0.42189(17) 0.3940(3)
H2 H 1.01660 0.42490 0.38470
C1 C 0.9659(3) 0.4193(2) 0.5362(3)
C2 C 0.8447(3) 0.4202(2) 0.2672(3)
C3 C 0.7329(3) 0.4021(3) 0.2777(4)
C4 C 0.7499(3) 0.4042(3) 0.4342(4)
C5 C 0.6308(3) 0.4473(3) 0.1817(4)
H3 H 0.62250 0.44810 0.08070
H4 H 0.55520 0.42980 0.17380
C6 C 0.6474(4) 0.5159(4) 0.2401(7)
H5 H 0.64130 0.51660 0.33170
H6 H 0.58520 0.54360 0.16580
H7 H 0.72670 0.53170 0.26040
C7 C 0.7229(12) 0.3296(5) 0.2317(18)
C8 C 0.7952(11) 0.2811(7) 0.3256(15)
H8 H 0.85400 0.29140 0.42410
C9 C 0.7814(13) 0.2177(6) 0.2755(18)
H9 H 0.83080 0.18460 0.33980
C10 C 0.6954(14) 0.2027(5) 0.1314(19)
H10 H 0.68600 0.15940 0.09720
C11 C 0.6231(13) 0.2512(8) 0.0375(14)
H11 H 0.56430 0.24100 -0.06100
C12 C 0.6369(12) 0.3147(7) 0.0876(17)
H12 H 0.58750 0.34780 0.02330
```

9. References

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